Thermochimica Acta, 95 (1985) 7–14
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ADDITIONAL THERMODYNAMIC RELATIONSHIPS ON COMPLEXATION EQUILIBRIA IN VARIOUS SOLVENTS *

DOMENICO DE MARCO **, GABRIELLA MAUCERI and ANTONINO MARCHESE
Institute of Analytical Chemistry, University of Messina, Via dei Verdi, 98100 Messina (Italy)

(Received 25 March 1985)

ABSTRACT

Complex formation in solution comes from the displacement reactions of solvent molecules through donor–acceptor interactions. ΔH and ΔS parameters are due to interactions between substrates and to solvent action, so that enthalpy and entropy changes depend on the same process (at least partially). Compensative and, in some cases, cooperative interdependence between ΔH and ΔS for several complexation equilibria in various solvent media are shown.

INTRODUCTION

In the gas phase, a complexing reaction is the addition of ligand L on substrate A

$$A + L = A\text{–}L \qquad (1)$$

The A–L formation comes from electrostatic and covalent interactions and from their reciprocal short-range influence on the respective coordinating abilities.

The change inferred in the system by eqn. (1) has well-defined ΔH and ΔS values so that a reaction can be represented (not biunivocally) by an ordered couple (ΔH, ΔS).

Every species is solvated in solution and reaction (1) is no longer an associative process but a displacement reaction where solvent-coordinated molecules are expelled by interaction between reagents. Then model (2) [1–3] for a complexing reaction in solvent medium must consider:

(1) the solvation of the reagents,

(2) mutual interaction between reagents,

(3) solvent–solvent interactions (which have a very varied influence on complexation equilibria [4]).

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* This work was presented to Workshop on "Metodologie analitiche ed equilibri chimici in solventi organici", Modena, Italy, 1984.

** Author to whom correspondence should be addressed.

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$$\begin{tikzcd} A_g + & L_g + S_g = & A\text{-}L_g \arrow[d] & + S_g \arrow[d] \\ AS_s + \arrow[u] & LS_s = \arrow[u] & (A\text{-}L)S_s & + S_s \end{tikzcd} \qquad (2)$$

where S = solvent molecule. Strong solute–solvent interactions (as in strongly coordinating solvent) lead to highly structured systems with a low entropy and enthalpy. Macroscopic parameters (such as the dielectric constant of the medium) are, at the end, poorly correlated with the solvation phenomena and other parameters relative to chemical equilibria in solution, because of the microscopic nature of the above-mentioned interactions. Enthalpy and entropy changes arise from several contributions. One part of ΔS is associated with solute–solute interactions. It has a negative sign (because of the associative nature of the complexing reaction (1)) and suffers from conformational terms on account of the ligand arrangement. The other part of the entropy change is due to the release of solvent molecules and involves the solvent structure. It can have positive values (counteracting the preceding values). At the same time, ΔH also consists of more than one term, one of which is associated with the solvent rearrangement. Therefore, the enthalpy and entropy changes are more interdependent on each other than they are dependent on the same phenomenon (in solution this can be the effect of the solvent molecules). Hence, the values of ΔH and ΔS for a set of homologous reactions have both a "residual" and a "proportional" term (the latter is connected with solvent action [5], and the model of their interdependence is derived both from the type of reaction and the type of solvent. In the $\Delta H, \Delta S$ plane, well-defined trends will exist where "homologous" reactions lie. Owing to limited ΔH and ΔS ranges, these trends can be approximated by a linear equation (at least as a first-order approximation). The intercept is the enthalpy change for a hypothetical isoentropy reaction (belonging to the specific trend) where the coordinated solvent is ejected into the bulk of the solvent. The linear dependence coefficient has the physical dimensions of temperature. The existence of ΔH vs. ΔS relationships involves the existence of ΔH vs. $T\Delta S$ relationships. In this latter case, the linear dependence coefficient is dimensionless, but depends on temperature. In our opinion the first case must be preferred because the relationships are invariant in all temperature ranges where enthalpy and entropy change can be considered constant.

RESULTS

In Figs. 1A and B, a set of successive complexing reactions of Ag(I) with thiocarbonyl ligands (thiourea, *N*-methyl-thiourea, *N*-ethyl-thiourea, *N*,*N*′-diethyl-thiourea, *N*-phenyl-thiourea, *N*′,*N*′-diphenyl-thiourea and thiobenzanilide) in protic solvents (H_2O, CH_3OH) is reported [6]. ΔH and ΔS values were obtained from the dependence of ΔG on the temperature at

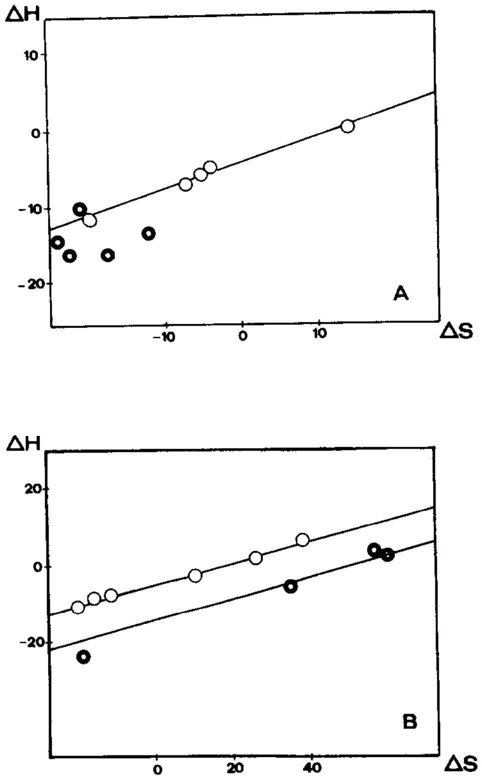

Fig. 1. Plots of ΔH vs. ΔS for successive complexing reactions of Ag(I) in water (A) and in methanol (B) at $\mu = 0$ (from ref. 5).

$\mu = 0$ (enthalpy changes are in kcal mol^{-1} and entropy changes in cal K^{-1} mol^{-1}). In water, the stepwise coordination of the second and third ligands

$$AgL_n^+ + L = AgL_{n+1}^+ (n = 1 \text{ or } 2) \tag{3}$$

shows a very sharp linear single trend, while the coordination of the first molecule of ligand

$$Ag^+ + L = AgL^+ \tag{4}$$

does not seem to have a linear structure. The least-squares fitting gives the following linear relationship

$$\Delta H = -3.97(0.4)\,{}^* + 0.33(0.03)\Delta S \quad (R = 0.98) \tag{5}$$

(in the fitting, the heavy circles near the line drawn in Fig. 1 are not considered). In CH_3OH (Fig. 1B) there are two distinct and parallel trends

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* Standard deviations are reported in parentheses.

which persist and are in the same sequence in C_2H_5OH, nC_3H_7OH and $(CH_3)_2CO$ (not reported in the figures). The equations for these trends are, respectively

in CH_3OH

$$\Delta H = -13.4(0.5) + 0.29(0.00)\Delta S \quad (R = 1) \tag{6a}$$

$$\Delta H = -4.43(0.3) + 0.28(0.00)\Delta S \quad (R = 1) \tag{6b}$$

in C_2H_5OH

$$\Delta H = -13.9(0.9) + 0.26(0.03)\Delta S \quad (R = 1) \tag{7a}$$

$$\Delta H = -3.90(0.2) + 0.28(0.01)\Delta S \quad (R = 1) \tag{7b}$$

in nC_3H_7OH

$$\Delta H = -12.98(0.4) + 0.30(0.03)\Delta S \quad (R = 1) \tag{8a}$$

$$\Delta H = -4.9(0.1) + 0.30(0.00)\Delta S \quad (R = 1) \tag{8b}$$

in $(CH_3)_2CO$

$$\Delta H = -15.7(1.1) + 0.29(0.01)\Delta S \quad (R = 1) \tag{9a}$$

$$\Delta H = -5.21(0.1) + 0.29(0.00)\Delta S \quad (R = 1) \tag{9b}$$

The lowest trend (a) is relative to the formation of monocoordinated ligand (4) and it is about -10 Kcal mol^{-1} different from the highest trend (relative to the second and third coordinations as in water). The difference in the intercepts is due to the nature of the coordinate bond between Ag(I) and the thiocarbonyl ligands which has a large π back-bond contribution causing a great difference in parameters relative to the first and second coordination. The very close correlations point out the low (or in any case invariant) contributions of conformational factors on the entropy term so that it is mainly determined by the solvent action. Linear dependence coefficients (all positive) show unfavourable enthalpy–entropy interactions more strongly in water than in other solvents (with a minimum in C_2H_5OH). The intercepts of the trends become more negative (≈ 1 kcal mol^{-1}) on passing from protic to aprotic solvents. The lack of correlation in the first coordination of Ag(I) in aqueous solution and its appearance in alcohols and acetone depend on the ability of the solvent to form hydrogen bonds with the solutes. Perhaps in water (as this solvent is very prone to bind via hydrogen bonds) the solvation states of the reagents and the product of eqn. (1) are the same. In alcohols and acetone, solvent molecules are more easily released from the solvation sphere of the reagents causing more favourable entropy changes, stressed by the lack of the solvent structure in alcohols and acetone with respect to water. It follows that the set of points, which comprises 20 e.u. in water, is moved towards higher entropy values and is scattered over a wider range in other solvents. In acetone it has the highest ΔS dispersion towards positive values and causes the consequent stabilization of tricoordinated complexes.

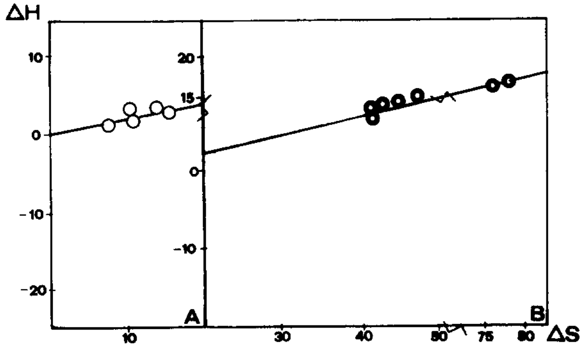

Fig. 2. Plots of ΔH vs. ΔS for the formation of monofluoro complexes of $3d$ divalent metal ions in water (A) and in methanol (B) (from ref. 6.).

In the formation of monofluoro complexes with divalent metal ions: Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) (Figs. 2A and B) [7], the linear coefficient (eqns. 10 and 11) of the trend is notably lower in CH_3OH than in water, contrary to the sequence for the Ag(I)–thiocarbonyl ligand complexes. Also in this case, the reagent desolvation process in the complexing reactions has positive enthalpy–entropy interaction. The intercept sequence ($CH_3OH < H_2O$) comes from the more positive ΔH value of the reagent solvation in methanol than in water.

In CH_3OH

$$\Delta H = -3.8(0.8) + 0.27(0.02)\Delta S \quad (R = 1) \tag{10}$$

In water

$$\Delta H = -0.35(1.6) + 0.2(0.13)\Delta S \quad (R = 0.7) \tag{11}$$

Figure 3 shows an interesting comparison between some complexing reactions in H_2O and DMSO for Zn(II), Cd(II) and Hg(II) with halides and SCN^- [4,8–11]. It is known that Zn(II) is a typical "a" or "hard" ion; Cd(II) has a borderline behaviour and Hg(II) is very soft [12]. In aqueous solution, the trends for the three ions are positive with different angular coefficients depending on the central ion and a minimum relative to Cd(II) complexes (eqns. 12–14b).

In water

$$\text{Zn(II)} \quad \Delta H = -0.28(0.5) + 0.34(0.05)\Delta S \quad (R = 1) \tag{12}$$

$$\text{Cd(II)} \quad \Delta H = -1.28(0.3) + 0.24(0.03)\Delta S \quad (R = 0.7) \tag{13}$$

$$\text{Hg(II)} \quad \Delta H = -14.8(1) + 0.74(0.2)\Delta S \quad (R = 0.8) \tag{14a *}$$

$$\Delta H = -2.25(0.6) + 0.45(0.2)\Delta S \quad (R = 0.9) \tag{14b *}$$

The two parallel trends observed previously in the Ag(I)–thiocarbonyl

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* According to the authors these values need to be improved by means of much more data.

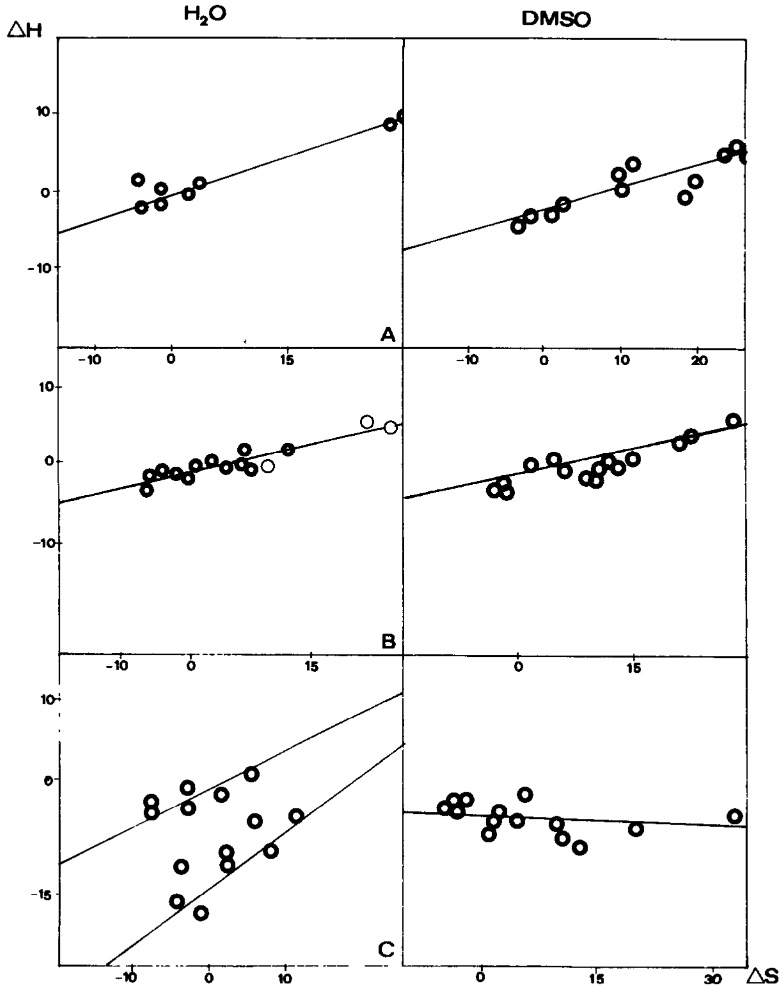

Fig. 3. Plots of ΔH vs. ΔS for the successive complexing reactions of Zn(II) (A), Cd(II) (B) and Hg(II) (C) in water and in DMSO (from refs. 4, 6, 9).

ligand soft–soft interactions are not found in Zn(II) and Cd(II) complexing reactions, but they reappear in the Hg(II) system discriminating stepwise coordinations I and II from III and IV. The intercepts become lower following the softness sequence and have a very sharp change from Cd(II) to Hg(II). In DMSO, the intercept order is the same as the previous one, but (as can be seen from the data), it is lower ($\approx$ 1–2 kcal mol^{-1}) for Zn(II) and Cd(II) with respect to water, while for Hg(II) it is higher ($\approx$ 10 kcal mol^{-1}). In DMSO

$$\text{Zn(II)} \quad \Delta H = -2.2(0.8) + 0.30(0.04)\Delta S \quad (R = 1) \tag{15}$$

$$\text{Cd(II)} \quad \Delta H = -2.35(0.5) + 0.26(0.04)\Delta S \quad (R = 0.9) \tag{16}$$

$$\text{Hg(II)} \quad \Delta H = -5.29(0.5) - 0.05(0.05)\Delta S \quad (R = 0.4) \tag{17}$$

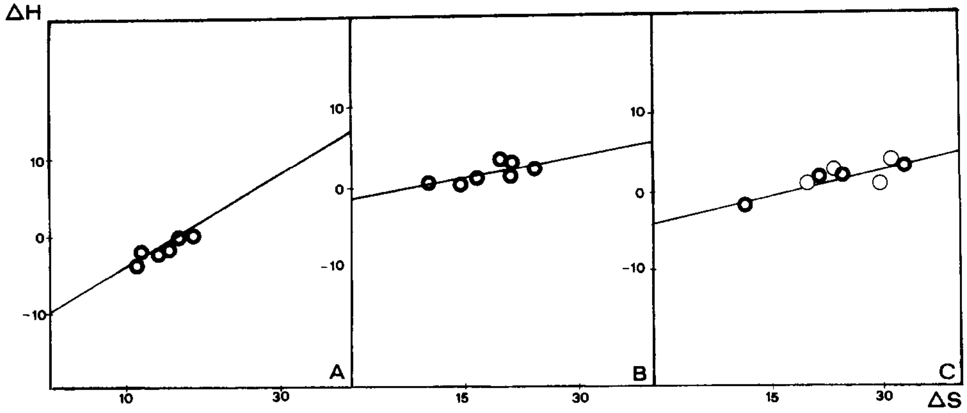

Fig. 4. Plots of ΔH vs. ΔS for the successive complexing reactions of Cu(I) in DMSO (A), in AN (B) and in PY (C) (from ref. 4).

The ΔH value for the Hg(II) stepwise complexing reactions in DMSO has a negative dependence on ΔS, showing a cooperative interaction between the two parameters, very different from their behaviour in water. ΔS values are more scattered in DMSO than in water. For Zn(II) and Hg(II) clusters, falling into different ΔS ranges, can be identified and their sequence (invariant for both acceptors) is consistent with the substrate–ligand charge neutralization. Compensative or cooperative relationships depend on the solvent nature because of the specific solute–solvent or solvent–solvent interactions.

Figure 4 shows that compensative or cooperative behaviour also depends on the central metal ion. In fact, for a soft acceptor, such as Cu(I) (in complexing reactions with halides and SCN^-) [4,13], compensative relationships (18)–(20) decreasing from DMSO to AN to PY without any change in the cooperative process can be seen.

Cu(I) in DMSO $\Delta H = -8.39(1.2) + 0.5(0.1)\Delta S$ $(R = 0.9)$ (18)

in AN $\Delta H = -3.22(1.5) + 0.22(0.06)\Delta S$ $(R = 0.8)$ (19)

in PY $\Delta H = -0.83(1.4) + 0.18(0.1)\Delta S$ $(R = 0.6)$ (20)

CONCLUSIONS

The existence of the relationship ΔH vs. ΔS depends on the overall contributions of several variables. By rationalizing these contributions and fixing some variables, it is possible to evaluate the behaviour of others.

The linear trends are certainly a specific case which derive from the "homogeneity" of the reactions studied. In this set of reactions we have

$$\Delta G = \Delta H_{\mathrm{int}} + (\tau - T)\Delta S \qquad (21)$$

where ΔH_{int} is the intercept of the trend equation in $(\Delta H, \Delta S)$ space and τ is a function of ΔS $(\tau = \partial\Delta H/\partial\Delta S) = \mathrm{f}(\Delta S))$ with the physical dimensions of temperature. According to eqn. (21), the influence of ΔS on chemical equilibrium is different depending on both τ and T. In the case of a linear model of the trend, τ is the angular coefficient of ΔH vs. ΔS relationships. With $\tau < 0$, $\tau - T < 0$; therefore, ΔS has an inverse influence on ΔG. With $\tau > 0$, $\tau - T \gtreqless 0$ (according to the Kelvin temperature value), and when $\tau - T = 0$, ΔS has no influence on the chemical equilibrium. The τ parameter in a compensative ΔH–ΔS process can be interpreted as the Kelvin temperature where the entropy change is exactly compensated by a corresponding enthalpy change.

ACKNOWLEDGEMENTS

Thanks are due to Italian M.P.I. for financial support.

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