Mechanism of Complex Formation in Methanol: Solvent Exchange Rates for some Bivalent Metal Ions

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Summary The kinetics of the formation and dissociation of metal(II) chloride complexes in the solvent methanol have been investigated; the rate determining step for the complex formation is shown to be the release of a co-ordinated methanol molecule from the inner co-ordination sphere of the metal ion and the relation between the enthalpy of activation and the entropy of activation for the solvent exchange is shown to be linear.

The formation and dissociation rate constants for the mono-chlorocomplexes of the bivalent metal ions of Ni, Co, Fe, and Mn in methanol solution have been determined from relaxation measurements using pressure-jump[1] and shock-wave techniques.[2] Solutions of the anhydrous metal chlorides showed a single concentration dependent relaxation time which could be fitted to the two step mechanism (1), in which K_0 is the outersphere equilibrium constant,

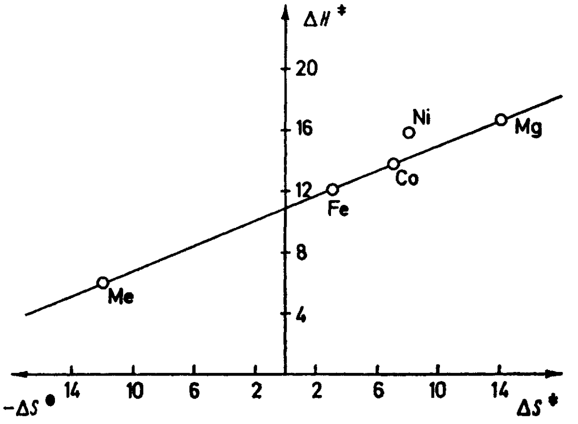

Figure. *Activation parameters for the methanol exchange from metal ions.*

Table

Equilibrium and rate constants for metal chlorides in methanol at 20 °C[a]

M^{2+}	K_0k_1 (M^{-1} s^{-1})	K_0 (M^{-1})	k_{-1} (s^{-1})	k_1 (s^{-1})	$K_1=k_1/k_{-1}$	k_0 (s^{-1})	$\Delta H^\ddagger$ (kcal)	$\Delta S^\ddagger$ (e.u.)
Ni^{2+}	$(7 \pm 1) \times 10^4$	170	$(1{\cdot}1 \pm 0{\cdot}1) \times 10^2$	$(4 \pm 0{\cdot}5) \times 10^2$	4	5×10^2 [b]	15·8[b]	8[b]
Co^{2+}	$(1{\cdot}2 \pm 0{\cdot}2) \times 10^6$	170	$(9 \pm 1) \times 10^3$	$(7 \pm 1) \times 10^3$	0·8	$1{\cdot}0 \times 10^4$ [b]	13·8[b]	7·2[b]
Fe^{2+}	$(3{\cdot}5 \pm 0{\cdot}5) \times 10^6$	170	$(1{\cdot}2 \pm 0{\cdot}1) \times 10^4$	$(2 \pm 0{\cdot}2) \times 10^4$	1·8	$3{\cdot}0 \times 10^4$ [c]	12[c]	3[c]
Mn^{2+}	$(2{\cdot}7 \pm 0{\cdot}3) \times 10^7$	170	$(3{\cdot}5 \pm 0{\cdot}5) \times 10^4$	$(2 \pm 0{\cdot}2) \times 10^5$	5·7	$3{\cdot}1 \times 10^5$ [c]	6·2[c]	−12[c]

[a] Values extrapolated to $\mu = 0$; [b] ref. 4; [c] ref. 5.

$$M^{2+} + Cl^- \overset{K_0}{\rightleftharpoons} M[MeOH]Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MCl]^+ \qquad (1)$$

k_1 the specific rate constant for the formation of the complex, and k_{-1} the dissociation rate constant. These calculated equilibrium and rate constants are given in the Table. The complexes do not follow the Irving-William's rule which predicts a steady increase for the stability constants from Mn to Ni. Instead, stability constants were found to decrease from Mn to Co and then increase for Ni. The evaluated rate constants, k_1, are approximately the same as the rate constant for the solvent exchange from the inner co-ordination sphere, k_0. The literature values for k_0 and associated activation parameters for the solvent exchange process are shown in the Table.

Values of k_1 are always similar to those of k_0; this shows that the rate determining step for the complex formation in all the studied systems is the release of a co-ordinated methanol molecule from the inner co-ordination sphere. Thus the mechanism which was originally proposed for the complex formation in water is also valid for methanol.[3]

The linear relation (Figure) between the activation enthalpy and the activation entropy for solvent exchange suggests that large activation enthalpies are counterbalanced by positive activation entropies. This results in only modest changes in rate constants for quite large changes in activation enthalpies. The general validity of this correlation is confirmed by the point for Mg (from ref. 6).

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