Registry No. $Co(NH_3)_5(DMF)^{3+}$, 31125-61-8; (dimethyl sulfoxide)pentaamminecobalt(III), 44915-85-7.

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Solvent Exchange at Some Bivalent Metal Ions

AIC60081H

Sir:

Solvent exchange at a metal ion is one of the fundamental reactions of metal ions in solution and often constitutes an important elementary step in a variety of processes taking place in solution, such as substitution reactions, redox reactions, and biochemical reactions involving metal ions or complexes. Solvent exchange at metal ions has been extensively studied and considerable data[1] are now available for making an effort to obtain a general picture of the phenomenon. Caldin and Bennetto[2] have discussed kinetic parameters of solvent exchange at some bivalent metal ions in relation to structural properties of solvents. They have shown an isokinetic relationship between the enthalpy and entropy of activation and interpreted the results in terms of a structural model for a solvated ion in solution.[3] They have also emphasized correlations of fluidity (viscosity/density) and the enthalpy of evaporation with kinetic parameters of solvent exchange.[2] An account of the Caldin–Bennetto viewpoint has recently been given[4] and more recently solvent effects on solvent exchange at nickel(II) ion have been discussed.[5]

In this communication a somewhat different approach is put forward: the enthalpy of activation of solvent exchange at some bivalent metal ions is correlated with the solvation enthalpy of metal ion and the enthalpy of evaporation of solvents.

A simple model based on the dissociation (D) mechanism is assumed and the solvent exchange at a metal ion is considered to involve the following four processes: (1) a solvent molecule dissociates from the metal ion; (2) this solvent molecule is incorporated in the bulk solvent; (3) another solvent molecule leaves the bulk solvent; (4) this latter solvent molecule approaches to the metal ion and is accommodated in an available coordination site of the metal ion vacated in process (1).

The energy for process (1) is assumed to be proportional to the free energy of *discharge* of the metal ion in the solvent, ΔG_d, which is given by the second term in the modified Born equation:[6]

$$\Delta G_d = -0.5N(ze)^2(r + r')^{-1}\epsilon^{-1} \qquad (1)$$

where N denotes Avogadro number, z the charge on the metal ion, e the electronic charge, r the crystal radius of the metal ion, r' the effective increment of radius characteristic of the solvent,[6,7] and ϵ the bulk dielectric constant of the solvent. From eq 1 we have immediately the corresponding enthalpy change, ΔH_d:

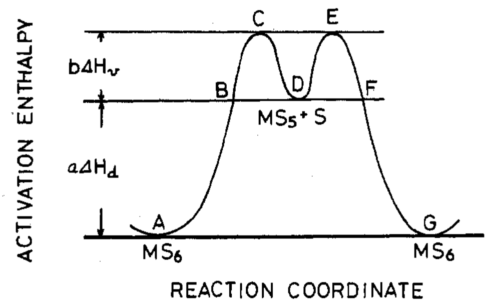

Figure 1. Solvent exchange at a metal ion. M: a metal ion; S: a solvent molecule. Charges are omitted.

$$\Delta H_d = -0.5N(ze)^2(r + r')^{-1}\epsilon^{-1}[1 + T(r + r')^{-1}\partial(r + r')/\partial T + T\,\partial \ln \epsilon/\partial T]_P \qquad (2)$$

ΔH_d is not an activation parameter but a thermodynamic quantity for the ion–solvent interaction per mole of a metal ion. We assume the activation enthalpy of dissociation of a solvent molecule from a metal ion is proportional to ΔH_d.

Process (2) is thought to be similar to evaporation–condensation; it would require first an energy comparable to the free energy of evaporation, ΔG_v, for the solvent to make a hole in the bulk solvent.[2] This energy would subsequently be almost compensated in the process of accommodation of the solvent molecule in the hole, a process similar to condensation. During the latter process an energy comparable to ΔG_v would be lost. Process (3) is a reverse process of process (2). Process (4) occurs spontaneously and is assumed to involve a decrease in energy proportional to that given by eq 1.

The enthalpy of activation for the solvent exchange process at a metal ion, $\Delta H^{\ddagger}_{ex}$, is then expressed as follows:

$$\Delta H^{\ddagger}_{ex} = a\Delta H_d + b\Delta H_v \qquad (3)$$

where a and b are constants. The reaction profile in terms of the activation enthalpy according to the above model is depicted in Figure 1: AB, process (1); BCD, process (2); DEF, process (3); FG, process (4).

Two differentials in eq 2 are now considered: $r^{-1}\,\partial r/\partial T$ is constant for a given metal ion and would be of the order of 10^{-5} K^{-1}, judging from values of the linear expansion of metals and metal salts.[8] The value $r'^{-1}\,\partial r'/\partial T$ is not available; it is expected to vary in parallel with the linear expansion of the solvent. On the other hand we know[8] that the linear expansion coefficient of most solid organic compounds is around 10^{-4} K^{-1}. Then taking the strong ion–solvent interaction into consideration, $(r + r')^{-1}\,\partial(r + r')/\partial T$ should be less than 10^{-4} K^{-1}. Therefore at 298 K the term $T(r + r')^{-1}\,\partial(r + r')/\partial T$ would not exceed 0.03 and its contribution to ΔH_d may be assumed to be unimportant.

The term $T\,\partial \ln \epsilon/\partial T$ is important in eq 2 as evident from Table I, in which some solvent properties are given. Thus ΔH_d may be approximated as:

$$\Delta H_d = -0.5N(ze)^2(r + r')^{-1}\epsilon^{-1}(1 + T\,\partial \ln \epsilon/\partial T)_P \qquad (4)$$

Data of solvent exchange at some bivalent transition metal ions are summarized in Table II. In making a choice among the available solvent exchange data, we prefer higher and more recent values of the enthalpy of activation obtained from measurements over a wider range of temperature. A trend is obvious in Table II: For the same solvent the activation

Table I. Solvent Properties of Some Solvents of Interest[a]

Solvent	Mp, K	Bp, K	ϵ	r',[c] nm	$T\,\partial \ln \epsilon/\partial T$	ΔH_v, kJ mol^{-1}
Acetonitrile (MeCN)	229.32	354.75	37.5	0.081	−1.52	33.23
Ammonia (NH_3)	195.5[b]	239.80[b]	16.90[b]	0.064[d]	−1.37	19.87[g]
N,N-Dimethylformamide (DMF)	212.72	426.2	36.71	0.068	−1.37	47.514
Dimethyl sulfoxide (DMSO)	291.69	462.2	46.68	0.067	−1.24[f]	52.89
Methanol (MeOH)	175.47	337.85	32.70	0.070[e]	−1.58[f]	37.43
Water (H_2O)	273.15	373.15	78.39	0.072	−1.37	43.991

[a] Unless otherwise noted, taken from J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley-Interscience, New York, N.Y., 1970. Mp: freezing point in K; Bp: boiling point in K; ϵ: dielectric constant at 298.15 K; r': effective increment of ionic radius in nm in the modified Born equation; $T\,\partial \ln \epsilon/\partial T$: value at 298.15 K determined graphically; ΔH_v: enthalpy of evaporation at 298.15 K in kJ mol^{-1}. [b] G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook", Academic Press, 1972. [c] Data summarized in ref 7. [d] No experimental value is available. The donor number (V. Gutmann, "Coordination Chemistry in Non-aqueous Solutions, Springer-Verlag, New York, N.Y., 1968) of ammonia has been estimated as 59 (M. Herlem and A. I. Popov, *J. Am. Chem. Soc.*, 94, 1431 (1972)). Then r' was estimated from its correlation with the donor number according to ref 7. [e] N. Tanaka, *Electrochim. Acta*, in press. [f] ln ϵ not being linearly related with temperature, the value is approximate. [g] "International Critical Tables", Vol. V, 1929, p 138.

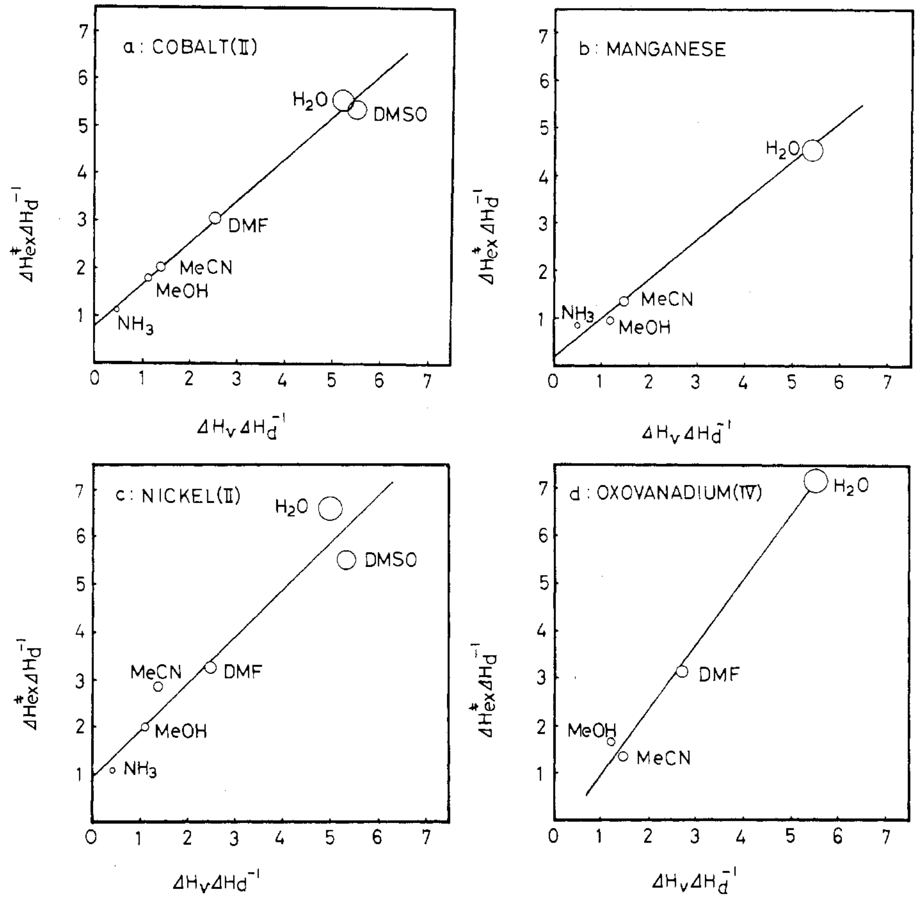

Figure 2. Activation enthalpy of solvent exchange at some bivalent metal ions correlated with ΔH_d and ΔH_v. Cf. Table I for the solvent abbreviation. Radius of circles corresponds to about ±2 kJ of uncertainty of $\Delta H^{\ddagger}_{ex}$.

enthalpy of solvent exchange is in the order nickel(II) > cobalt(II) > iron(II) > manganese(II). We note that this order is parallel with that of ligand field stabilization energy for these transition metal ions. Unexpectedly the activation enthalpy of water exchange is higher for manganese(II) ion than for iron(II) ion. The value for either of these metal ions should probably be revised.

Now we shall test the validity of the present model on these data tabulated in Table II. In Table III are given values of ΔH_d calculated from data given in Table I. From eq 3 we have immediately the following:

$$\Delta H^{\ddagger}_{ex}\Delta H_d^{-1} = a + b\Delta H_v \Delta H_d^{-1} \quad (5)$$

According to eq 5 the plot of $\Delta H^{\ddagger}_{ex}\Delta H_d^{-1}$ against $\Delta H_v\Delta H_d^{-1}$ should yield a straight line. Such plots are given in Figure 2 for cobalt(II), manganese(II), nickel(II), and oxovanadium(IV) ions. The correlation is obviously good for these metal ions.

The coefficients a and b involved in eq 3 will then be discussed. By means of the method of least squares, we determined values of a and b for these metal ions and the results are summarized in Table IV. The values of a are a little less than unity for cobalt(II), nickel(II), and iron(II) ions. This implies that the dissociation of *one solvent molecule* from these metal ions requires an activation enthalpy comparable to the enthalpy of the solvent dissociation *per mole of these metal ions*. This is not surprising because the solvent close to a metal ion is believed to have a dielectric constant considerably lower than the bulk solvent. For oxovanadium(IV) ion a is negative. No physical significance can be attached to the negative a value and the present model as it is may fail or some solvent exchange data may be in error for this oxocation; the correlation given in Figure 2d should be regarded

Table II. Activation Enthalpy of Solvent Exchange at Some Bivalent Metal Ions (kJ mol^{-1}) and Crystal Radius of These Metal Ions (nm)

Solvent	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
Acetonitrile (MeCN)	47.7[a]	40.6[g]	30.3[j]	68.4[m]	29.5[p]
Ammonia (NH_3)	46.8[b]		33.4[k]	46.0[n]	
N,N-Dimethylformamide (DMF)	56.8[c]			62.7[c]	54.8[q]
Dimethyl sulfoxide (DMSO)	51.0[d]			54.3[d]	
Methanol (MeOH)	57.7[e]	50.2[h]	28.4[h]	66.0[e]	50.2[r]
Water (H_2O)	47.2[f]	32.2[i]	36.8[l]	58.0[o]	57.3[s]
Crystal radius/nm	0.082	0.083	0.091	0.078	0.092[t]

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Table III. ΔH_d Values (kJ mol^{-1})

	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
MeCN	23.6	23.4	22.4	24.2	22.3
NH_3	41.7	41.4	39.3	42.9	39.0
DMF	18.7	18.6	17.6	19.2	17.5
DMSO	9.6	9.5	9.0	9.9	9.0
MeOH	32.4	32.2	30.6	33.3	30.4
H_2O	8.5	8.5	8.1	8.8	8.0

Table IV. Coefficients *a* and *b* in Equation 3

	Co^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	VO^{2+}
a	0.7705	0.7752[a] (0.9292)[b]	0.1629	0.9530	−0.4157
b	0.8730	0.6738[a] (0.5535)[b]	0.8747	0.9833	1.365

[a] Calculated with data for MeCN and MeOH. [b] Calculated with data for MeCN, MeOH, and H_2O.

as merely apparent. For manganese(II) *a* is much lower than for cobalt(II), nickel(II), and iron(II). We should await more solvent exchange data for this metal ion before we know definitively whether some solvent exchange data are not correct or the present model fails and some other mechanism should be considered to be involved in the solvent exchange of manganese(II) ion.

The value of *b* is not far from unity; process (2) is in effect similar to evaporation–condensation.

With the values of *a* and *b* given in Table IV $\Delta H^{\ddagger}_{ex}$ values can be reproduced according to eq 3. As seen from Table V, eq 3 reproduces $\Delta H^{\ddagger}_{ex}$ values for cobalt(II) ion to within ±3 kJ mol^{-1} which is within the claimed experimental error for most NMR studies (±2–4 kJ mol^{-1}). However, for the other metal ions the correlation is not as good as for cobalt(II) ion as evident from Figure 2.

Calculated values of the first and second terms of the right-hand side of eq 3 are also included in Table V. The contribution of the ΔH_d term is about twice as large as that of the ΔH_v term for the ammonia exchange, while for the exchange of the other solvents the ΔH_v term is more important than the ΔH_d term. Especially for the exchange of *N,N*-dimethylformamide, dimethyl sulfoxide, and water, the large ΔH_v term is leveled down by the small ΔH_d term. In consequence the activation enthalpy of the exchange of these solvents does not differ much despite the large differences in ΔH_d and ΔH_v.

Table V. Calculated $\Delta H^{\ddagger}_{ex}$ for Cobalt(II) Ion

	$a\Delta H_d$	$b\Delta H_v$	$\Delta H^{\ddagger}_{ex}$, kJ mol^{-1}		
			Calcd	Obsd	Difference
MeCN	18.18	29.01	47.2	47.7	−0.5
NH_3	32.13	17.35	49.5	46.8	+2.7
DMF	14.41	41.48	55.9	56.8	−0.9
DMSO	7.40	46.17	53.6	51.0	+2.6
MeOH	24.96	32.68	57.6	57.7	−0.1
H_2O	6.55	38.40	45.0	47.2	−2.2

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Registry No. Co^{2+}, 22541-53-3; Fe^{2+}, 15438-31-0; Mn^{2+}, 16397-91-4; Ni^{2+}, 14701-22-5; VO^{2+}, 20644-97-7; MeCN, 75-05-8; NH_3, 7664-41-7; DMF, 68-12-2; DMSO, 67-68-5; MeOH, 67-56-1; H_2O, 7732-18-5.

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Comments on the Reduction of Nitrate by Diammonium Oxopentachloromolybdate(V) in Dimethylformamide[1]

AIC60114T

Sir:

The reduction of nitrate by molybdenum(V) in DMF has recently been reported.[1] The source of the molybdenum(V) was $(NH_4)_2[MoOCl_5]$, and the interpretation of the observed