133. High-Pressure ^{17}O-NMR. Study of Vanadium(II) in Water: a Second Example of an Associative Interchange Mechanism (I_a) for Solvent Exchange on an Octahedral Divalent Transition-Metal Ion[1][2]

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(19.IV.82)

Summary

The water exchange of $[V(H_2O)_6]Cl_2$ in aqueous solution has been studied as a function of temperature and pressure (up to 250 MPa), by measuring the ^{17}O-FT-NMR. line-widths of the free water resonance at 8.13 MHz. The kinetic parameters obtained are $k_m^{298} = 87 \pm 4$ s^{-1}, $\Delta H^* = +61.8 \pm 0.7$ kJ mol^{-1} and $\Delta S^* = -0.4 \pm 1.9$ J mol^{-1} K^{-1}. A pressure-independent volume of activation $\Delta V^* = -4.1 \pm 0.1$ cm^3 mol^{-1} is obtained, suggesting an associative interchange (I_a) mechanism for this early divalent metal ion.

Introduction. - Our recent high-pressure ^1H-, ^{17}O- and ^{13}C-NMR. investigations of the mechanisms for solvent exchange on labile transition metal ions led to the conclusion that a dissociative interchange mechanism (I_d) is not the rule for these symmetric exchange reactions, and that, contrary to general belief, a trend appears throughout the series, with a changeover occurring from I_a for the earlier members to I_d for the later ones [2-4]. This evidence was essentially based on the results obtained for Mn^{2+} in water and methanol, and we have decided to seek further confirmation by extending our investigations to an earlier member of the series, V^{2+}. In this paper, we report a study of the temperature- and pressure-dependence of the water exchange rate on $[V(H_2O)_6]^{2+}$ in aqueous solution, determined by ^{17}O-FT-NMR. spectroscopy.

Experimental. - The perchlorate anion, usual counter-ion in solvent exchange studies, can easily be reduced by vanadium(II), and this process is rapid at the high temperatures required to obtain accurate kinetic information from NMR. data. For this reason, we decided to replace perchlorate by chloride in this study. There are apparently no formation constants reported in the literature for

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[1] Part 15 of the series: High-Pressure NMR. Kinetics. For Part 14 see [1].

[2] Presented in part at the 8th AIRAPT Conference, Uppsala, Sweden, August 17-22, 1981.

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0018-019X/82/5/1385-06$01.00/0

chloride complexes of V^{2+} in water, and this is probably due to the poor stability of these chloro-complexes. To further check this point, we have measured the UV./VIS. spectrum of $[V(H_2O)_6]Cl_2$ as a function of temperature. At 298 K, the absorption bands and extinction coefficients correspond to those of $[V(H_2O)_6](ClO_4)_2$ [5] [6], and these bands do not shift with temperature, giving us confidence that no chloride complexes are formed. Furthermore, the extinction coefficient at 415 nm, a region of minimum absorbance for the divalent species, was also measured for $[V(H_2O)_6]Cl_3$ at 353 K, and compared with the extinction coefficient for the divalent species at the same wavelength. This comparison showed that, at 353 K, less than 2% of the vanadium is present in the sample solutions as the trivalent species. This preliminary study clearly shows that the reaction we observe in solutions of VCl_2 is really the water exchange.

$VCl_2 \cdot 2\,H_2O$ was prepared by reduction of VCl_3 *(Fluka)* over Zn,Hg-amalgam, and dried *i.v.* The elemental analysis of the vanadium, chloride and water content gave satisfactory results.

The solutions were prepared in an inert atmosphere by direct dissolution of the appropriate amount of $VCl_2 \cdot 2\,H_2O$ in ^{17}O-enriched water (25.5 atom-%, ^1H-normalized, *Yeda*, multidistilled *i.v.* before use). Two acidified solutions were prepared for the variable-temperature work (0.676 *m*, and 0.724 *m* in vanadium, 0.170 *m* and 0.314 *m* in HCl), and two for the high-pressure work (0.735 *m* and 0.656 *m* in vanadium, 0.278 *m* and 0.199 *m* in HCl).

The transverse relaxation rate $1/T_2$ was determined by ^{17}O-FT-NMR. spectroscopy at 8.13 MHz, as a function of temperature, between 267 and 392 K, and pressure, up to 250 MPa. The experimental procedure for these measurements has already been discussed in earlier publications [3] [7]. The titanium high-pressure bomb used has been described elsewhere [2].

Tables of experimental data at variable temperature and pressure are available from the authors.

Results and discussion. – As a first step, we have repeated the early variable-temperature CW-NMR. work of *Olson et al.* [8], on a slightly extended temperature range, using FT-NMR. The data are shown in *Figure 1.* They were analyzed using a four-parameters nonlinear least-squares fitting routine. In this treatment, $1/T_{2r}$, the reduced bulk water relaxation rate is related to the measured relaxation rate $1/T_2$ by *Equation 1* [9], where P_m is the ratio of moles of water in

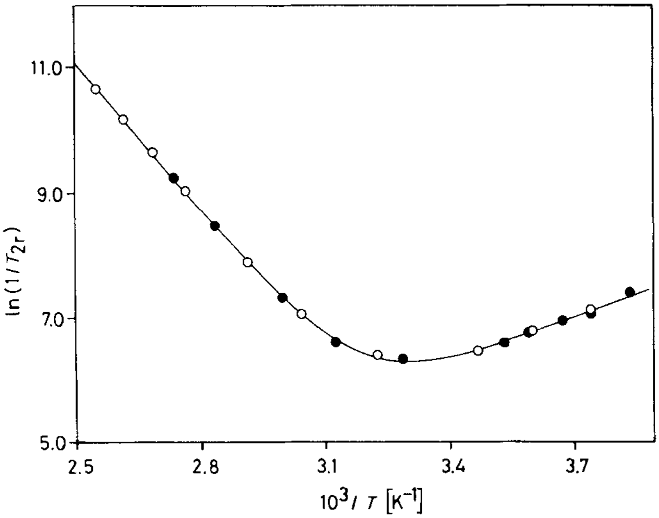

Fig. 1. *Experimental and calculated ln* $1/T_{2r}$ vs. $10^3/T$ ((○) $P_m = 0.0680$; (●) $P_m = 0.0725$)

the bound site to the total moles of water and $1/T_{2s}$ is the relaxation rate of water in a reference $ZnCl_2$ solution.

$$\frac{1}{T_{2r}}=\frac{1}{P_m}\left(\frac{1}{T_2}-\frac{1}{T_{2s}}\right) \tag{1}$$

At low temperatures, the water exchange is too slow to contribute to the observed line-width, and the only important effect is the interaction between V^{2+} and the outer-sphere water molecules. At temperatures above 303 K, the free and bound waters start to exchange noticeably, becoming the rate-determining factor in the relaxation process. In this region of faster relaxation, the so-called *Swift-Connick* equation [9] reduces to a simplified form, *i.e. Equation 2*, in which τ_m is the residence time of a water molecule on the paramagnetic site, described by *Equation 3*, and T_{2os} is the relaxation time due to the outer-sphere term, which is expressed by *Equation 4*.

$$\frac{1}{T_{2r}}=\frac{1}{\tau_m}+\frac{1}{T_{2os}} \tag{2}$$

$$\frac{1}{\tau_m}=k_m=\frac{kT}{\mathrm{h}}\exp\left(-\frac{\Delta H^*}{RT}+\frac{\Delta S^*}{R}\right) \tag{3}$$

$$\frac{1}{T_{2os}}=A_{os}\exp\left(E_{os}/RT\right) \tag{4}$$

The data treatment resulted in the ΔH^*, ΔS^*, A_{os}- and E_{os}-values listed in *Table 1*, where the kinetic parameters obtained by *Olson et al.* [8] using a similar data treatment, are also shown. The difference in the activation parameters can be explained by the larger temperature scale used in this study, resulting in a better definition of the slow-exchange domain, and by the use of FT-NMR. instead of CW-NMR. (where the widths of the first absorption mode side-band or the derivative of the absorption mode signal are measured). As discussed earlier, ΔS^* is rather sensitive to any small systematic error and it is thus not surprising to have such different values, although this parameter is often used for mechanistic assignments.

Table 1. *Kinetic parameters derived for the water exchange on V^{2+} at variable temperature and pressure*[a])

	Ref. [8]	This work
k_m^{298} [s^{-1}]	90 ± 20	87 ± 4
ΔH^* [kJ mol^{-1}]	+ 68.6 ± 2.5	+ 61.8 ± 0.7
ΔS^* [J mol^{-1} K^{-1}]	+ 23.0 ± 6.3	− 0.4 ± 1.9
A_{os} [s^{-1}]		0.13 ± 0.04
E_{os} [kJ mol^{-1}]		20.4 ± 0.7
ΔV^* [cm^3 mol^{-1}]		− 4.1 ± 0.1
$10^2\,\Delta\beta^*$ [cm^3 mol^{-1} MPa^{-1}]		− 0.0 ± 0.1

[a]) Errors quoted are standard deviations.

The pressure-dependence of the water-exchange rate between the V^{2+}-center and the bulk solvent was measured in the so-called slow-exchange region, in two separate runs at 350.3 and 350.8 K. The measured line-widths were corrected for quadrupolar relaxation, considering the slight pressure dependence of this term [7]. At the temperatures of the measurements, the outer-sphere term, $1/T_{2\mathrm{os}}$, only contributes to less than 0.3% to the relaxation rate, and could therefore be neglected in the data treatment *(Eqn. 2)*. The results were analyzed using the usual nonlinear least-squares fit of all the data to both *Equations 2* and *5*, with k_P and k_0 being the rate constants at pressure P and zero, respectively, ΔV_0^* is the zero-pressure

$$\ln k_\mathrm{P} = \ln k_0 - \frac{(\Delta V_0^*)\mathrm{P}}{RT} + \frac{(\Delta\beta^*)\mathrm{P}^2}{2\,RT} \qquad (5)$$

volume of activation, and $\Delta\beta^*$ is the compressibility of activation. The k_0-values for both data sets were also parameters in the fit, and the results of the two experiments were analyzed simultaneously. The experimental and calculated data are shown in *Figure 2*. The data treatment yielded a volume of activation of $\Delta V_0^* = -4.1 \pm 0.1$ cm^3 mol^{-1}, with a compressibility of activation of $10^2 \cdot \Delta\beta^* = -0.0 \pm 0.1$ cm^3 mol^{-1} MPa^{-1}. The volumes obtained for the pressure-independent volume of activation, ΔV^*, and for $\Delta\beta^*$ are listed in *Table 1*.

Following the criteria for the attribution of a mechanism that have been exposed in earlier publications from this laboratory [4] [7], we can conclude that this clearly negative volume of activation is undoubtedly reflective of a concerted mechanism with associative character ($\mathrm{I_a}$). Looking at *Table 2*, where all the known ΔV^* for water exchange on divalent metal ions are summarized, it seems clear that the observed trend does not extend beyond Mn^{2+}. This is of course not a surprise, if

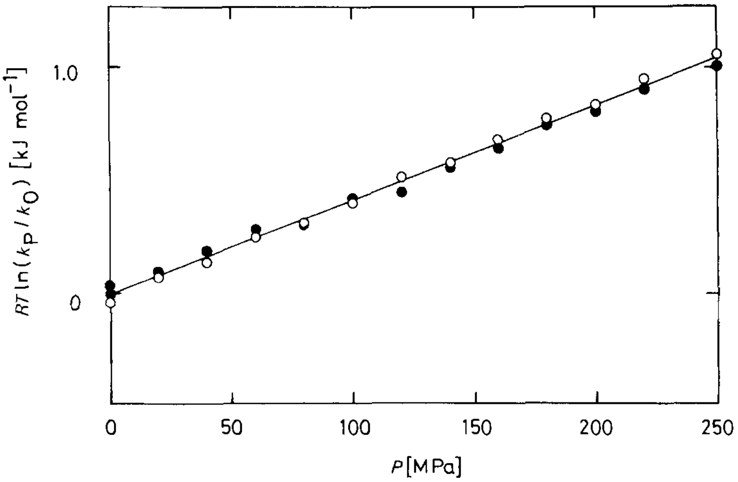

Fig. 2. *Experimental and calculated* $RT\ln(k_\mathrm{P}/k_0)$[kJ mol^{-1}] vs. *pressure* ((●) $P_\mathrm{m} = 0.0669$, $T = 350.3$ K; (○) $P_\mathrm{m} = 0{,}0747$, $T = 350.8$ K)

we refer to the rationals we have developed earlier to explain the associative-dissociative changeover occurring along the series [4] [7] [10]. That is, to recapitulate, the existing parallel between the gradual tending towards dissociative character going from Mn^{2+} to Ni^{2+} and both the decrease in ionic radius and the increase in occupancy of the non-bonding t_{2g}-orbitals of the central cation. According to those arguments, V^{2+} being smaller than Mn^{2+} ($r_i(Mn^{2+}) = 0.82$ Å, $r_i(V^{2+}) = 0.79$ Å) with the same t_{2g}-occupancy, the water exchange on this ion should have a less pronounced associative character. But, going from Mn^{2+} (d^5) to V^{2+} (d^3), there is also a difference to be taken into account, namely, the occupancy of the e_g-orbitals: whereas the later members of the series (d^5 to d^8) all have these two σ^*-antibonding orbitals singly occupied, and therefore present the same mechanistic character from this standpoint, V^{2+} has empty e_g-orbitals. This should consequently result in V^{2+} showing less dissociative character. Considering the volumes of activation obtained for Mn^{2+} and V^{2+}, we can conclude that the steric effect (a seven-coordinate transition state is less favourable for a smaller central ion) totally compensates this electronic effect, or even slightly predominates over it. This is further supported by results obtained at variable pressure for substitution reactions on low-spin Fe^{2+}, which are known to occur *via* a truly *D*-mechanism [11]. This ion, t_{2g}^6, can be compared with Ni^{2+}, $t_{2g}^6 e_g^2$. Regarding only electronic effects, low-spin Fe^{2+}, in view of its lack of e_g-electrons, should exhibit a less dissociative character towards substitution reactions. It is obviously not true, and in this particular case also, the steric factor is predominant: the low-spin Fe^{2+}-ion, much smaller in size than the Ni^{2+}-ion ($r_i(Fe^{2+}) = 0.61$ Å, $r_i(Ni^{2+}) = 0.70$ Å), is also much more dissociative in nature.

Finally, it would be desirable to compare the results of our water-exchange study with those obtained in complex-formation studies of V^{2+} in aqueous solutions, to seek for possible entering-group effects as one would expect for an I_a-mechanism. Unfortunately, there is very little information on V^{2+}-complexation reactions in water (see *Table 3*), part of it still remaining unpublished [12] [16].

Table 2. *Volumes of activation* ΔV^* [$cm^3\ mol^{-1}$] *for water exchange on divalent metal ions at 298 K*a)

V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
−4.1b)	−5.4	+3.8	+6.1	+7.2

a) Ref. [3] and this work. b) At 350 K.

Table 3. *Rate constants for complex-formation reactions with* V^{2+} *in water at 298 K*

Ligand	k_f [$M^{-1}\ s^{-1}$]	Technique	Reference
SCN^-	9 ± 1	'Stopped-flow'	[12]
	15 ± 2	'Temp.-jump'	[13]
	28 ± 3	'Stopped-flow'	[14]
1,10-Phenanthroline	3.0	VIS. spectr.	[15]
2,2′-Bipyridine	0.3	VIS. spectr.	[16]
2,2′,2″-Tripyridine	0.8	VIS. spectr.	[17]

If we constrain the discussion to only unidentate ligands (for reasons explained previously [3]), we are left with a unique ligand, the thiocyanate anion, and three different studies showing widely spread rate constants, not allowing any comparison with the water-exchange rate. It is clear that a better understanding of complex formation with the early divalent first-row transition ions requires more work, and we have currently undertaken stopped-flow studies, both at variable temperature and variable pressure in this field.

This work was supported by the *Fonds National Suisse de la Recherche Scientifique.*

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