Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam – Printed in The Netherlands

WATER-EXCHANGE KINETICS IN LABILE AQUO AND SUBSTITUTED AQUO TRANSITION METAL IONS BY MEANS OF ^{17}O NMR STUDIES

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(Received November 2nd, 1970)

CONTENTS

ABBREVIATIONS

Tiron	4,5 dihydroxybenzene-1,3-disulfonate	Terpy	2,2′,2″-terpyridyl
IDA	iminodiacetate	bipy	2,2′-bipyridyl
SS	5-sulfosalicylate	dien	diethylenetriamine
phen	*ortho*-phenanthroline	trien	triethylenetetramine
mal	malonate	tren	β, β′, β″-triethyltriaminoamine
en	ethylenediamine	EDTA or Y	ethylenediaminetetraacetate

A INTRODUCTION

Several reviews have appeared which discuss the uses of NMR methods to study water exchange kinetics in aqueous metal ion solutions[1] and the importance of these results in attempting to understand net substitution processes in labile systems[2]. A moderate amount of NMR data, largely from our laboratories, is now available concerning the kinetics of water exchange in partially substituted aquo ions. It is the purpose of this review to bring together the current results, consider correlating them, and to mention some related matters suggested by the NMR work. Inferences about water-exchange kinetics have, of course, been drawn from the large amount of work on net substitution reactions [1–3], but these are not reconsidered in detail in this discussion.

B. CONSIDERATION OF EXPERIMENTAL MEASUREMENTS, THEORY, AND INTERPRETATION

(i) Theory of the NMR method for water-exchange kinetics

We are concerned here with relating measurements of line broadenings and shifts for ^{17}O in solvent or bulk water, produced by paramagnetic (usually) water-containing metal ion complexes, to the kinetics of water exchange between solvent and bound water molecules in the first coordination sphere of a metal ion Discussions of the general subject are numerous[1] and only a brief account will be given here The procedures and equations used for the studies are based on the work of Swift and Connick[4]. Some modifications we have used are given by Dodgen et al.[5]. The basic equations for two sites, as we use them, are as follows where $T_{2p'}$ is a molar line-broadening function and Q is the molar shift function

$$T_{2p'} \equiv \frac{2\,[\mathrm{M}]}{\gamma\Delta'} = \frac{[\mathrm{M}]\,\tau_{\mathrm{H_2O}}\,[(1/T_{2\mathrm{M}} + 1/\tau_{\mathrm{M}})^2 + \Delta\omega_{\mathrm{M}}^{\,2}]}{[1/T_{2\mathrm{M}}^{\,2} + 1/T_{2\mathrm{M}}\tau_{\mathrm{M}} + \Delta\omega_{\mathrm{M}}^{\,2}]}$$

$$Q \equiv \frac{TS\,[\mathrm{H_2O}]}{[\mathrm{M}]} = \frac{T\,[\mathrm{H_2O}]\,\Delta\omega_{\mathrm{M}}}{\omega_0\,[\mathrm{M}]\,\tau_{\mathrm{H_2O}}\,\tau_{\mathrm{M}}\,[(1/\tau_{\mathrm{M}} + 1/T_{2\mathrm{M}})^2 + \Delta\omega_{\mathrm{M}}^{\,2}]}$$

The symbols used have the following meanings [M] is the concentration of the aquo metal ion complex, $[H_2O]$ is the concentration of solvent water, τ_{H_2O} is the mean lifetime for water exchange in bulk water ($\tau_{H_2O} = [H_2O]$/rate of exchange), T_{2M} is the spin–spin relaxation time for ^{17}O bound to the metal ion, τ_M is the mean lifetime for exchange of a bound water molecule (n[M]/rate of exchange, where n is the number of water molecules bound/metal ion), $\Delta\omega_M = (\omega_M - \omega_{obs}) \simeq (\omega_M - \omega_0)$ for dilute solutions, where ω_M is the NMR absorption frequency (rad/sec) for a bound water, ω_{obs} is the frequency observed for bulk water in the given solution and ω_0 is the frequency observed for bulk water in the absence of the paramagnetic metal ion, γ is the magnetogyric ratio for ^{17}O (3628 $\text{gauss}^{-1} \cdot \text{sec}^{-1}$), Δ' is the observed line broadening ($W_{obs} - W_0$) where W_{obs} is the full line width at half-maximum in the NMR absorption curve for the paramagnetic solution and W_0 the same quantity for the reference or blank, T is the absolute temperature and occurs because $\Delta\omega$ is assumed to follow Curie's Law and $S = \Delta\omega_{obs}/\omega_0$ ($\Delta\omega_{obs} = \omega_{obs} - \omega_0$). Thus, S and Δ' can be thought of as the experimental observables in general In some cases, T_{2M} and $\Delta\omega_M$ may be directly measured and also used to help extract τ_M or τ_{H_2O} which contain the kinetic information

It should be noted that the treatment based on Swift and Connick's equations is valid only for two-site or parallel two-site situations. Further, only solutions dilute in the paramagnetic ion (< 0.5 *M* perhaps) are precisely treated. The equations for the dilute solution three-site situation have been presented[6]. In principle, the kinetic information can be obtained either from line broadening or shift measurements or a combination of both, which latter approach seems preferable. Limiting forms of the equations are useful, but it is desirable to fit the data finally using the complete equations

(ii) Experimental aspects of the NMR measurements

Various kinds of equipment and techniques of measurement are used The use of derivative curves or side-band techniques is common with commercial equipment. Our experiments have been mainly done using a single-coil method[5,7]. In all cases, care is required to ensure the proper use of the spectrometer. Problems of field and frequency stability, phasing, modulation parameters, Rf power level (avoidance of saturation), good temperature control of sample etc., and others must be considered. Signal averaging can help to increase signal–noise ratios.

A reference solution is needed in making broadening and shift measurements at each temperature. The nature of this reference is less critical if one can work with relatively large line broadenings and shifts. If this is not possible, the reference solution should be chosen to resemble the working solution as closely as possible.

Possible outer-sphere line broadening and line shifts should be looked for and taken into account if found. These seem to be quite small in general when protons are not being studied.

(iii) Treatment of data

The parameters of kinetic interest usually have to be extracted from a rather complex function. Although the usual non-linear least squares computer treatment have been used, they are not ideally suited to the problem at hand Variations in the individual parameters over a range of values should be tried to get a proper assessment of the influence of each on the results. The relative importance and precision of measurements of each parameter depends on the temperature. To date, we have preferred to use the computer to calculate curves which can be compared visually with the experimental curves, adjusting parameters systematically to give the best fit to the more precise data. Because of the inherent difficulties in the measurements, rate constants will rarely be reliable to better than ± 5% and $\Delta H^{\ddagger}$ values to ± 0.5 kcal/mole even in favorable cases.

(iv) Chemical aspects of the measurements

In systems where several species exist in equilibrium, a knowledge of the formation constants and enthalpy of formation values is needed under prevailing conditions Uncertainties in these quantities are reflected in the absolute errors present in the end results reported. Species present may change over the range of temperatures used and if so can cause misleading interpretations. Often the isomeric structures present are not known with any certainty.

C. RESULTS

(i) General comments

The available data are collected in Table 1 The rate constant k_1 is defined by the relation $R = nk_1\,[\mathrm{M}]$, where R is the observed rate of water exchange, n is the number of kinetically equivalent, exchanging water molecules and M refers to the particular metal complex species involved. The quantity A, from the electron–nuclear spin interaction term $AI\cdot S$, is reported as A/h (h = Planck's constant) and is calculated from

$$A/h = T(\Delta\omega_M/\omega_0)(3k/2\pi)(\gamma_N/S(S+1)g_{\mathrm{eff}}\beta)$$

Here T is the absolute temperature, k the Boltzmann constant, γ_N the nuclear magnetogyric ratio, S the spin quantum number and $g_{\mathrm{eff}}\beta$ is consistent with μ_{eff} for the metal complex with $\mu_{\mathrm{eff}} = g_{\mathrm{eff}}\,[S(S+1)]^{1/2}$. Here μ_{eff} is the magnetic moment in Bohr magnetons, β is the Bohr magneton in cgs units and g_{eff} is the observed "g-factor". The other symbols have been defined previously Errors indicated are estimates based on the precision of measurement and uncertainties in quantities used in the data treatment. They are thought to be conservatively assigned

TABLE 1

Water exchange data

System [a]	k_1 (25°C) (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	A/h (Hz)	Ref
VO^{2+} pH ca 1, $\mu < 0.3$, ClO_4^- anion	Equatorial water 5×10^2	13.7	3.8×10^6	8
VO (IDA), pH ca. 4, low μ	1.2×10^5	11.7	2.8×10^6	8
VO $(SS)^-$ pH ca. 4, low μ	1.5×10^5	10.8	4.5×10^6	8
VO $(Tiron)^{2-}$, pH ca 4, low μ	5.3×10^5	11.8	4.9×10^6	8
Mn $(H_2O)_6{}^{2+}$ pH ca. 4, low μ	$2.3\ (\pm 0.2) \times 10^7$	9 ± 1	$7\ (\pm 0.1) \times 10^6$	21
Mn $(H_2O)_4$ $(phen)^{2+}$ pH ca. 4. low μ	$5.3\ (\pm 0.7) \times 10^7$	9 ± 2	$1\ (\pm 0.5) \times 10^7$	21
Mn $(H_2O)_2$ $(phen)_2{}^{2+}$	$1.2\ (\pm 0.2) \times 10^8$	9 ± 2	$2\ (\pm 0.6) \times 10^7$	21
Co $(H_2O)_6{}^{2+}$, 0.1 M Co $(ClO_4)_2$	$2.6\ (\pm 0.2) \times 10^6$	11.9 ± 0.7	1.35×10^7	22
Co $(H_2O)_5Cl^+$ dil. HCl	$1.7\ (\pm 0.3) \times 10^7$	13.8 ± 0.7	1.35×10^7	22
Co $(H_2O)_6{}^{2+}$, pH ca. 4, 2 M NH_4NO_3	$2.24\ (\pm 0.05) \times 10^6$	10.3 ± 0.2	$1.20\ (\pm 0.02) \times 10^7$	14
Co $(H_2O)_5NH_3{}^{2+}$ 2 M NH_4NO_3	$1.6\ (\pm 0.2) \times 10^7$	12.6 ± 0.6	$1.2\ (\pm 0.1) \times 10^7$	14

TABLE 1 (continued)

Co $(H_2O)_4(NH_3)_2{}^{2+}$ 2 *M* NH_4NO_3	6.5 (±1) × 10^7	9.4 ± 1.5	1.2 (±0.1) × 10^7	14
Co $(H_2O)_4$ mal° μ ca 0.3	2.2 (±0.4) × 10^7	12.9 ± 0.8	1.2 (±0.1) × 10^7	14
Co $(H_2O)_2(mal)_2{}^{2-}$ μ ≃ 0.3	> 10^8			14
Ni $(H_2O)_6{}^{2+}$ 0.1 *M* $HClO_4$, μ ca. 0.4	2.7 × 10^4	11.6		23
Ni $(H_2O)_6{}^{2+}$, 0.1 *M* $HClO_4$ μ ca. 0.2 – 0.7	3.0 (±0.3) × 10^4	10.8 ± 0.5	1.9 × 10^7	24
Ni $(H_2O)_6{}^{2+}$ 6.5 *M* $LiClO_4$ pH ca. 7	4.1 (±0.5) × 10^4	9.6 ± 1	2.8 (±0.5) × 10^7	19
Ni $(H_2O)_6{}^{2+}$, μ = 0.5 pH ca. 6	4.4 (± 0.2) × 10^4	10.3 × 0.5	2.2 (±0.4) × 10^7	25
Ni $(H_2O)_6{}^{2+}$, μ = 0.4 – 1.0 pH ca. 3	3.4 (±0.1) × 10^4	12.1 ± 0.3		26
Ni $(H_2O)_6{}^{2+}$, 2 *M* NH_4NO_3 pH ca. 5	3.6 (±0.2) × 10^4	12.3 ± 0.5	2.3 (±0.2) × 10^7	11
Ni $(H_2O)_6{}^{2+}$, 10^{-3} *M* HCl μ = 0.3 → 1.4	3.2 (±0.2) × 10^4	12.1 ± 0.5	2.1 (±0.1) × 10^7	27
Ni $(H_2O)_5(NH_3)^{2+}$ 2 *M* NH_4NO_3	2.5 (±0.2) × 10^5	10.6 ± 0.5	2.5 (±0.2) × 10^7	11
Ni $(H_2O)_4(NH_3)_2{}^{2+}$ 2 *M* NH_4NO_3	6.1 (±0.6) × 10^5	7.8 ± 0.5	1.9 (±0.2) × 10^7	11
Ni $(H_2O)_3(NH_3)_3{}^{2+}$ 2 *M* NH_4NO_3	2.5 (±0.3) × 10^6	10.2 ± 0.7	2.6 (±0.2) × 10^7	11
Ni $(H_2O)_4en^{2+}$, μ = 0.5	4.4 (±0.2) × 10^5	10.0 ± 0.5	2.2 (±0.2) × 10^7	25
Ni $(H_2O)_2en_2{}^{2+}$, μ = 0.5	5.4 (±0.3) × 10^6	9.1 ± 0.5	2.3 (±0.2) × 10^7	25
Ni $(H_2O)_5Cl^+$, 7 *M* LiCl	1.4 (±0.3) × 10^5	8 ± 1	3.5 (±1) × 10^7	19
Ni $(H_2O)_2(NCS)_4{}^{2-}$, 8 *M* KNCS	1.1 (±0.1) × 10^6	6 ± 0.6	2.0 (±0.2) × 10^7	20
Ni $(H_2O)_3(terpy)^{2+}$ pH ca. 3, low μ	5.2 (±0.4) × 10^4	10.7 ± 0.4		26
Ni $(H_2O)_4(bipy)^{2+}$ 10^{-3} *M* HCl, low μ	4.9 (±0.5) × 10^4	12.6 ± 0.5	1.6 (±0.2) × 10^7	27
Ni $(H_2O)_2(bipy)_2{}^{2+}$ 10^{-3} *M* HCl, low μ	6.6 (±0.8) × 10^4	13.7 ± 1	3.8 (±0.5) × 10^7	27
Ni $(H_2O)_3(dien)^{2+}$ pH ca 8, low μ	1.2 (±0.1) × 10^6	5.5 ± 0.5	2.3 × 10^7	28
Ni $(H_2O)_2(trien)^{2+}$ pH ca. 8, low μ	2.9 (±0.3) × 10^6	7 ± 0.5	2.1 × 10^7	28
Ni $(H_2O)_2(tren)^{2+}$ pH ca. 7, low μ	6.0 (±0.6) × 10^5 1.0 (±0.1) × 10^7	8 ± 1		28
Ni $(H_2O)(EDTA)^{2-}$	7.0 (±0.5) × 10^5	8.0 ± 0.5	2.6 (±0.2) × 10^7	29
Ni $(H_2O)(HEDTA)^-$	2 (±0.1) × 10^5	9.8 ± 0.3	2.3 (±0.1) × 10^7	

The VO (IV) aquo species is unique in having one relatively non-labile oxygen, one rapidly exchanging water and four (equatorial) moderately labile water molecules Labilizing effects of the ligands used are quite large. These are discussed in detail by Wuthrich and Connick[8] in terms of structures and electron donor effects and their discussion will not be repeated here. Similar arguments will be used for the Ni and Co systems discussed later in the review.

Very little data are available on the Mn(II) complexes. Exchange rates are near the upper limit of present day ^{17}O NMR techniques and labilizing effects will be hard to measure. The phen ligand produces only a small effect as will be discussed later It might be noted that the enthalpies of activation are fairly large though generally smaller than for Co and Ni. The aquo ion data are very much like those for $Mn(NH_3)_6{}^{2+}$ in liquid ammonia[9], an observation which is even more striking for Co and Ni examples[5b].

Most of the available results refer to Ni(II) and Co(II) species. These will be discussed in the next section in a variety of ways. Comparison of these metals is of considerable theoretical interest. No detailed and systematic studies on effects of ionic strength (μ), added salts, solvent mixtures, and pH have been made. The data listed do suggest that at least small effects can be expected upon varying μ and pH Probably the Ni(II) systems warrant some detailed physico-chemical studies.

In general the bound water molecules behave as if they are kinetically equivalent with the nickel–tren and nitrilo triacetate[10] (NTA) systems being exceptions. Detection conditions for non-equivalence will vary considerably depending on the detailed NMR behavior found as well as on the equilibrium properties relating species and the kinetic parameters for the particular water molecules Some of the results reported may be averages of similar values One might generally expect to see clearly differences in k_1 values of a factor of 3 and in $\Delta H^{\ddagger}$ of 2–3 kcal/mole and smaller ones in favorable circumstances In many cases no clear-cut evidence exists as to the isomer(s) present

(ii) More specific consideration of the cobalt and nickel data

Considering the k_1 values at 25°C, a simple correlation was found[11] when log k_1 (25°C) was plotted vs. H_2O bound/M^{2+}. In general, log k_1 (25°C) increases roughly linearly as H_2O/M^{2+} decreases for Ni(II) and Co(II) examples with the ligands Cl^-, NH_3, malonate, en, dien, and tren as shown in Fig. 1. Some extrapolations in temperature are made and because of the variability in $\Delta H^{\ddagger}$ the correlation typically works best at one temperature only The ligands NCS^-, bipy, terpy, *o*-phen, and EDTA characteristically (considering the few examples) do not produce as large an increase in k_1 (25°C) as the above correlation predicts (terpy, for example, is about 1/100 as effective as three NH_3 groups). The small increases in log k_1 (25°C), however, are still roughly linear in H_2O/Ni. The above observations can be considered in conventional terms by regarding the complexes to be largely ionic in nature with electron-donating or withdrawing effects of the ligands altering the effective metal ion charge. These effects would be expected to be roughly additive. Good electron donors should enhance the rate of water exchange. Funahashi and Tanaka[12] have correlated some rates of substitution with the E_n (electron donating) parameter of Edwards[13]. In general, E_n values are not available for all the

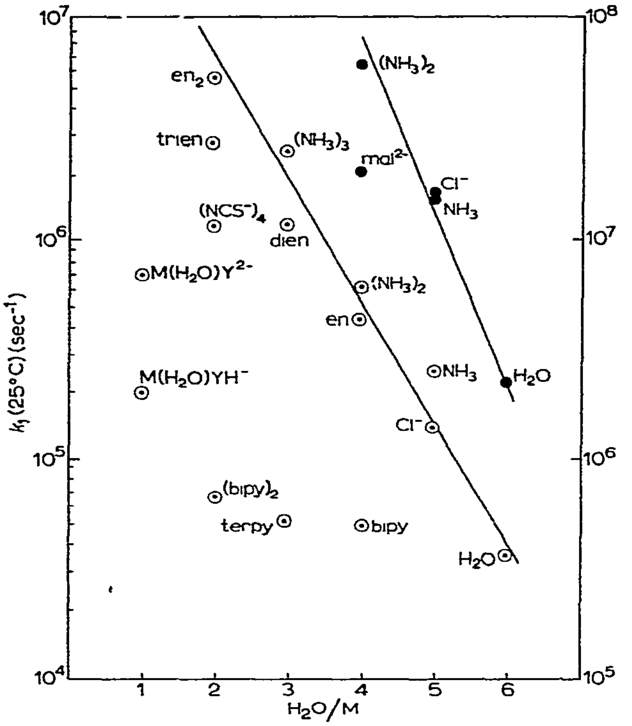

Fig. 1. Semilogarithmic plot of log k_1 (25°C) vs. H_2O/M for cobalt and nickel systems. Right hand scale and • refer to cobalt data while left hand scale and ○ refer to nickel. Y is EDTA

ligands of interest If one assumes that NH_3 and the other amines have the same E_n value, the correlation is only approximate The more complex amines deviate by producing smaller effects, in general, then NH_3 Chloride is not consistent between cobalt and nickel, it should be about two-thirds as effective as NH_3. Using twice the E_n value of acetate for malonate predicts about the observed results.

The ligands bipy, terpy, and phen (in the Mn(II) case) produce little effect. These observations can be rationalized by postulating significant back pi-bonding to the ligand, compensating for sigma donation. Thiocyanate may then be an intermediate case with somewhat less back-bonding

The EDTA systems are interesting and will be described in a bit more detail under (iii) Based on the malonate result for cobalt, one might expect more rate enhancement than is observed. Protonation of the free acetate arm considerably reduces the enhancement. Comparison of these highly chelated systems with the simpler ones may not, of course, be particulary valid.

One might expect some spectral correlations if electron donating — withdrawing effects are involved. The spectra, however, are complex and it is not easy to obtain proper parameters Simple correlations with 10*Dq*. in general, do not work. Hoggard[14] has suggested the use of Jϕrgensen's "optical electronegativities". Although there are many difficulties in application of these ideas, some success seems to be possible and perhaps warrants further investigation.

That single temperature data can be misleading is a well-known but often largely ignored fact. While the $\Delta H^{\ddagger}$ values are not as precise as may be desired, they are not grossly in error and qualitative trends can be discussed. In the VO^{2+} system the ligand labilization of water is accompanied by some reduction in $\Delta H^{\ddagger}$ although the greatest labilizing effect at 25°C is for the system with the least reduction in $\Delta H^{\ddagger}$. In the Mn(II) examples the $\Delta H^{\ddagger}$ values are not precise but are similar as are the rates. In the cobalt(II) systems the Cl^-, NH_3, and malonate ligands (mono-complexes) *increase* or do not change $\Delta H^{\ddagger}$, while bound water is being labilized. For the diammine Co(II) a significant reduction in $\Delta H^{\ddagger}$ occurs. For Ni(II) the $\Delta H^{\ddagger}$ values to some extent follow the trend in k_1 though not in any regular way. Perhaps the main value of these parameters at this time is to emphasize how little is really understood in detail about the kinetic properties of similar species and the importance of entropy and solvation effects.

A comparison of the cobalt and nickel $\Delta H^{\ddagger}$ values is of special interest. For the hexaaquo ions cobalt has a lower $\Delta H^{\ddagger}$ by ca. two kcal/mole (in 2 *M* NH_4NO_3). In the case of the hexaammine species in liquid ammonia[5b] both have $\Delta H^{\ddagger} = 11 \pm 0.5$ kcal/mole. In the other systems, cobalt has the *higher* value. Various theoretical considerations have suggested that the faster Co(II) rates (about 100X at 25°C) are due to a *lower* $\Delta H^{\ddagger}$ for a common mechanism. Solvation effects are usually assumed to be identical for cobalt and nickel. If these ideas are correct (and they may not be), one may wish to consider that the mechanisms are indeed not the same for these metals, as was suggested earlier[5b]. The high $\Delta H^{\ddagger}$ and positive $\Delta S^{\ddagger}$ for cobalt may reflect greater dissociative character (four-coordinate cobalt?) for cobalt.

(iii) Some special observations

The implications of ligand effects on solvent exchange kinetics for substitution processes have been recently discussed by Hewkin and Prince[2]. Although most of the data cited here were not available to them their general conclusions are not particularly altered. The observation of more than one water-exchange rate in the Ni(II)-tren and NTA systems does, of course, require some new thought concerning substitution in the relevant complexes.

Margerum et al.[3] have revised the substitution data using ammonia to replace bound water in nickel. Treating the observed substitution rate constant as a product of an outer-sphere constant and the rate constant for water exchange they estimate "k_1" values which can be compared with the ^{17}O NMR results. These are as follows (^{17}O NMR result given first): for $Ni(H_2O)_4en^{2+}$ 4.4×10^5, 1.8×10^5; for $Ni(H_2O)_2en_2{}^{2+}$ 5.4×10^6, 2.1×10^8, for $Ni(H_2O)_3dien^{2+}$ 1.2×10^6, 8.6×10^5, for $Ni(H_2O)_2trien^{2+}$ 3.8×10^6, 3.6×10^6, for $Ni(H_2O)_3tren^{2+}$ 7×10^5 and 6×10^4, 7.8×10^6. The agreement is about as good as usually found except for the en_2 case. A similar result is found for terpyridine substituting on $Ni(H_2O)_3terpy^{2+}$ where the usual estimate of k_1 is 100–200 times too large[15].

The shift data for the ^{17}O resonance in bulk water for Ni(II) and Co(II), but not VO^{2+}, solutions imply fairly constant A/h values (for a constant μ_{eff}) for metal–oxygen coupling regardless of substitution in octahedral species. The main exceptions appear to be

$Ni(H_2O)_5Cl^+$ and $Ni(H_2O)_2(bipy)_2{}^{2+}$; however, these values may not be well-determined An important implication is that at least an approximate idea of the number of bound water molecules in a species can be obtained from such shift measurements Earlier Morgan et al [16] had made use of the assumption of constant A/h to obtain equilibrium data. The $Ni(H_2O)EDTA^{2-}$ species has received, in this way, strong support in our high pH studies. A shift in the $^{17}OH_2$ resonance at high pH was observed and using Higginson and Samuels[17] results for the abundance of the species a "normal" A/h value is obtained suggesting an octahedral complex with one unprotonated acetate arm replaced by a water molecule

In the nickel–tren system, the existence of two forms has been reported[18] A minor species at 25°C suggested to be planar is postulated in addition to the normal octahedral one. In our work, ^{17}O shift measurements at high temperature do show an abnormal decrease consistent with the endothermic formation of a slow-exchanging or diamagnetic species. Again, shift measurements have promise of revealing more detail on the nature of species present in solution.

The ligand tren appears to bind in four coordination positions to nickel(II) It is easily seen from models that the two remaining water molecules are not structurally equivalent. Discovery of two water-exchange rates is perhaps not surprising in view of the earlier observations[10] on nitrilotriacetate but is still a rarity The substitution of NH_3 [3] appears to be for the more rapidly exchanging water as would be expected

A subject of some importance which has not received much experimental attention concerns equilibria such as

$$Ni(H_2O)_5Cl^+ + H_2O \rightleftharpoons Ni(H_2O)_6{}^{2+} + Cl^-$$

By use of NMR methods, exchange kinetics for both free H_2O and Cl^- can be determined[19]. If *only* the above process occurs, water and chloride exchange must follow the same kinetics in detail In this particular case, and the similar $Ni(H_2O)_2(NCS)_4{}^{2-}$ system[20] the situation is more complicated than a single replacement equilibrium permits The question of direct ligand replacement can be studied if suitable systems can be found. Preferably, only a single metal ion species should be present

D. CONCLUSION

A significant amount of water-exchange data now exists and it can be understood approximately in conventional terms. The nechanisms for exchange are not proven and the order with respect to solvent remains unknown It clearly is desirable to obtain more precise activation parameters for exchange as well as for net substitution processes Comparisons between different metals give promise of revealing some unexpected results. In addition to kinetic information, the ^{17}O NMR methods can be very helpful in understanding the nature of partially substituted aquo ions and their solutions

ACKNOWLEDGEMENTS

The studies made at Washington State University were made possible by generous support from the U.S. Atomic Energy Commission, the Washington State University Research Committee, and the National Science Foundation through an Institutional Grant.

REFERENCES

1 T R. Stengle and C H Langford, *Coord. Chem. Rev* 2 (1967) 349, E.F. Caldin, *Fast Reactions in Solution*, Blackwell, Oxford, 1964.
2 D J. Hewkin and R H Prince, *Coord. Chem Rev* . 5 (1970) 45, A. McAuley and J. Hill, *Quart Rev.*, 23 (1969) 18
3 J.P. Jones, E J Billo and D W Margerum, *J Amer Chem. Soc* , 92 (1970) 1875 and references therein.
4 T.J. Swift and R E Connick, *J Chem Phys.*, 37 (1962) 307, 41 (1964) 2553
5 (a) R Murray, H.W. Dodgen and J P Hunt, *Inorg Chem.*, 3 (1964) 1576;
(b) H H. Glaeser, H.W Dodgen and J P Hunt, *Inorg Chem.*, 4 (1965) 1061.
6 N.S. Angerman and R B. Jordan, *Inorg Chem.*, 8 (1969) 1824
7 H.H. Glaeser, G A Lo, H.W Dodgen and J P. Hunt, *Inorg Chem* , 4 (1965) 206.
8 K. Wuthrich and R E Connick, *Inorg Chem* , 6 (1967) 583, 7 (1968) 1377.
9 M Grant, H W. Dodgen and J P. Hunt, *J Amer Chem Soc* , 91 (1969) 6318
10 R.E Connick, private communication
11 A G. Desai, H.W. Dodgen and J.P Hunt, *J Amer Chem Soc* , 92 (1970) 798
12 S Funahashi and M. Tanaka, *Inorg Chem* , 8 (1969) 2159.
13 J.O. Edwards, *J Amer. Chem. Soc.*, 78 (1956) 1819.
14 P. Hoggard, *Ph D Thesis*, Washington State University, 1970
15 R H. Holyer, C D Hubbard, S F A. Kettle and R.G. Wilkins, *Inorg Chem.*, 5 (1966) 622.
16 A H Zeltman, N A Matwiyoff, and L O Morgan, *J Phys Chem.*, 72 (1968) 121.
17 W.C E. Higginson and B. Samuel, *J. Chem Soc* , (1970) 1579
18 R.G. Wilkins, R. Yelin, D W. Margerum and D C Weatherburn, *J Amer. Chem. Soc.*, 91 (1969) 4326
19 S.F. Lincoln, F. Aprile, H W. Dodgen and J P. Hunt, *Inorg Chem.*, 7 (1968) 929.
20 R B Jordan, H W. Dodgen, and J P. Hunt, *Inorg. Chem* , 5 (1966) 1906.
21 M. Grant, H.W. Dodgen and J.P. Hunt, *Inorg. Chem.*, 10 (1971) 71.
22 A.H. Zeltman, N A. Matwiyoff and L.O. Morgan, *J. Phys. Chem.*, 73 (1969) 2689.
23 T.J. Swift and R.E. Connick, *J. Chem. Phys.*, 37 (1962) 307.
24 R.E. Connick and D. Fiat, *J. Chem. Phys.*, 44 (1966) 4103.
25 A.G. Desai, H.W. Dodgen, and J.P. Hunt, *J. Amer. Chem. Soc.*, 91 (1969) 5001.
26 D. Rablen and G. Gordon, *Inorg. Chem.*, 8 (1969) 395.
27 M. Grant, H.W. Dodgen and J.P. Hunt, *J. Amer. Chem. Soc.*, 92 (1970) 2321.
28 D.P. Rablen, unpublished work in these laboratories.
29 M. Grant, H.W. Dodgen and J.P. Hunt, *Chem. Commun.*, (1970) 1446.