[Ir(PPh$_3$)$_2$(NO)$_2$][18] complexes have Ir–N–O angles of 124, 125, and 164°; yet these iridium compounds have N–O infrared absorptions at 1680, 1720, and 1715–1760 cm^{-1},[19] respectively. Also, Enemark[20] recently found that the Ni–N–O angle and the N–O infrared peak in Ni(PPh$_3$)$_2$(NO)N$_3$, which was prepared from Feltham's Ni(PPh$_3$)$_2$(NO)Cl,[4] are 153° and 1710 cm^{-1}, respectively.

Since the infrared and electronic spectra and the magnetism on the [Ni(triphosphine)(NO)]$^+$ cations did not provide a definitive interpretation about the nature of these complexes, Eller and Corfield[21] determined the structure of [Ni(tep)(NO)]BF$_4$. The cation, shown in Figure 2, has a C_3 axis, and the nickel atom is surrounded in a pseudotetrahedral fashion by three phosphorus atoms and a linearly bonded nitrosyl group. The Ni–N distance, 1.58 (1) Å, is very short as compared to other M–N distances involving first transition series metal nitrosyls, which usually have M–N distances in the range 1.70–1.80 Å.[17,22] The short Ni–N bond in [Ni(tep)(NO)]$^+$ signifies a large

amount of multiple-bond character in the Ni–NO linkage and is much more consistent with NO$^-$ than with a NO$^-$ group.[10,23] The pseudotetrahedral geometry around nickel, the short Ni–N bond, and the diamagnetism of the complex all favor a formulation of the metal as Ni(0) and the nitrosyl group as NO$^+$.

The [Ni(tpp)NO]$^+$ and [Ni(tep)NO]$^+$ cations are isoelectronic with Ni[P(OC$_2$H$_5$)$_3$]$_4$,[24] Ni(CO)$_4$, and Co(CO)$_3$NO.[16] The two nickel(0) complexes are colorless, whereas Co(CO)$_3$NO is red, similar to the [Ni(triphosphine)NO]$^+$ compounds. As the [Ni(tpp)-NO]$^+$, [Ni(tep)NO]$^+$, and Co(CO)$_3$NO complexes all contain a d^{10} electronic configuration, the deep red colors exhibited by these complexes must arise from an M → NO charge transfer or from an n → π^* transition within the NO group.[25]

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Solvent Effects in Coordination Kinetics. II. Outer-Sphere Effects in Solvent–Ammonia Exchange on Nickel(II) in Methanol–Water Mixtures[1]

By F. R. SHU and D. B. RORABACHER*

The temperature-jump relaxation method has been used to study the kinetics of solvent–ammonia exchange on Ni(II) as a function of methanol–water solvent composition. In this study inner-sphere effects have been minimized by complexing the nickel ion with a quinquedentate ligand leaving only one coordination site available for exchange. As studied at 25°, $\mu = 0.3$ *M*, both the anation and solvation rate constants are observed to increase with increasing methanol content of the solvent, the increases being particularly dramatic as anhydrous methanol is approached. The results do not correlate to previously proposed structural properties of the bulk solvent but can be accounted for by changes in the inner- and outer-sphere composition. The simplest interpretation which accounts for the formation (anation) rate constant trend indicates that this rate constant is directly related to the distribution of the two species containing either water or methanol at the sixth coordination site with methanol being 10–20 times more labile than water as a leaving group. To explain the trend in the dissociation (solvation) rate constant, however, it is concluded that significant solvent matrix effects exist. The observed behavior is shown to be consistent with a model in which the outer-sphere solvation shell is preferentially occupied by water molecules while methanol exerts a stronger influence than water in assisting the dissociation of the nickel–ammonia bond. Either a "pull" mechanism or a "push" mechanism may be used to explain the observed phenomena with some preference being given to the former process.

Introduction

A decade ago Eigen first demonstrated that ligand substitution reactions on octahedrally solvated metal ions proceed by a dissociative mechanism.[2] In the intervening years much additional evidence has been gathered to support the hypothesis that the rupture of a

metal–solvent bond represents the rate-determining step in nearly all such reaction processes.[3,4]

Despite the broad implications of the dissociative mechanism for any ligand–solvent exchange process involving octahedral metal ions, the vast majority of definitive kinetic studies have been carried out in aqueous solution.[3,4] More recently several related studies have been carried out in other coordinating solvents

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resulting in the general conclusion that the dissociative mechanism is applicable to these solvent systems as well.[1,5–10] However, an extensive comparison by Bennetto and Caldin of the kinetics of the Ni(II)–bipy reaction with the kinetics of solvent–solvent exchange in a wide variety of pure nonaqueous solvents has led to the suggestion that solvent structural effect also play a major role in governing ligand-exchange rates.[8] Based on the comparative data, these workers have proposed a detailed model—involving a concerted rearrangement of the surrounding solvent molecules—to account for the manner in which structural effects contribute to the substitution process.[8b]

In a correlated study, Bennetto and Caldin also investigated the kinetics of the Ni(II)–bipy reaction in mixed methanol–water solvents.[9] The resulting trend in the formation rate constant has again been phrased in terms of the solvent structure. However, this interpretation contrasts sharply with our recent study on the Ni(II)–NH₃ reaction in the same mixed solvents

$$NiS_6{}^{2+} + NH_3 \underset{k^{Ni-NH_3}}{\overset{k_{Ni}{}^{NH_3}}{\rightleftharpoons}} Ni(NH_3)S_5{}^{2+} + S \qquad (1)$$
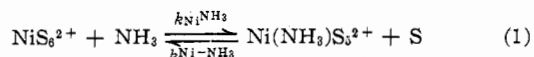
where the observed formation rate constant behavior was attributed to inner coordination sphere effects as the coordinated solvent molecules, S, changed in stepwise fashion from water to methanol.[1]

Our interpretation was largely influenced by the observation that the formation rate constant for reaction 1 exhibited a pronounced maximum at 80–85 wt % methanol, quantitatively paralleling the fractional concentration of the mixed-solvated species $Ni(H_2O)_5$-$(CH_3OH)^{2+}$ as determined by an independent solvation study. The exceptional lability of this solvated species relative to all others led to the formulation of a general hypothesis regarding inner-sphere effects upon the six-coordinate ground state relative to the presumed five-coordinate transition state. This interpretation appears to be supported by subsequent studies in which corresponding behavior has been observed for reactions involving other ligands[11a] and other metal ions (*viz.*, Co(II)[11b]) in methanol–water mixtures.

A comparison of the kinetic results obtained from the ammonia[1] and bipyridyl[9] studies reveals both distinct similarities and intriguing differences. Thus, whereas the formation rate constants for both mono complexes decrease notably in the region 90–100 wt % (83–100 mol %) methanol, the dramatic increase in the region of 50–85 wt % (35–75 mol %) methanol noted for the ammonia reaction is replaced by a plateau in the bipyridyl system.

The selection of ammonia as the ligand for our previous study[1] was motivated by the desire to avoid steric as well as electrostatic effects.[12,13] In view of

recent studies in this laboratory on steric effects in coordination kinetics[13,14] it is tempting to conclude that the differing behavior of the bipyridyl reaction may be attributable to complicating steric factors associated with this bulky ligand, perhaps even involving a shift of the rate-determining step to the point of the second coordinate-bond formation.[14] Considering the vast quantity of nonaqueous kinetic data assimilated by Bennetto and Caldin using the bipyridyl ligand (as well as the more limited results of Pearson and Ellgen[5]) which has formed the basis of their proposed model on solvent structural effects, the implications of this latter suggestion are of such magnitude that a more definitive investigation on the influence of methanol–water solvents upon ligand substitution behavior at the Ni(II) ion would appear to be a matter of exceptional importance.

In the present study an attempt has been made to minimize inner-sphere effects so that the influence of the bulk solvent may be isolated. To that end, a quinquedentate ligand has been complexed to the Ni(II) ion leaving a single coordination site available for solvent–ammonia exchange

$$NiZS + NH_3 \underset{k^{NiZ-NH_3}}{\overset{k_{NiZ}{}^{NH_3}}{\rightleftharpoons}} NiZ(NH_3) + S \qquad (2)$$
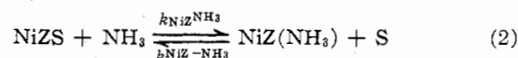
where Z represents the quinquedentate ligand. The choice of an appropriate quinquedentate ligand was guided largely by the need to obtain a strongly complexing agent whose exchange would not compete with that of ammonia. The use of a strongly complexing polyamine such as tetraethylenepentamine (tetren) was ruled out on the basis that ammonia exchange on the resultant $Ni(tetren)^{2+}$ complex is apparently too fast to observe even with the temperature-jump relaxation method employed.[15] Based on available aqueous data for ammonia exchange kinetics on Ni(II) complexes,[15,16] N-hydroxyethylethylenediamine-N,N',N'-triacetate ion (HEEDTA) was employed as the complexing quinquedentate ligand.

The results obtained indicate that both the formation and dissociation rate constants for ammonia exchange on the Ni^{II}–HEEDTA complex increase as the methanol content of the solvent is increased. This behavior is in dramatic contrast to that observed for both ammonia and bipyridyl exchange on the hexasolvated Ni(II) ion[1,9] indicating that the earlier studies were, in fact, largely influenced by inner-sphere effects as we previously proposed. Whereas the presence of significant solvent matrix effects are indicated in the present study—particularly upon the dissociation reaction in highly methanolic solvents—these effects appear to be much different from the structural effects suggested by Bennetto and Caldin in the mixed solvents. The possible source of these effects and their implications for the preceding studies are considered.

Experimental Section

Reagents.—Acidified HEEDTA, obtained as reagent grade crystals (LaMont Laboratory, Dallas, Tex.), was recrystallized from hot ethanol–water. Stock solutions of the Ni^{II}–HEEDTA complex were prepared by dissolving a stoichiometric weighed

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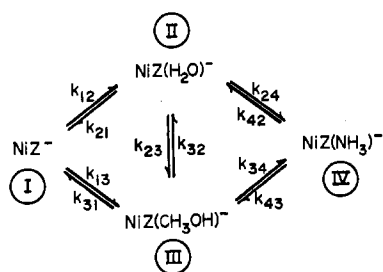
Figure 1.—Schematic representation of the five coupled reactions considered in treating the Ni(II)–HEEDTA–NH$_3$ system where Z represents the HEEDTA anion and species I represents the sexadentate Ni(HEEDTA)$^-$ complex ion.

amount of HEEDTA in a standard Ni(ClO$_4$)$_2$ solution. Reagent grade ammonium perchlorate, used as the source of NH$_3$ in solution, was recrystallized once from deionized water maintaining the solution under 75° to prevent decomposition. All other reagents were identical with those used in the previous study.[1]

Kinetic Measurements.—All methanol–water solvents were prepared on a weight per cent basis and are so reported in the remainder of this paper. Acidity measurements were made using the nonaqueous pH* scales of deLigny and coworkers,[17] appropriate to each solvent composition, as previously described.[18] Ionic strength was maintained at 0.3 M using NaClO$_4$. The temperature-jump relaxation spectrometer previously described[1,13] was used for all kinetic relaxation measurements with the final temperature achieved being calibrated at 25.0 ± 0.2°. All relaxation times in this study were within the time interval before the onset of internal convection.

Results

The absorbance change accompanying the temperature-induced shift in equilibrium 2 was too small to measure directly. Therefore, as in earlier temperature-jump studies involving solvent–ammonia exchange on Ni(II),[1,12,13,15,16] reaction 2 was coupled to an acid-base indicator, HIn, *via* the ammonia–hydrogen ion equilibrium

$$H^+ + NH_3 \xrightleftharpoons{K_H} NH_4^+ \qquad (3)$$

$$H^+ + In^- \xrightleftharpoons{K_I} HIn \qquad (4)$$
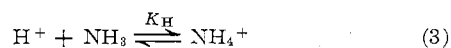
and the change in the In$^-$ concentration was monitored spectrophotometrically. With the indicators used in this study, reactions 3 and 4 are sufficiently rapid to be considered in equilibrium at all times relative to reaction 2.

Consideration of the exchange of water and methanol at the sixth coordination position of NiZS$^-$ and the possibility of coordination by the hydroxyethyl group of HEEDTA to produce the sexadentate complex NiZ$^-$ yield the reaction scheme depicted in Figure 1 which indicates the possibility of five coupled relaxations. Since the indicator being monitored is coupled to ammonia according to reactions 3 and 4, however, interconversion among species I, II, and III will not be detected directly. Furthermore, as discussed in the previous study,[1] it may be assumed that the interconversion among these three species is very rapid relative to substitution by ammonia (except in solvents nearly depleted in one solvent component) so that these species may be considered to be in rapid equilibrium. Thus the single observed relaxation is presumed to represent the sum of reactions II → IV and

III → IV. (Note that the interconversion I → IV is statistically unfavorable[19] and is not considered.) The kinetic behavior of this observed relaxation is consistent with the rate equation

$$\frac{d[NiZ(NH_3)^-]}{dt} = k_{NiZ}{}^{NH_3}[NiZS^-][NH_3] - k^{NiZ-NH_3}[NiZ(NH_3)^-] \qquad (5)$$

The corresponding relaxation equation can be represented as[12]

$$1/\tau = k_{NiZ}{}^{NH_3}\left\{\frac{[\overline{NiZS}]}{1 + \alpha} + [\overline{L}]\right\} + k^{NiZ-NH_3} \qquad (6)$$

where τ represents the relaxation time, $[\overline{NiZS}]$ and $[\overline{L}]$ represent the equilibrium concentrations of NiZS$^-$ and NH$_3$, respectively, and α represents the rate of change in concentration of free, unprotonated ammonia relative to the change in concentration of NiZS$^-$ as previously defined.[1,12,13]

An iterative computer program with the χ^2 error treatment was employed to calculate the formation and dissociation rate constants from experimental relaxation times.[20] Since equilibrium constant values for reaction 2 are not available (other than in aqueous solution[21]), the values initially inserted for $[\overline{NiZS}]$ and $[\overline{L}]$ in solving eq 6 were based on the assumption that the amount of mixed complex formed was negligible. The rate constant values calculated in this manner were then used to approximate an equilibrium constant value ($K_{NiZL} = k_{NiZ}{}^{NH_3}/k^{NiZ-NH_3}$), which allowed a recalculation of $[\overline{NiZS}]$ and $[\overline{L}]$. The iterative process was continued until successive K_{NiZL} values were constant to within 1%.

Mixed-mode protonation constants for ammonia ($K_H{}^{m*} = [NH_4^+]/a_H{}^*[NH_3]$) at 0.3 M ionic strength were determined by potentiometric titration as previously described.[18] Although the values obtained in intermediate methanol–water solvent compositions showed a general lack of reproducibility[22] and appear to be somewhat low (perhaps due to the use of a different glass electrode), this matter was not pursued further after calculations established that the use of protonation constant values differing by 0.3 log unit (the maximum error presumed in these values[22]) did not affect the final resolved rate constants by more than 10% which represents the approximate level of error inherent in the temperature-jump measurements themselves. The experimentally obtained protonation constants actually used in the calculations are listed in Table I. Also listed are mixed-mode protonation con-

Table I

MIXED-MODE PROTONATION CONSTANTS FOR AMMONIA AND SULFONPHTHALEIN INDICATORS USED IN THIS STUDY AT 25°, $\mu = 0.3$ M (NaClO$_4$)

[CH$_3$OH], wt %	Log $K_H{}^{m*}$	Log $K_I{}^{m*}$	[CH$_3$OH], wt %	Log $K_H{}^{m*}$	Log $K_I{}^{m*}$
0	9.24	7.8^b	80	8.73	7.2^e
25	9.05	8.1^b	90	9.11	7.8^e
50	8.68	7.3^c	95	9.73	8.3^e
65	8.63	6.8^d	99	10.57	9.2^e
70	8.65^a	6.9^e			

^{a} Interpolated value. ^{b} Phenol Red. ^{c} Bromothymol Blue. ^{d} Bromocresol Purple. ^{e} Chlorophenol Red.

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TABLE II

KINETIC RELAXATION DATA FOR THE Ni(HEEDTA)(S)⁻⁻–NH₃ SYSTEM AT 25°, $\mu = 0.3\ M$ (NaClO₄)

C_M, mM	C_L, mM	X, mM	pH*	$1/\tau$, sec⁻¹	C_M, mM	C_L, mM	X, mM	pH*	$1/\tau$, sec⁻¹
		0% CH₃OH					70% CH₃OH		
106.8	44.1	94.5	7.81	87.0	54.1	26.8	48.4	7.03	115.0
85.4	44.1	75.5	7.80	68.0	48.7	26.8	43.5	7.05	101.0
74.8	44.1	67.2	7.69	59.0	40.1	26.8	35.5	7.10	88.0
64.1	44.1	57.1	7.75	54.0	33.8	26.8	29.9	7.12	77.0
53.4	44.1	47.1	7.82	44.0	24.3	26.8	21.3	7.20	57.0
42.7	44.1	38.0	7.78	36.0	16.2	26.8	14.4	7.21	43.0
32.0	22.0	29.7	7.87	31.0	10.8	13.4	10.2	7.09	33.0
27.8	22.0	25.9	7.87	27.0	5.4	13.4	5.3	7.08	21.0
21.4	22.0	20.2	7.81	24.0			80% CH₃OH		
10.7	22.0	10.5	7.92	15.0	41.4	21.8	36.8	7.18	124.0
		25% CH₃OH			37.3	21.8	33.3	7.15	112.0
82.9	42.1	69.1	7.91	57.0	33.2	21.8	29.7	7.13	103.0
74.5	42.1	63.5	7.79	55.0	29.0	21.8	25.8	7.19	92.0
66.2	42.1	54.4	7.95	49.0	24.9	21.8	22.3	7.16	78.0
57.9	42.1	47.6	7.94	45.0	20.7	21.8	18.2	7.30	66.0
49.6	42.1	42.0	7.82	41.0	16.6	21.8	15.0	7.18	54.0
43.4	21.1	39.3	7.84	37.0	12.4	21.8	11.3	7.17	50.0
33.1	42.1	28.7	7.77	30.0	10.4	10.4	9.7	7.29	45
24.8	42.1	21.8	7.79	23.0	8.3	10.4	7.8	7.31	38.0
16.5	21.1	15.4	7.91	18.0	4.1	10.4	4.1	7.25	21.0
8.3	21.1	8.4	7.94	13.0			90% CH₃OH		
		50% CH₃OH			41.0	21.2	38.2	7.64	165.0
58.9	30.0	50.8	7.30	78.0	36.9	21.2	34.5	7.63	160.0
53.0	30.0	45.3	7.34	62.0	32.8	21.2	30.6	7.68	152.0
47.0	30.0	40.3	7.33	71.0	28.7	21.2	26.9	7.66	142.0
41.2	30.0	35.0	7.37	58.0	24.6	21.2	23.2	7.60	117.0
35.3	30.0	30.4	7.30	42.0	20.5	21.2	19.4	7.60	98.0
29.4	30.0	25.4	7.30	43.0	16.4	21.2	15.6	7.69	74.0
23.6	30.0	20.8	7.24	35.0	12.3	21.2	11.9	7.56	83.0
17.8	30.0	15.6	7.37	31.0	8.2	10.6	8.0	7.63	55.0
14.7	15.0	13.5	7.37	26.0	4.1	10.6	4.2	7.72	43.0
11.8	15.0	10.9	7.43	21.0			95% CH₃OH		
5.9	15.0	5.8	7.42	16.0	40.4	18.9	37.2	8.43	184.0
		65% CH₃OH			36.3	18.9	33.9	8.24	177.0
53.1	24.4	48.3	7.00	97.0	32.3	18.9	30.2	8.23	166.0
47.8	24.4	42.6	7.18	72.0	28.3	18.9	26.5	8.26	150.0
42.5	24.4	38.3	7.08	70.0	24.2	18.9	22.7	8.22	137.0
37.2	24.4	33.5	7.10	61.0	20.2	18.9	19.1	8.22	125.0
31.9	24.4	28.8	7.08	58.0	16.1	18.9	15.3	8.25	104.0
26.5	24.4	23.9	7.11	43.0	12.1	18.9	11.6	8.21	85.0
21.2	24.4	19.4	7.04	39.0	8.1	9.5	7.8	8.23	68.0
15.9	24.4	14.5	7.16	30.0	4.0	9.5	4.1	8.31	49.0
10.6	12.2	10.1	7.12	23.0			99% CH₃OH		
13.3	12.2	12.6	7.11	31.0	40.6	20.2	39.0	9.07	219.4
5.3	12.2	5.2	7.17	15.0	36.5	20.2	35.2	9.13	168.6
					32.5	20.2	31.4	9.06	159.8
					28.4	20.2	27.4	9.02	186.0
					24.3	20.2	23.6	9.08	145.8
					20.3	20.2	19.8	9.10	145.6
					16.2	20.2	16.0	9.15	116.7
					12.2	20.2	12.1	9.06	98.2
					8.1	10.1	7.9	8.99	91.0
					4.1	10.1	4.2	9.08	65.1

stants for the acid–base indicators ($K_I^{m*} = [\text{HIn}]/a_H^* \cdot [\text{In}^-]$) used in this study as determined from spectrophotometric data.

The experimentally determined relaxation times for each of the nine solvent compositions studied are listed in Table II. These data are plotted according to eq 6 in Figures 2–4. The formation and dissociation rate constants obtained from these plots are tabulated in Table III with the experimental standard deviations indicated.

The ratio of the aqueous rate constants ($K_{NiZL} = 125\ M^{-1}$) is in good agreement with the experimentally determined equilibrium constant for reaction 2 in aqueous solution ($K_{NiZL} = 100\ M^{-1}$).[21] Since the previously reported study on the aqueous system[16] yielded a

much lower equilibrium constant ($K_{NiZL} = 35\ M^{-1}$), the disagreement in formation rate constant values between that study ($k_{NiZ}^{NH_3} = 2.9 \times 10^2\ M^{-1}\ \text{sec}^{-1}$) and the current work ($k_{NiZ}^{NH_3} = 7.8 \times 10^2\ M^{-1}\ \text{sec}^{-1}$) may stem from the fact that the earlier value is too low,[28] although the theoretical fit generated in the following section indicates that the "correct" value may be intermediate between the two experimentally obtained values.

Discussion

In the previous paper[1] involving the study of reaction 1, where solvent molecules comprise the inner

(23) An independent evaluation has yielded $k_{NiZ}^{NH_3} = 7 \times 10^2\ M^{-1}$ sec⁻¹: L. G. Jambor and D. B. Rorabacher, unpublished results.
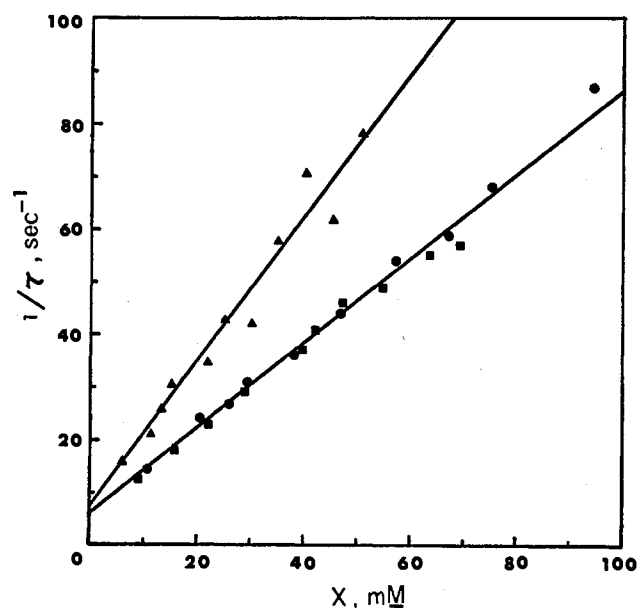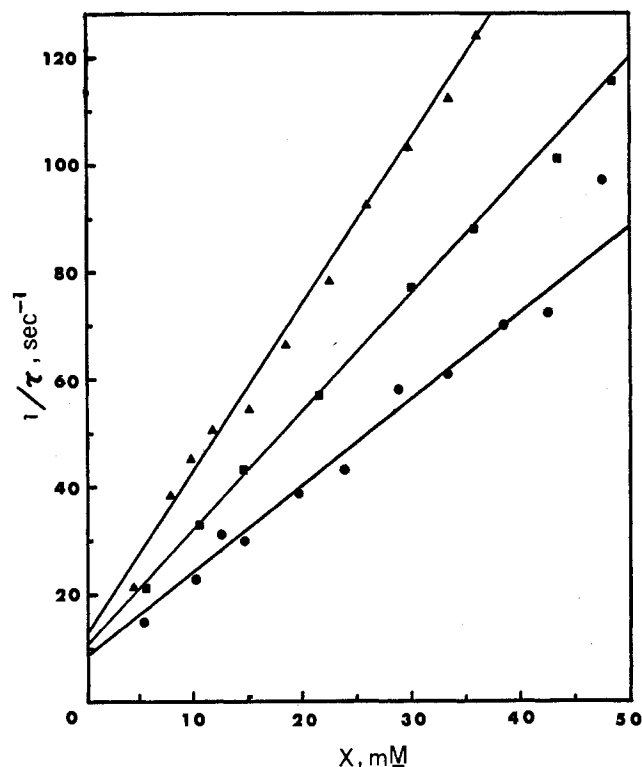
Figure 2.—Plots for the resolution of rate constants for the Ni(II)–HEEDTA–NH$_3$ system at 25°: ●, 0% CH$_3$OH; ■, 25% CH$_3$OH; ▲, 50% CH$_3$OH. (X represents the coefficient for $k_{\text{NiZ}}^{\text{NH}_3}$ in eq 6.)

Figure 4.—Plots for the resolution of rate constants for the Ni(II)–HEEDTA–NH$_3$ system at 25°: ●, 90% CH$_3$OH; ■, 95% CH$_3$OH; ▲, 99% CH$_3$OH. (X represents the coefficient for $k_{\text{NiZ}}^{\text{NH}_3}$ in eq 6.)

TABLE III
FORMATION AND DISSOCIATION RATE CONSTANTS FOR THE Ni(HEEDTA)(NH$_3$)$^-$ COMPLEX IN METHANOL–WATER MIXTURES AT 25°, μ = 0.3M (NaClO$_4$)

[CH$_3$OH], wt %	$10^{-3}k_{\text{NiZ}}^{\text{NH}_3}$, M^{-1} sec^{-1}	$k^{\text{NiZ}-\text{NH}_3}$, sec^{-1}	$K = k_{\text{NiZ}}^{\text{NH}_3}/k^{\text{NiZ}-\text{NH}_3}$, M^{-1}
0	0.78 ± 0.02	6.2 ± 0.6	125
25	0.79 ± 0.02	6.3 ± 0.5	125
50	1.37 ± 0.08	7.5 ± 1.6	183
65	1.58 ± 0.08	8.0 ± 1.4	199
70	2.19 ± 0.04	9.8 ± 0.6	223
80	3.11 ± 0.13	12.8 ± 1.8	242
90	3.63 ± 0.22	25.0 ± 4.6	145
95	4.04 ± 0.13	34.8 ± 2.6	116
99	4.39 ± 0.52	48.0 ± 14.0	91

each solvent composition. The values thus estimated appear to be constant within the large experimental error arising from uncertainties in the equilibrium constant values up to about 90% methanol after which a significant decrease is apparent. The normalized trends for the two rate constants are illustrated in Figures 5 and 6.

Both of these observations are consistent with the previously postulated inner-sphere effects: the substitution of methanol for the stronger water ligand initially provides a more labile leaving ligand for the enhancement of the formation rate but, as additional methanol molecules are incorporated into the inner coordination sphere, the cumulative effect is to destabilize the five-coordinate intermediate (or transition state) relative to the six-coordinate complex ion resulting in a rate *decrease* in both the formation and dissociation processes as the solvent approaches the anhydrous condition.[1]

As illustrated by the normalized plots in Figures 5 and 6, the data for the current study on reaction 2

Figure 3.—Plots for the resolution of rate constants for the Ni(II)–HEEDTA–NH$_3$ system at 25°: ●, 65% CH$_3$OH; ■, 70% CH$_3$OH; ▲, 80% CH$_3$OH. (X represents the coefficient for $k_{\text{NiZ}}^{\text{NH}_3}$ in eq 6.)

coordination sphere, the value of the formation rate constant was reported to pass through a maximum value in the region of 80–85% methanol. The rate constant then decreased sharply as anhydrous methanol was approached. Although the dissociation rate constants were not obtained directly in that study, approximate values can be calculated from the formation rate constants and equilibrium constants reported for
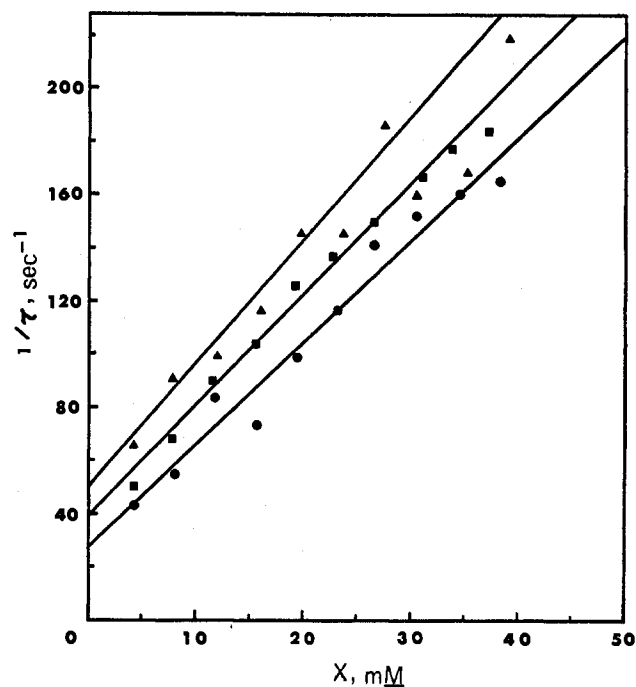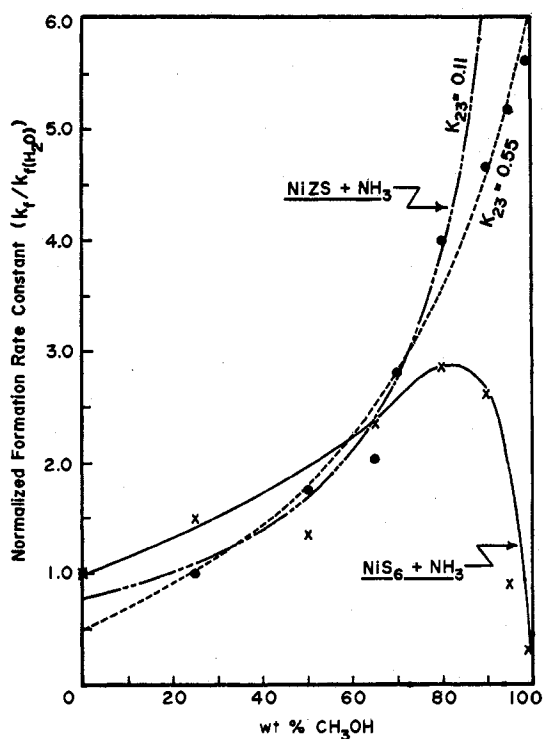
Figure 5.—Normalized plots of the formation rate constants for NiZS$^-$ and NiS$_6$$^{2+}$ reacting with ammonia at 25° as a function of solvent composition in methanol–water mixtures. Upper curves represent theoretical fits to the NiZS$^-$ experimental data according to eq 10 using the solvation equilibrium constants indicated: ●, NiZS$^-$ data from this study; ×, NiS$_6$$^{2+}$ data from ref 1.
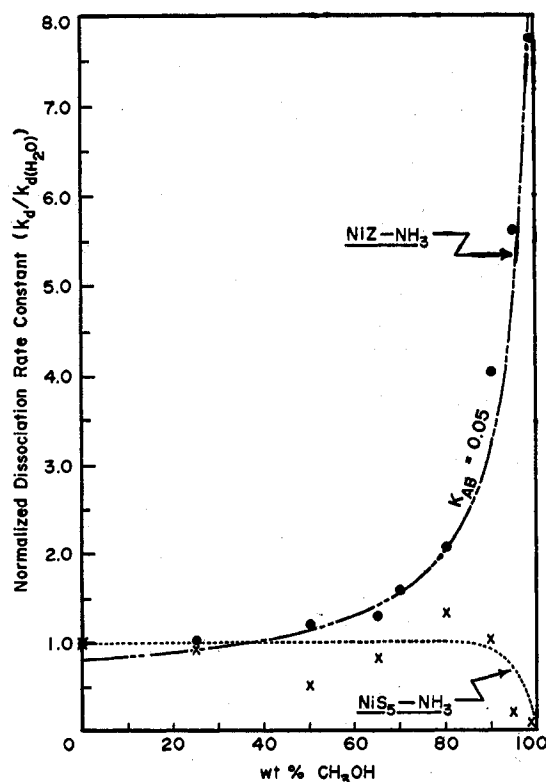

Figure 6.—Normalized plots of the dissociation rate constants for NiZ(NH$_3$)$^-$ and Ni(NH$_3$)S$_5$$^{2+}$ at 25° as a function of solvent composition in methanol–water mixtures. The upper curve represents the iterated fit to the NiZ(NH$_3$)$^-$ experimental data according to eq 13: ●, NiZ(NH$_3$)$^-$ data from this study; ×, Ni(NH$_3$)S$_5$$^{2+}$ data from ref 1.

show an *increase* in both the formation and dissociation rate constants as the percentage of methanol in the solvent is increased. Thus, with an inner-sphere composition which is presumed to be constant, *the dominant trends in highly methanolic solvents are opposite to those observed in the previous work.*

The dramatic contrast in behavior between the two studies reemphasizes the marked influence of the inner sphere upon the rate constants for solvent–ammonia exchange on the hexasolvated Ni(II) ion as noted in the previous study. The behavior of the formation rate constant observed in this study may also be attributable to changes in the solvent species occupying the sixth coordination site. The trend in the dissociation rate constant illustrated in Figure 6, however, gives strong evidence that solvent matrix effects are also operative in these reactions. The implications of these observations are examined below.

Structure of the Ni^{II}-HEEDTA Complex.—The trends observed in the current study cannot be presumed to be entirely free of inner-sphere effects unless HEEDTA acts consistently as a quinquedentate ligand in all solvent compositions. Therefore, the structure of the Ni^{II}-HEEDTA complex is of considerable importance.

Although no direct structural study of the Ni^{II}-HEEDTA complex in solution has been reported, the extent of bonding in this complex can be inferred from the results of related studies on metal complexes of ethylenediamine-N,N,N',N'-tetraacetate ion (EDTA). For the Ni^{II}-EDTA complex, an X-ray crystallographic study indicates that EDTA acts as a quinquedentate ligand having one uncomplexed acetato group, with a water molecule occupying the sixth coordination site.[24] This structure, which probably remains unchanged in solution,[25] is rationalized by considering the relief in steric strain which results from having one unbonded acetato group.[26] Since a nickel–alcoholic oxygen bond is weaker than a nickel–carboxylic oxygen bond, it is generally considered that, for Ni^{II}-HEEDTA in aqueous solution, the alcoholic oxygen remains unbonded to the Ni(II) ion.[27]

If HEEDTA were to retain less than five-coordinate bonds to the Ni(II) ion on a time-averaged basis, the kinetics of solvent–ammonia exchange might not be greatly affected since it has already been suggested that the influence of water and carboxylic oxygen upon the lability of other coordinated donor atoms is relatively equivalent.[16,28] Thus, in predominantly aqueous solvents, the rate of solvent–ammonia exchange should be roughly equivalent whether HEEDTA acts as a quadridentate or quinquedentate ligand.

Furthermore, if a quadridentate chelate complex were prevalent, the eventual inclusion of methanol into a nonexchanging coordination site should have the effect

(24) G. S. Smith and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 556 (1959).

(25) R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); **37**, 1326 (1965).

(26) Similar behavior has been observed even when stronger donor atoms are placed in the terminal positions; thus, for the sexadentate ligand $N,N,-N',N'$-tetrakis(2-aminoethyl)ethylenediamine (penten), one terminal nitrogen is much more easily detached from Ni(II) than is the case for the corresponding ligand N,N,N',N'-tetrakis(2-aminoethyl)-1,3-diaminopropane (ptetraen) where steric strain has been relieved: P. Paoletti, R. Walser, A. Vacca, and G. Schwarzenbach, *Helv. Chim. Acta*, **54**, 243 (1971).

(27) *E.g.*, T. J. Bydalek and D. W. Margerum, *Inorg. Chem.*, **2**, 678 (1963).

(28) H. Hoffmann, personal communication.

of decreasing both the formation and dissociation rates based on the conclusions of the previous study.[1] Since this is opposite to the trends observed in Figure 6, it is concluded that any inner-sphere effects resulting from the contribution of a quadridentate species to the exchange rates are swamped out by other influences and this species is disregarded in the subsequent discussion.

As the methanol content of the solvent is increased, the tendency for HEEDTA to act as a sexadentate ligand may also be enhanced.[29] Since the dissociation rate is observed as a first-order process, the k^{NiZ-NH_3} values should be unaffected by the presence of a sexadentate complex. However, by lowering the concentration of the available $NiZS^-$ species, the formation of sexadentate NiZ^- (species I in Figure 1) should cause a net decrease in the observed second-order formation rate constant. Therefore, the existence of this latter species is considered in discussing the formation rate behavior.

Solvent Effects on the Formation Rate Constant.—As suggested earlier, the observed formation rate constant in each solvent composition must surely be a function of the solvent species occupying the sixth coordination site. If no other effects were present, the formation rate could be represented by the sum of the processes designated by the rate constants k_{24} and k_{34} in Figure 1, *viz.*

$$k_{NiZ}^{NH_3}[NiZS^-][NH_3] = k_{24}[NiZ(H_2O)^-][NH_3] + k_{34}[NiZ(CH_3OH)^-][NH_3] \quad (7)$$
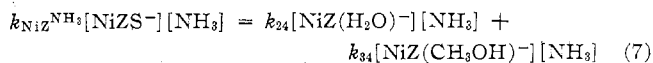
Defining the thermodynamic solvation equilibrium constant between species II and III (Figure 1) as

$$K_{23} = \frac{[NiZ(CH_3OH)^-][H_2O]}{[NiZ(H_2O)^-][CH_3OH]} = K_{23}'\frac{[H_2O]}{[CH_3OH]} \quad (8)$$

and establishing the material balance condition

$$[NiZS^-] = [NiZ(H_2O)^-] + [NiZ(CH_3OH)^-] \quad (9)$$

(in which the sexadentate species is assumed negligible) yields the derivation

$$k_{NiZ}^{NH_3}(1 + K_{23}') = k_{24} + k_{34}K_{23}' \quad (10)$$

If the substitution process is truly dissociative in nature and the rupture rates for the nickel–solvent bonds are unaffected by changes in the solvent environment (*i.e.*, k_{24} and k_{34} are independent of solvent composition), eq 10 predicts a linear relationship between the terms $k_{NiZ}^{NH_3}(1 + K_{23}')$ and K_{23}'. Unfortunately, it has not proved possible to determine a reliable value for K_{23} (and hence K_{23}') experimentally. A consideration of the statistical differences in solvent exchange on $NiZS^-$ and the hexasolvated Ni(II) ion leads to the approximation $K_{23} \approx 0.11$[30] *if it can be assumed that the inner-sphere influence exerted by HEEDTA does not greatly alter the relative preference of Ni(II) for water over methanol as a ligand.*

Using this K_{23} value, a linear plot of eq 10 is obtained for the experimental formation rate constant data over the solvent range 0–80% methanol as illus-
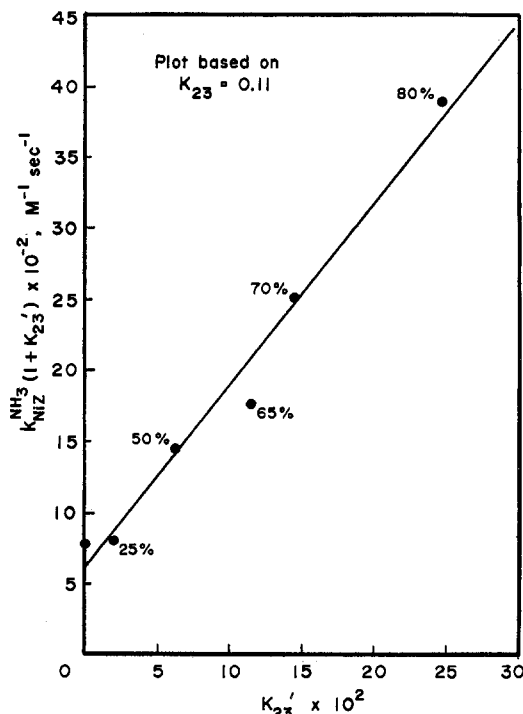
(29) Note, *e.g.*, that many strained chelate compounds which are unstable in water can be prepared by using alcoholic solvents: P. Pfeiffer and E. Lubbe, *J. Prakt. Chem.*, **136**, 321 (1933); P. Pfeiffer, *Naturwissenschaften*, **35**, 190 (1948).

(30) This value is calculated as $K_{23} = K_1'/6$ where the latter constant is defined as $K_1' = [Ni(H_2O)_5(CH_3OH)^{2+}][H_2O]/[Ni(H_2O)_6^{2+}][CH_3OH]$ and has been evaluated from spectrophotometric measurements as $K_1' = 0.66$.[1]

Figure 7.—Plot for the resolution of the individual formation rate constants for $NiZ(H_2O)^-$ and $NiZ(CH_3OH)^-$ reacting with ammonia based on eq 10 using $K_{23} = 0.11$.

trated in Figure 7 while the values for 90, 95, and 99% methanol show marked deviations. The resolved rate constants calculated by the least-squares method from this plot are $k_{24} = 6.1 \times 10^2$ and $k_{34} = 12.8 \times 10^3 M^{-1}$ sec^{-1}. (Interestingly, the resulting ratio of k_{34}/k_{24} is almost identical with the corresponding nickel–methanol and nickel–water bond rupture rate constants calculated in the preceding study[1] where water molecules comprised the inner sphere, which might be interpreted as lending credibility to the assumption made above that HEEDTA does not greatly alter the relative rates.)

The marked deviations of the experimental formation rate constants determined in 90, 95, and 99% methanol solvents from the linear relationship established in Figure 7 may be attributable to the formation of the sexadentate species NiZ^- in accordance with the preceding discussion on the structure of the Ni^{II}–HEEDTA complex. On the other hand, the premise that the value of K_{23} for Ni^{II}–HEEDTA differs from the corresponding constant for the solvated Ni^{II} ion only by a statistical factor may be open to question—particularly since the inner-sphere influence of coordinated HEEDTA upon the dissociation of the Ni–H_2O and Ni–NH_3 bonds does not appear to be equivalent.[16]

By arbitrarily selecting K_{23} values in increments of 0.05 unit, it is found that a "best fit" to the entire set of formation rate constant data is obtained for $K_{23} = 0.55$. The associated resolved rate constant values are then $k_{23} = 4.0 \times 10^2 M^{-1}$ sec^{-1} and $k_{34} = 4.7 \times 10^3 M^{-1}$ sec^{-1}.

The theoretical fit to the experimental formation rate constant data is illustrated in Figure 5 using both sets of resolved constants. The fit obtained using the latter set of constants is sufficiently good to support the conclusion that there is no apparent real evidence of a sexadentate species in significant concentrations.

Although the influence of outer-sphere and bulk solvent effects upon the formation rate constant cannot be ruled out—particularly in the highly methanolic solvents—the foregoing discussion indicates that a consistent interpretation of the experimental data can be formulated without invoking matrix effects. This stands in sharp contrast to the dissociation rate behavior as discussed below.

Solvent Effects on the Dissociation Rate Constant.— As depicted in Figure 1, the dissociation rate constant obtained experimentally represents the same bond-rupture process in all solvent compositions regardless of the nature of the incoming ligand. If reaction 2 is predominantly dissociative in nature, the dramatic increase in the dissociation rate constant in 70–99% methanol leads to the unavoidable conclusion that solvent matrix effects are involved since it has already been established that feasible variations in the degree of coordination by HEEDTA (*i.e.*, quadridentate bonding) cannot account for the observed trends.

It is readily demonstrated that a direct relationship between the dissociation rate constant and bulk solvent fluidity, as originally proposed by Bennetto and Caldin,[8a] does not account for the present data. Moreover, since the trend in both the dissociation and formation rate constants for reaction 2 is totally different from the formation rate constant trend observed by Bennetto and Caldin for the Ni(II)–bipy reaction, it is obvious that the more detailed arguments based on solvent structure, which were proposed by these authors to explain their results as a function of methanol–water solvent composition,[9] cannot be applicable to the present system.

Whereas some structural effects may be significant in the Ni(II)–bipy system, a comparison with the solvated Ni(II)–NH₃ results would suggest that the several alterations in the $\Delta H^*–\Delta S^*$ relationship noted by Bennetto and Caldin can largely be attributed to changes in the nature of the inner coordination sphere on the Ni(II) ion—an aspect which was largely ignored by them. The differences between the ammonia and bipyridyl studies could then be accounted for by steric effects associated with the latter ligand.[14] Thus, while solvent structural effects may contribute to the dissociation rate constant trend obtained in this work, the appearance of this trend as a continuous curve (Figure 6) indicates that a much simpler explanation may account for the gross features observed—*e.g.*, either a direct interaction of the surrounding bulk solvent with the leaving ligand or some type of an associative process.

As an example of the former category, the "solvating power" concept proposed by Grunwald and Winstein[31] and extended by Brownstein[32] has been used to provide an empirical correlation of several phenomena to solvent composition. However, use of the solvating parameters published by these authors for methanol–water solvents does not provide a fit to our data if the outer-sphere solvent composition is assumed to resemble that of the bulk solvent.[20]

Although it has never been conclusively established that solvation processes of the type under discussion are unaffected by the nature of the entering solvent

molecule, associative processes generally show a decrease in rate constant as the nucleophilicity of the incoming group decreases barring the existence of overriding steric effects. Since methanol is generally considered a weaker coordinating ligand than water and is also larger in bulk, it would not be expected to be more effective than water in assisting the dissociation of ammonia.

As an interesting combination of the associative process and outer-sphere interactions, the Sn2FS (substitution nucleophilic bimolecular front side) mechanism has been widely applied to interpret the dissociation rate constants for various aquation reactions.[33,34] As applied to the reaction under study, this mechanism would suggest that an incoming solvent molecule could hydrogen bond to the coordinated ammonia ligand, thereby assisting the dissociation of the leaving ammonia and placing the incoming solvent molecule in the proper position for Sn2 substitution. As a presumed example of this mechanism, Adamson[34a] has studied the solvolysis of the Reineckate ion, *trans*-$Cr(NH_3)_2(NCS)_4^-$, and has suggested that methanol as well as water can assist the dissociation of NCS⁻, although the solvolysis rate was observed to *decrease* slightly in methanolic solvents as contrasted to the marked increase noted in this study.[35]

The suggestion that the hydrogen-bonded solvent molecule also acts as a nucleophilic displacing agent appears to be inconsistent since the nucleophilicity of a donor atom should be effectively lowered while it is engaged in hydrogen bonding. Moreover, in the case of solvolysis reactions, the surrounding solvent molecules in the outer sphere provide a ready supply of entering groups and the preponderant evidence suggests that such solvation processes are uninfluenced by the nature of the entering groups.[3,4] Thus, a dissociative process would appear to be more reasonable.

In a more recent investigation of Reineckate ion aquation in acetone–water mixtures, Langford and White[36] have reached similar conclusions regarding the dissociative nature of solvolysis while lending support to the concept that the dissociation of the leaving thiocyanate group is solvent assisted. As a point of particular significance, these authors used proton nmr to establish that *the complex ion is preferentially solvated by acetone in the outer sphere*.[37] From subsequent kinetic investigations they concluded that the aquation process (*i.e.*, the substitution of a coordinated thiocyanate ligand by a solvent water) is second order with respect to the outer-sphere water concentration. These results were interpreted in terms of a dissociative pro-

(33) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 3.

(34) (a) A. W. Adamson, *J. Amer. Chem. Soc.*, **80**, 3183 (1958); (b) A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

(35) It is interesting to contrast the Sn2FS mechanism to the internal conjugate base (ICB) mechanism which has been proposed to account for anation reactions in aqueous solution involving multidentate ligands: ref 12; *cf.* D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, **8**, 1498 (1969); D. B. Rorabacher and D. B. Moss, *ibid.*, **9**, 1314 (1970). In that mechanism a basic donor atom of an incoming ligand is postulated to hydrogen bond to a proton of a coordinated water molecule to stabilize the outer-sphere complex and labilize other coordinated solvent molecules. That mechanism has been phrased in terms of a dissociative process, however, and similar arguments can be brought to bear on the proposed Sn2FS mechanism.

(36) C. H. Langford and J. F. White, *Can. J. Chem.*, **45**, 3049 (1967).

(37) Similar evidence for preferential outer-sphere solvation by a noncoordinating solvent component was reported by Frankel[10] for Ni(II) ion in dimethylformamide–nitromethane mixtures.

(31) S. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

(32) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

cess where one water molecule is postulated to assist in "pulling off" a thiocyanate ion while a second water moves in to occupy the vacated site. The second-order dependence on outer-sphere water is then presumed to result from the fact that the lifetime of the five-coordinate species is shorter than the time required for reorganization of the outer sphere so that the incoming water must be available in the outer sphere at the time the coordination site is vacated.

We suggest that the dissociation of ammonia from the Ni^{II}–HEEDTA can be accounted for in similar terms. Thus the relative constancy of the dissociation rate constant in the 0–70% methanol solvent region suggests preferential solvation by water at the exchange site while the sharp increase in the rate constant values above 80% methanol indicates that methanol is more effective in assisting the dissociation of ammonia.

This proposal can be quantitatively tested against the experimental data if the preferential outer-sphere solvation of Ni(HEEDTA)(NH$_3$)$^-$ can be described by a thermodynamic equilibrium constant related to the bulk solvent concentrations of the two solvent components as has been previously assumed for inner-sphere solvation (eq 8)

$$K_{AB} = \frac{[\text{NiZ(NH}_3)\cdots\text{H}_2\text{O}][\text{CH}_3\text{OH}]}{[\text{NiZ(NH}_3)\cdots\text{CH}_3\text{OH}][\text{H}_2\text{O}]} = K_{AB}'\frac{[\text{CH}_3\text{OH}]}{[\text{H}_2\text{O}]} \quad (11)$$

The species NiZ(NH$_3$)$\cdots$H$_2$O and NiZ(NH$_3$)$\cdots$CH$_3$OH represent species where water and methanol, respectively, are hydrogen bonded to the coordinated ammonia or otherwise specifically situated in an influential location in the outer sphere. If each such species exhibits a specific rate constant, the dissociation rate may be expressed as

$$k^{\text{NiZ}-\text{NH}_3}[\text{NiZ(NH}_3)] = k_{(\text{H}_2\text{O})}{}^{\text{NiZ}-\text{NH}_3}[\text{NiZ(NH}_3)\cdots\text{H}_2\text{O}] + k_{(\text{CH}_3\text{OH})}{}^{\text{NiZ}-\text{NH}_3}[\text{NiZ(NH}_3)\cdots\text{CH}_3\text{OH}] \quad (12)$$

Substitution of eq 11 into eq 12 yields an expression similar to eq 10, *i.e.*

$$k^{\text{NiZ}-\text{NH}_3}(1 + K_{AB}') = k_{(\text{H}_2\text{O})}{}^{\text{NiZ}-\text{NH}_3} + k_{(\text{CH}_3\text{OH})}{}^{\text{NiZ}-\text{NH}_3}K_{AB}'$$
$$(13)$$

Plotting eq 13 using arbitrary values of K_{AB} in increments of 0.05 (*i.e.*, K_{AB} = 0.05, 0.10, etc.) reveals that the smallest least-squares residue is obtained for K_{AB} = 0.05 for which values of $k_{(\text{H}_2\text{O})}{}^{\text{NiZ}-\text{NH}_3}$ = 5 sec^{-1} and $k_{(\text{CH}_3\text{OH})}{}^{\text{NiZ}-\text{NH}_3}$ = 80 sec^{-1} are obtained. Substituting the foregoing values into eq 12 yields the theoretical curve shown in Figure 6. The fit of this curve to the experimental data is seen to be within the limits of experimental error.

As illustrated in Figure 8, the apparent differing effectiveness of methanol and water in assisting the nickel–ammonia dissociation process can be attributed either to a "pull" mechanism (a dissociative process) or a "push" mechanism (an associative process). However, as has been argued above, it is difficult to justify the greater effectiveness of methanol in terms of an associative process in view of its greater bulk and its supposed lower nucleophilicity relative to water. By contrast, assignment of the observed behavior to a "pull" mechanism, in which the solvent molecule in question is hydrogen bonded to the leaving ammonia group, bears a striking parallel to the explanation which we have previously proposed to account for preferential proton solvation in mixed methanol–water mixtures.[18]
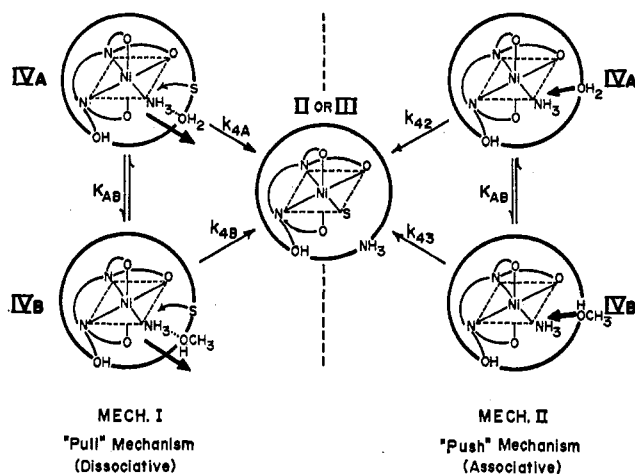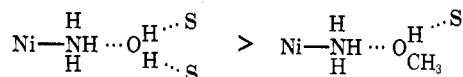

MECH. I
"Pull" Mechanism
(Dissociative)

MECH. II
"Push" Mechanism
(Associative)

Figure 8.—Schematic representation of proposed mechanisms for the replacement of ammonia in Ni(HEEDTA)(NH$_3$)$^-$ (species IV; *cf.* Figure 1) by a solvent molecule to produce Ni(HEEDTA)(H$_2$O)$^-$ or Ni(HEEDTA)(CH$_3$OH)$^-$ (species II or III, respectively; *cf.* Figure 1). In each mechanism the species designated as IVA and IVB differ only in the nature of the solvent molecule (H$_2$O or CH$_3$OH, respectively) located at a specific active site in the outer solvation sphere (represented by the solid circles), the two species being presumed to be in rapid equilibrium as described by the thermodynamic equilibrium constant, K_{AB}. The two mechanisms, to the left and right of the vertical dashed line, are intended to illustrate the proposed alternatives for the apparent solvent-assisted dissociation either by "pulling off" the ammonia *via* hydrogen bonding (mechanism I) or by "pushing" *via* a displacement reaction (mechanism II).

Thus the apparent greater effectiveness of methanol in "pulling off" an ammonia is in line with the suggestion that methanol is intrinsically more basic than water (*i.e.*, CH$_3$OH$_2$$^+$ is more stable than H$_3$O$^+$ *in an isolated state*[18]). The apparent preferential solvation by water at the exchange site corresponds to the proposal that H$_3$O$^+$ represents a more stable species than CH$_3$OH$_2$$^+$ *in the bulk solvent* due to the availability of an additional hydrogen to promote the formation of a more extensive hydrogen-bonded network leading to a greater total solvation energy, *i.e.*

$$\text{Ni}-\overset{\text{H}}{\underset{\text{H}}{\text{NH}}}\cdots\text{O}\overset{\text{H}\cdots\text{S}}{\underset{\text{H}\cdots\text{S}}{}} > \text{Ni}-\overset{\text{H}}{\underset{\text{H}}{\text{NH}}}\cdots\text{O}\overset{\text{H}\cdots\text{S}}{\underset{\text{CH}_3}{}}$$

In proposing the foregoing explanation, it should be noted that the role of the solvent in assisting the dissociation of ammonia may also be phrased in the more passive terms of Grunwald and Winstein[31] and Brownstein[32] wherein the various solvent species may be conceived to "solvate" the ammonia to a greater or lesser degree thereby influencing the nickel–ammonia bond stretch leading to complete bond rupture. In fact, the fit of eq 13 to the experimental data, as shown in Figure 6, gives no indication of the specific type of interaction existing between the inner-sphere ammonia and the outer-sphere solvent molecules. From any standpoint, however, it is evident that more than one solvent molecule may be affecting the dissociation process. In such a case a succession of outer-sphere solvation equilibria should be considered which, by reference to Figure 6, might lead to a slight improvement in the fit of the theoretical curve to the experimental data.

Within the context of the hydrogen-bonding explanation, the differing affinity for hydrogen-bond formation

to be expected for various leaving groups leads one to anticipate large differences in the relative dissociation rate constant trends as a function of solvent composition upon altering the nature of the leaving group. This factor could then account for the reversal in the relative effect of methanol and water upon the dissociation rate in the current system as contrasted to that reported by Adamson for the Reineckate ion (where NCS$^-$ as the leaving group would serve as a proton acceptor[34a])—a reversal which is difficult to explain within the context of an associative process or of solvent structural effects. Further studies on this aspect are planned.

In view of the evidence supporting the existence of significant outer-sphere effects upon the dissociation of the nickel–ammonia bond, it remains to reconsider the possibility that such effects are also present to a significant degree in the formation rate constant trends observed in this and the previous study.[1] If outer-sphere methanol and water were to have the same relative effect upon nickel–water and nickel–methanol bond dissociation rates as is apparent for nickel–ammonia, then a major contribution to the formation rate constant trend observed in this study could be attributable to changes in the outer-sphere composition.

This could lead to the conclusion that the inherent differences in the two nickel–solvent dissociation rate constants are much less than indicated by the values resolved from ignoring outer-sphere effects (*cf.* Figures 5 and 7). By the same token, however, it must then be concluded that inner-sphere effects leading to the observed decrease in nickel–solvent and nickel–ammonia bond dissociations upon replacing coordinated water by methanol[1] are much larger than previously assumed. Thus, to whatever extent outer-sphere effects (including structural effects) are important in nickel–ligand bond rupture rate constants in methanol–water solvents, the magnitude of inner-sphere effects previously reported must be increased accordingly.[38]

(38) Note Added in Proof.—Suggestive evidence for an interaction between Ni(HEEDTA)S$^-$ and the indicator Chlorophenol Red in solvents of high alcoholic content was brought to our attention by Richard W. Taylor prior to going to press. We are grateful to him and to Louis G. Jambor for subsequently rechecking the relaxation data under alternative conditions in confirming the validity of the original results as reported in Table III of this paper.

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Kinetics of the Exchange Reaction between 1,10-Phenanthroline and Triethylenetetraminenickel(II)

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The kinetics of the ligand substitution of 1,10-phenanthroline (phen) and triethylenetetraminenickel(II) (Ni(trien)$^{2+}$) has been studied spectrophotometrically over the pH range of 4.9–6.7 at 25°. The reaction involves an initial rapid formation of a mixed-ligand intermediate, Ni(trien)(phen)$^{2+}$, which then goes on to products. The reaction is first order in Ni(trien)(phen)$^{2+}$ and zero order in phenanthroline. Experimental rate constants for the dissociation of trien are $k^{\mathrm{NiHTP}} = 3.4 \times 10^{-3}$ sec^{-1} and $k_{\mathrm{H}}{}^{\mathrm{NiHTP}} = 5.3 \times 10^2$ M^{-1} sec^{-1}. By comparison to the Ni(trien)$^{2+}$ system, a mechanism is proposed in which breakage of the last trien bond to nickel is rate determining, followed by the rapid addition of two phenanthroline molecules. Formation rate constants for $k_{\mathrm{HT}}{}^{\mathrm{NiP}}$ and $k_{\mathrm{H_3T}}{}^{\mathrm{NiP}}$ are both calculated from the above dissociation constants and predicted from the Eigen mechanism. Comparison of these values with the corresponding ones for the Ni(trien)$^{2+}$ system shows that coordinated phenanthroline enhances the internal conjugate base effect by a factor of 80.

Introduction

The mechanism of nickel polyamine formation and dissociation reactions has been thoroughly studied.[1-5] The dissociation involves the following two steps repeated sequentially:[3] nickel–nitrogen bond breakage followed by nickel–solvent bond formation. This sequence continues until the polyamine has completely dissociated from the nickel ion. Excluding strongly acidic conditions, the rate-determining step is the last nickel–nitrogen bond rupture. Similarly, the rate-determining step for the formation reaction is the rate

of metal–water loss immediately preceding the first nickel–nitrogen bond formation.

The effect that coordinated nitrogens have upon rate of nickel–water substitution has also been studied.[6-14] Polyamine nitrogens appear to accelerate water loss[7-10] whereas aromatic ones do not.[11-14]

Rorabacher[15] has shown that the experimentally measured rate of formation of some metal polyamines

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