mation nor central bond lengths, but depend markedly upon central bond angles.

Simple interpretations in terms of s–s bond orders, related to the popular "carbon-s-character" approach, do not appear to hold in all cases, even qualitatively. The results given in the tables are not meant to provide specific numbers to compare with actual data, but rather to suggest the trends in couplings to be expected for certain geometrical alterations.

Acknowledgment. The author wishes to thank the Applied Sciences Department for their assistance.

Solvent Effects in Coordination Kinetics. I. Inner-Sphere Effects in the Reaction of Solvated Nickel(II) Ion with Ammonia in Methanol–Water Mixtures

W. J. MacKellar and D. B. Rorabacher*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received November 6, 1970*

Abstract: The kinetics of solvated Ni(II) ion reacting with ammonia have been studied using the temperature-jump relaxation method in methanol–water mixtures ranging from 0 to 99% methanol (by weight). The ammonia protonation constants and Ni(II)–ammine stepwise stability constants have also been determined in each solvent composition studied. The kinetic results show a distinct maximum in the formation rate constant for the nickel(II)–monoammine complex in the vicinity of 80–90% methanol. In conjunction with Ni(II) solvation measurements, these results indicate that $Ni(H_2O)_5(CH_3OH)^{2+}$ (5:1 species) is the most labile species of solvated Ni(II) ion in these solvents. The rate constant for nickel–methanol bond rupture in this species is then estimated to be $k_{5:1}{}^{Ni-CH_3OH} = (7\text{–}8) \times 10^5\ sec^{-1}$, approximately 800 times larger than the rate constant established for the same bond rupture in $Ni(CH_3OH)_6{}^{2+}$ and 20 times larger than the rate constant for nickel–water bond rupture in $Ni(H_2O)_6{}^{2+}$. A general theory is proposed in terms of the dissociative mechanism to account for the kinetic behavior of all labile solvated metal ions in both pure and mixed coordinating solvents.

Alcoholic solvents were first applied to the kinetic studies of coordination reactions in order to permit the use of low temperatures for slowing down reactions which were considered "instantaneous" in water.[1] Currently, the use of such nonaqueous solvents has come under renewed interest as a means of investigating the role of the solvent itself in influencing reaction rates.

The dissociative mechanism proposed by Eigen to explain the kinetic behavior of aqueous complex formation reactions[2] predicts a multifaceted role for the solvent in influencing reaction rates. As generalized here for any labile octahedrally solvated metal ion

$$MS_6{}^{a+} + L^{b-} \underset{}{\overset{K_{os}}{\rightleftharpoons}} \underset{\text{outer-sphere complex}}{MS_6{}^{a+}\cdots L^{b-}} \xrightarrow[\text{rate-determining step}]{k^{M-S}}$$

$$\underset{\text{short-lived intermediate}}{MS_5{}^{a+}\cdots L^{b-}} \xrightarrow{\text{(fast)}} MLS_5{}^{(a-b)+} \quad (1)$$

This mechanism involves the rupture of a metal–solvent coordinate bond (designated by the rate constant k^{M-S}) as the rate-determining step to form a short-lived intermediate of lower coordination number, MS_5, followed by rapid insertion of a nearby ligand into the vacated coordination site.

The short lifetime indicated for the MS_5 species requires that the entering ligand must be in the second coordination sphere (outer sphere) at the time of the metal–solvent bond rupture in order to compete successfully with the surrounding solvent molecules for the vacant site. As a result, the extent of outer-sphere complex formation, also dependent on the properties of the solvent matrix, directly influences the reaction rate. Thus, the observed overall formation rate constant, $k_M{}^L$, can be equated to the product of the outer-sphere equilibrium constant, K_{os},[3,4] and the rate constant for metal–solvent bond rupture, *viz.*

$$k_M{}^L = K_{os}k^{M-S} \quad (2)$$

both of the terms on the right being solvent dependent. The general dissociative mechanism is represented pictorially in Figure 1.

The weaker coordinating ability of alcoholic oxygen as a donor atom compared to aqueous oxygen led to the initial speculation that, for octahedrally solvated metal ions such as Ni(II) ion, "a dissociative mechanism in which $Ni(H_2O)_5{}^{2+}$ and $Ni(CH_3OH)_5{}^{2+}$ are formed should *always be more rapid for methanol than for water*."[5] Evidence from nmr studies, however, indicates that the reverse order is observed for solvent-exchange reactions when pure solvents are involved, *i.e.*,

---

[1] J. Bjerrum and K. G. Poulsen, *Nature (London)*, **169**, 463 (1952); *cf.* J. Bjerrum, K. G. Poulsen, and I. Poulson, *Proc. Symp. Coord. Chem., 1953*, 51 (1954).

[2] (a) M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 373; (b) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

[3] (a) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958); (b) M. Eigen, W. Kruse, G. Maass, and L. deMaeyer, *Progr. React. Kinet.*, **2**, 287 (1964).

[4] D. B. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 228.

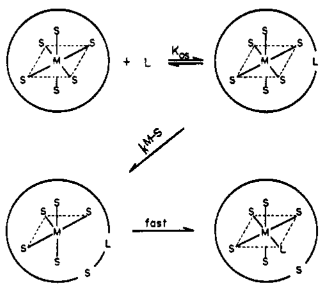


Figure 1. Schematic representation of the dissociative mechanism as proposed for a labile, octahedrally solvated metal ion, MS_6, reacting with a ligand, L (see mechanism 1). The circle surrounding the solvated metal ion represents the next adjacent layer of solvent molecules (outer sphere).

$k^{Ni-H_2O}(aq) > k^{Ni-CH_3OH}(CH_3OH)$.[6] This result thus appears to be in direct contradiction to the predictions of the dissociative mechanism.

More recently, Pearson and Ellgen have found that nickel ion reactions with both neutral and uninegative anionic ligands are indeed slower in methanol than in water,[7] the methanol results being in good agreement with the nmr value for the nickel–methanol bond rupture rate constant, k^{Ni-CH_3OH}, in accordance with eq 2. Owing to the influence of the solvent dielectric upon the value of K_{os}, these workers concluded that, *for reactions involving anionic ligands*, the observed complex formation rate constants might pass through a maximum value in intermediate methanol–water mixed solvents, presuming that the increase in K_{os} might precede the decrease in k^{M-S}. This prediction was supported by limited data on the Ni(II)–SCN^- reaction. On the basis of rate measurements with bipyridyl, however, it was implied that neutral and cationic ligands would be expected to exhibit continually decreasing rate constants as the methanol content of the solvent is increased, since the K_{os} value would be expected to remain nearly constant for neutral ligands and would continually decrease for cationic ligands. The bipyridyl study has since been extended by Bennetto, Bulmer, and Caldin,[8] whose results show a more complex behavior but corroborate the general decrease in formation rate constant with increasing methanol content.

In addition to the evidence by Pearson and Ellgen, limited solvent-exchange studies have indicated a dramatic increase in the value of k^{M-S} for both Ni(II) and Co(II) upon the addition of small amounts of water to the methanolic solvents.[6,9] To date no satisfactory proposals have been offered to explain this effect. Moreover, the slower solvent-exchange rate for $Ni(CH_3OH)_6^{2+}$ and $Co(CH_3OH)_6^{2+}$ relative to $Ni(H_2O)_6^{2+}$ and $Co(H_2O)_6^{2+}$ remains unexplained.

We have undertaken a series of investigations in mixed alcohol–water solvents involving the influence of changing solvent composition upon the rates and mechanisms of coordination reactions, including those involving both neutral and positive ligand species. In the current study the reaction kinetics of solvated Ni(II) ion with ammonia have been measured in methanol–water solvents containing 0, 25, 50, 65, 80, 90, 95, and 99% methanol (by weight) using the temperature-jump relaxation method. For this initial study, ammonia was selected as the ligand of choice on the basis of its single donor atom, small size, and lack of net charge—thereby minimizing steric and electrostatic complications. Furthermore, the kinetic study of the formation of the nickel(II)–monoammine complex in aqueous solution has already been demonstrated to give excellent agreement between experimental and theoretical rate constant values in accordance with eq 2.[4]

In contrast to the implications of earlier studies in methanol–water mixtures, the results show a distinct maximum in the formation rate constant value in the vicinity of 80–90% methanol. In conjunction with correlated solvation equilibrium data, these results are quantitatively resolved to yield the relative rates of the contributing solvated Ni(II) species in the region of 0–90% methanol. A general theory is then proposed to account for the behavior of the k^{M-S} values for all labile solvated metal ion species in methanol–water solvents, which appears to be applicable to other solvent systems as well.

Experimental Section

Reagents. $Ni(ClO_4)_2$ was prepared by treating $NiCO_3$ with $HClO_4$, precipitating, and recrystallizing. Sodium methoxide, used for protonation constant and stability constant determinations, was prepared by treating sodium metal with absolute methanol followed by the addition of water to adjust the solvent composition. Ammonium perchlorate, which served both for ionic strength control and as the source of NH_3 in solution, and all other chemicals were reagent grade and used without further purification. All mixed methanol–water solvents were prepared on a weight per cent basis using absolute methanol (99.98%, J. T. Baker Chemical Co.) and distilled deionized water. $Ni(ClO_4)_2$ solutions were standardized by titration with standard EDTA solution, while ammonium perchlorate solutions were prepared by weighing the salt and titrating potentiometrically with standard base solution.

Acidity Measurements. The pH* scales of deLigny and coworkers for methanol–water mixtures,[10] equivalent to the pH scale for aqueous media as defined by the National Bureau of Standards, permitted the measurement of thermodynamically significant acidity values for all solvents. All pH* measurements were made using either a Sargent Model DR or a Corning Model 12 expanded-scale pH meter equipped with commercial glass and saturated calomel electrodes. To limit transfer of the internal aqueous KCl solution from the calomel electrode to the nonaqueous solvents, an internal agar salt bridge was prepared. The pH* readings were standardized for each solvent composition using the appropriate oxalate and succinate standard buffer solutions prepared according to deLigny's specifications.[10] The two buffers agreed within 0.07 pH* unit or less in all solvents, the meter being set to average the two deviations.

Temperature-Jump Measurements. The temperature-jump relaxation spectrometer used in this work was a single-beam instrument constructed by the Messanlagen Studiengesellschaft mbH of Goettingen, Germany, in conjunction with a Tektronix Type 549 storage oscilloscope. Anticipated difficulties with spontaneous cavitation in the more alcoholic solvents proved to be minimal and, when it occurred within the monitoring light path, was readily detectable so that such runs were discarded. A more serious problem was the increased rate of convection upon temperature reequilibration in the highly alcoholic media resulting from the decreased viscosity of these solvent mixtures. Coupled with the diminished relaxation rates, this phenomenon severely limited the accuracy of the study in 99% methanol and made it impossible to attempt measurements on the nickel–ammonia reaction in anhydrous methanol without drastically altering the conditions.

---

(6) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058, 1066, 2686 (1964).

(7) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

(8) H. P. Bennetto, R. Bulmer, and E. F. Caldin in "Hydrogen-Bonded Solvent Systems," A. K. Covington and P. Jones, Ed., Taylor and Francis, London, 1968, p 335.

(9) T. E. Rogers, J. H. Swinehart, and H. Taube, *J. Phys. Chem.*, **69**, 134 (1965).

(10) C. L. deLigny, P. F. M. Luykx, M. Rehbach, and A. A. Weinecke, *Recl. Trav. Chim. Pays-Bas*, **79**, 699, 713 (1960).

The rate constant notations used throughout this paper are based on the following conventions: (i) metal ion subscripts plus ligand superscripts (*e.g.*, $k_{\mathrm{M}}{}^{\mathrm{L}}$) are used to designate complex formation rate constants between the two species indicated, (ii) metal-ligand superscripts (*e.g.*, $k^{\mathrm{M-L}}$) are used to designate dissociation rate constants involving rupturing of the coordinate bond between the two species indicated, and (iii) numerical and letter subscripts are used to distinguish rate constants for processes which are identical except for alterations in the inner solvation sphere.

Results

In all solvent mixtures studied, the kinetic behavior of the reversible nickel-ammonia reaction system was found to be consistent with second-order dependence for the formation reaction and first-order for complex dissociation in accordance with the rate equation

$$\frac{-\mathrm{d}[\mathrm{Ni}^{2+}]}{\mathrm{d}t} = k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}[\mathrm{NiS_6}^{2+}][\mathrm{NH_3}] - k^{\mathrm{Ni-NH_3}}[\mathrm{Ni(NH_3)S_5}^{2+}] \quad (3)$$

At detectable reactant concentrations (greater than 10^{-4} *M*) and at or near room temperature the reaction proceeds too rapidly to permit its study by classical kinetic methods. Therefore, as in the aqueous study,[4] the temperature-jump relaxation method was applied.

As previously discussed for the aqueous work, the spectrophotometric changes for the desired reaction were insufficient to permit accurate monitoring of the reactant concentrations so that it was necessary to couple the desired reaction with an acid-base indicator system.

$$\mathrm{NiS_6}^{2+} + \mathrm{NH_3} \underset{k^{\mathrm{Ni-NH_3}}}{\overset{k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}}{\rightleftharpoons}} \mathrm{Ni(NH_3)S_5}^{2+} + \mathrm{S} \quad (4)$$

$$\mathrm{H}^+ + \mathrm{NH_3} \overset{K_{\mathrm{H}}{}^{\mathrm{C}}}{\rightleftharpoons} \mathrm{NH_4}^+ \quad (5)$$

$$\mathrm{H}^+ + \mathrm{In}^- \overset{K_{\mathrm{I}}{}^{\mathrm{C}}}{\rightleftharpoons} \mathrm{HIn} \quad (6)$$

The mathematical treatment for this coupled system has been discussed previously[4] and shown to yield the relaxation equation (with a slight change in notation from that used in ref 4)

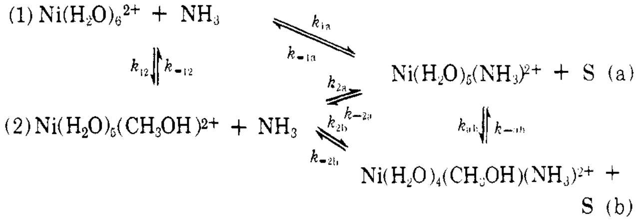
$$1/\tau = k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}([\bar{\mathrm{M}}]/(1 + \alpha) + [\bar{\mathrm{L}}]) + k^{\mathrm{Ni-NH_3}} \quad (7)$$

where τ is the relaxation time, $[\bar{\mathrm{M}}]$ and $[\bar{\mathrm{L}}]$ are the molar concentrations of uncomplexed Ni(II) ion and unprotonated ammonia, respectively, at the final temperature, and α is defined by

$$\alpha = \frac{K_{\mathrm{H}}{}^{\mathrm{C}}[\mathrm{H}^+](K_{\mathrm{I}}{}^{\mathrm{C}}[\mathrm{In}^-] + K_{\mathrm{I}}{}^{\mathrm{C}}[\mathrm{H}^+] + 1)}{K_{\mathrm{H}}{}^{\mathrm{C}}[\mathrm{NH_3}](K_{\mathrm{I}}{}^{\mathrm{C}}[\mathrm{H}^+] + 1) + K_{\mathrm{I}}{}^{\mathrm{C}}([\mathrm{In}^-] + [\mathrm{H}^+]) + 1} \quad (7a)$$

In eq 7a the terms $K_{\mathrm{H}}{}^{\mathrm{C}}$ and $K_{\mathrm{I}}{}^{\mathrm{C}}$ represent the protonation constants, in reciprocal molar concentration units, for ammonia and the indicator, respectively, as defined by reactions 5 and 6.

In the mixed-solvent systems the situation is further complicated by the fact that several mixed-solvated species of Ni(II) ion may be present, so that the observation of multiple coupled relaxation processes might be anticipated. Thus, even when only two solvated species of Ni(II) are present in solution, as many as five coupled relaxations might be observed, corresponding to the processes



(8)

It should be noted, however, that the use of a coupled acid-base indicator for monitoring the reaction system eliminates the possibility for direct observation of the relaxation processes corresponding to changes in solvation (k_{12} and k_{ab}).

In pure aqueous solution, where only the aquated species are present, the relaxation process corresponding to the ammoniation of hexaaquonickel(II) ion ($k_{1\mathrm{a}}$) can be unambiguously identified and the one observed relaxation time has been demonstrated to yield rate constants from eq 7 which are in excellent agreement with the dissociative mechanism.[4] As the concentration of methanol in the solvent is increased, however, no new relaxations are observed within the accessible time range (10 μsec to 1 sec) even when the concentration of partially methanolated species far exceeds that of the aquonickel ion. Instead, the mean lifetime of the one observable relaxation process decreases up to approximately 80–90% methanol and then increases sharply as the methanol content of the solvent is further increased such that the limiting value as pure methanol is approached is consistent with the value to be anticipated for $\mathrm{Ni(CH_3OH)_6}^{2+}$ on the basis of the solvent-exchange data, if a dissociative process is involved. Furthermore, the amplitude of the one observed relaxation curve does not differ greatly from one solvent composition to another (for equivalent reactant concentrations), indicating that the effective concentrations of the contributing reactive species are not changing significantly.

These observations point to the fact that the solvent-exchange processes (corresponding to k_{12}, k_{-12}, and k_{ab}, $k_{-\mathrm{ab}}$) are rapid relative to the ligand-substitution processes, a conclusion which is consistent with all related observations in view of the large excess of both solvent components relative to the concentration of free ligand. Based on this assumption, the resulting coupled relaxation expression can be shown to resolve to eq 7, where $[\bar{\mathrm{M}}]$ now represents the total concentration of all solvated Ni(II) species and the rate constants $k_{\mathrm{Ni}}{}^{\mathrm{NH_3}}$ and $k^{\mathrm{Ni-NH_3}}$ represent the weighted averages of the rate constants $k_{1\mathrm{a}}$, $k_{2\mathrm{a}}$, etc., and $k_{-1\mathrm{a}}$, $k_{-2\mathrm{a}}$, etc., respectively.

Protonation and Stability Constants. The required equilibrium constant values for the mixed methanol-water solvents have been determined in separate studies.[11] The protonation constants for $\mathrm{NH_3}$ and selected sulfonephthalein indicators in each solvent composition were determined by pH* potentiometric titrations as described in detail elsewhere.[11a] The values for all pertinent protonation constants are listed in Table I.

For determination of the stepwise formation constants for nickel-ammine complexes, potentiometric

---

(11) (a) D. B. Rorabacher, W. J. MacKellar, F. R. Shu, and S. M. Bonavita, *Anal. Chem.*, 43, 561 (1971); (b) D. B. Rorabacher, W. J. MacKellar, and R. W. Taylor, unpublished results.

Table I. Equilibrium Constants Pertinent to the Nickel–Ammonia Study [25°, μ = 0.10 M (NH_4ClO_4)]

CH_3OH, wt %	CH_3OH, mol fraction	Log K_H^C	Log K_1^C	Log K_1^a	Log K_2^b
0	0	9.21	7.2[c]	2.72	2.17
25	0.1578	9.04	7.7[c]	2.93	2.32
50	0.3599	8.74	5.54[d]	3.13	2.61
65	0.5108	8.63	5.81[d]	3.18	2.13[f]
80	0.6922	8.73	6.3[d]	3.05	2.49
90	0.8350	9.07	6.89[d]	3.12	2.61
95	0.9144	9.38	6.64[e]	3.37	2.55
99	0.9824	10.04	7.44[e]	3.26	2.53

[a] Relative standard deviation (from computer fit) ≤1.6%, except 12% for 99% CH_3OH. [b] Relative standard deviation (from computer fit) ≤5%, except 11% for 65% CH_3OH and 18% for 99% CH_3OH. [c] Bromthymol blue indicator. [d] Bromcresol green indicator. [e] Bromphenol blue indicator. [f] This value appears to be low.

Table II. Relaxation Data for the Nickel–Ammonia System [25°, μ = 0.10 M (NH_4ClO_4)]

C_M, mM	A, mM	$1/\tau$, sec^{-1}
0% CH_3OH, pH = 6.96		
1.00	1.29	10.5
2.00	2.01	14.4
4.00	3.47	21.8
6.00	4.93	28.8
8.00	6.39	33.3
10.00	7.85	40.3
50% CH_3OH, pH* = 6.00		
1.51	1.36	16.4
3.02	2.59	19.2
4.54	3.82	23.0
7.56	6.29	33.8
9.07	7.52	38.3
10.58	8.76	51.8
13.61	11.23	72.0
15.12	12.47	82.2
80% CH_3OH, pH* = 6.54		
0.81	0.87	9.6
1.62	1.35	14.4
2.43	1.84	22.9
3.24	2.33	23.0
4.05	2.83	28.8
4.86	3.32	35.9
5.67	3.81	48.0
6.48	4.31	63.9
7.29	4.81	57.5
8.10	5.30	65.8
95% CH_2OH, pH* = 6.70		
2.40	1.94	9.4
4.81	3.78	13.6
9.61	7.47	22.9
12.01	9.32	32.9
14.42	11.18	38.3
16.82	13.03	45.2
19.22	14.89	57.5
21.62	16.74	67.7
24.03	18.61	74.4
25% CH_3OH, pH* = 6.94		
0.79	1.09	11.5
1.58	1.60	13.6
2.37	2.10	17.1
3.16	2.61	23.0
3.95	3.11	25.6
4.73	3.62	28.9
5.52	4.13	32.5
6.31	4.64	33.8
7.10	5.15	37.1
7.89	5.67	42.7
65% CH_3OH, pH* = 6.60		
1.47	1.33	18.5
2.94	2.07	28.8
4.40	2.83	38.4
5.87	3.58	46.0
7.38	4.37	47.0
8.81	5.12	57.5
10.27	5.89	67.7
11.74	6.67	72.0
13.21	7.46	82.2
14.68	8.25	96.0
90% CH_3OH, pH* = 7.02		
1.60	1.37	12.8
3.21	2.25	20.1
4.81	3.16	32.4
6.41	4.06	47.0
8.02	4.97	54.9
9.62	5.89	63.9
11.22	6.82	77.7
12.82	7.75	90.3
14.43	8.69	96.0
16.03	9.63	105
99% CH_3OH, pH* = 7.25		
7.39	6.71	9.2
15.85	13.35	16.4
31.71	26.66	31.0
47.56	40.01	54.1

Table III. Formation Rate Constants for the Nickel–Monoammine Complex in Methanol–Water Mixtures [25°, μ = 0.10 M (NH_4ClO_4)]

CH_3OH, wt %	$k_{Ni}^{NH_3} \times 10^{-3}$, M^{-1} sec^{-1}
0	4.46
25	6.69
50	(5.98)
65	10.4
80	12.7
90	11.6
95	4.01
99	1.33

titrations of the ammonium perchlorate solutions with standard base were repeated in the presence of Ni(II) ion.[11b] The successive stability constant values were then calculated using a modified form of the Bjerrum $\bar{n}_L$ function ($\bar{n}_L$ representing the average number of ligands bound to the central nickel ion) by means of a computer program[12] which tested various theoretical models involving one to six successive stability constants. For each model the weighting of each data point was iterated until a best fit of the theoretical model to the data points was obtained, as indicated by a minimum value for the summation of the squares of the residuals for all titration points.

For solvent compositions up to and including 90% methanol, the model based on four successive stability constants yielded the best fit, whereas that based on three constants produced the optimal fit for 95 and 99% methanol.

It should be noted at this point that no correction for the hydrolysis of Ni(II) ion was made in these calculations. Hydrolysis did, in fact, occur during the addition of the third and fourth ammonia ligand in every case studied; consequently, the K_3 and K_4 values are, in all cases, in error and actually represent values which allow the best fit for the entire titration curves. In this manner better values for K_1 and K_2 were obtained, while the actual K_3 and K_4 values are relatively meaningless and are not recorded. The results obtained for K_1 and K_2 are listed in Table I. (Small variations in K_1 and reasonably large variations in K_2 did not significantly affect the values obtained for the formation rate constants as described in the following paragraph.)

Relaxation Measurements. In each solvent mixture studied a series of individual solutions was made up at a constant pH* and ammonia concentration, with varying nickel ion concentration covering a tenfold range. The relaxation data for the individual solutions studied are reported in Table II. Each $1/\tau$ value reported represents a median of approximately six separate relaxation curves (*i.e.*, six replicate temperature jumps per solution) and A is the concentration term in eq 7.

$$A = [\bar{M}]/(1 + \alpha) + [\bar{L}] \tag{9}$$

According to eq 7 a plot of the $1/\tau$ values should be linear, with a slope equal to the formation rate constant for the nickel–monoammine complex and an intercept equal to its dissociation rate constant. For conditions where the dissociation rate constant is much smaller than the product of A times the formation rate constant, gross inaccuracies may result in the intercept value. This situation prevailed in this study, so dissociation rate constants could not be determined accurately from the relaxation measurements. The results for the formation rate constants are listed in Table III for the data obtained graphically from the individual runs. The observed behavior of the formation rate constant as a function of weight per cent methanol is shown in Figure 2.

---

(12) L. P. Varga, *Anal. Chem.*, 41, 323 (1969).

Discussion

Mechanism Considerations. The general dissociative mechanism involving prior ion-pair formation, as shown in Figure 1, has been affirmed for nickel complex formation reactions in aqueous media many times over[13] and has been demonstrated specifically for the reaction of hexaaquonickel(II) ion with ammonia.[4] As noted in the introduction, the available data in pure methanol are essentially limited to the studies of Pearson and Ellgen involving nickel complex formation with six ligands (including molecular and anionic ligands)[7] plus the recently reported results of Dickert, Hoffmann, and Jaenicke for Ni(II) reacting with SCN^- and Cl^-.[14] These workers found a general agreement with the ion-pair dissociative mechanism as depicted by eq 1 and 2 when the experimental formation rate constants were compared with the rate constant for methanol exchange on the nickel ion as reported by Luz and Meiboom.[6]

Since the dissociative mechanism appears to be operative in both pure water and pure methanol for reactions involving solvated Ni(II) ion reacting with simple unidentate ligands, it is reasonable to assume that the mixed-solvated species also react by this mechanism. Proceeding on this basis, the dependence of metal–solvent bond ruptures on metal solvation and bulk solvent composition may be investigated.

From eq 2 it is apparent that the rate maximum noted in Figure 2 for nickel–monoammine formation in the intermediate solvent range could be attributed to the outer-sphere equilibrium term, the metal–solvent bond-rupture rate constant, or a combination of both factors. Therefore, each must be considered on an individual basis in order to elucidate the effect of solvent on the observed formation rate.

Effect of K_{os} on Observed Rate Constants. The outer-sphere equilibrium constant, K_{os}, can be derived from diffusion equations[3] and, *in the case of uncharged ligands* such as ammonia, has been shown to simplify to[4]

$$K_{os} = {}^4/_3\pi a^3 N_A \times 10^{-3} \tag{10}$$

where a represents the center-to-center distance between the two reacting species in the outer-sphere complex (in centimeters) and N_A represents Avogadro's number. Therefore, the following relationship for the K_{os} terms in the two pure solvents results.

$$\frac{K_{os_{CH_3OH}}}{K_{os_{H_2O}}} = \frac{a^3{}_{CH_3OH}}{a^3{}_{H_2O}} \tag{11}$$

If reasonable values for a_{CH_3OH} and a_{H_2O} are selected, then an estimate can be made of the effect of K_{os} on the formation rate of the reaction in the two pure solvents. If a value of 4 Å is chosen for a_{H_2O} and 5 Å for a_{CH_3OH} (a larger value being chosen in methanol owing to the increased van der Waals radius for the hexamethanolic nickel ion, as suggested by Pearson and Ellgen[7]), according to eq 11 a twofold increase in observed complex formation rate attributable to the K_{os} value should be noted when the reaction takes place in anhydrous methanol relative to that observed in water. For mixed alcohol–water solvents, water is much preferred in the nickel inner coordination sphere.[15] Thus this anticipated rate enhancement arising from the K_{os} contribution should only become appreciable in solvents of very low water content, since molecular models indicate that the increased crowding about the central metal ion does not occur appreciably until three or more methanol molecules are physically present in the inner coordination sphere. It can also be shown that any other reasonable selection of reactive radii for $Ni(H_2O)_6{}^{2+}$ and $Ni(CH_3OH)_6{}^{2+}$ yields comparative K_{os} ratios. Therefore, it is apparent that the K_{os} term in eq 2 is not a dominant factor in the observed rate phenomena and, for species containing only one or two methanol molecules in the inner coordination sphere, the K_{os} value is assumed to be identical with that calculated for $Ni(H_2O)_6{}^{2+}$.

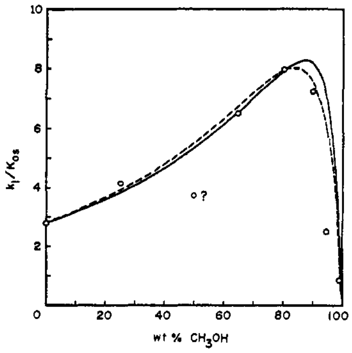


Figure 2. Variability of the formation rate constant as a function of bulk solvent composition for the reaction of $NiS_6{}^{2+}$ with NH_3. As plotted on the ordinate, a constant value of $K_{os} = 0.16$ has been divided into the experimental $k_{Ni}{}^{NH_3}$ values, the resulting values presumed to approximate the rate constant for nickel–solvent bond rupture. The solid line represents the theoretical fit calculated with eq 24 based on the resolved rate constants obtained using an estimated minimum value for $k_{4:2}{}^{M-S} \approx 1 \times 10^3$ sec^{-1} and the solvation constants $K_1' = 0.66$ and $K_2' = 0.067$. The dashed line is similarly calculated using the iterated solvation constants $K_1' = 0.62$ and $K_2' = 0.14$.

Contribution of the Inner Coordination Sphere to Observed Rate Constants. Since the outer-sphere equilibrium constant is assumed to have little effect upon the rate constant for reactions such as nickel–monoammine complex formation, from eq 2 the observed variation of $k_{Ni}{}^{NH_3}$ with changes in solvent composition must be primarily affected by the dissociation rate constant k^{M-S} for the nickel–solvent bond. This would imply that the observed formation rate constant is altered according to the composition of the nickel ion inner coordination sphere. Luz and Meiboom have reported that the rate of methanol exchange on the nickel ion is accelerated by the addition of water,[6] although they were unable to determine the composition of the inner solvation sphere accompanying this acceleration.

If a quantitative interpretation of k^{M-S} values in the methanol–water solvent compositions studied is to be effected, solvation equilibrium constant values are required in order to determine the relative concentration of each individual solvated nickel ion species present at the solvent compositions studied. The individual sol-

---

(13) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 55 (1965); R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(14) F. Dickert, H. Hoffmann, and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, 74, 500 (1970).

(15) R. F. Pasternack and R. A. Plane, *Inorg. Chem.*, 4, 1171 (1965).

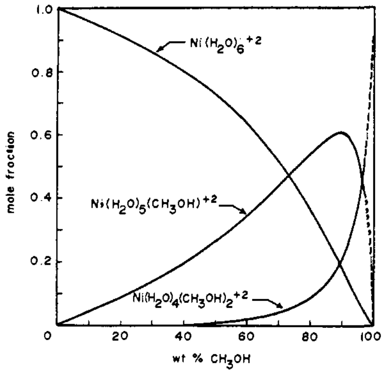


Figure 3. Mole fractional distribution of solvated nickel ion species as calculated using the solvation constants $K_1' = 0.66$ and $K_2' = 0.067$ (ref 17). (Species with more than two coordinated methanol molecules were neglected in the resolution of these values, leading to significant error in the distribution of species existing above about 95% methanol.)

vation equilibrium constants can be expressed as

$$K_j' = \frac{[\mathrm{Ni(H_2O)_{6-\mathit{j}}(CH_3OH)_{\mathit{j}}}^{2+}][\mathrm{H_2O}]}{[\mathrm{Ni(H_2O)_{6-(\mathit{j}+1)}(CH_3OH)_{\mathit{j}-1}}^{2+}][\mathrm{CH_3OH}]} \quad (12)$$

where $1 \leq j \leq 6$.

Many workers have found that water is strongly preferred to alcohol in the inner coordination sphere of transition metal ions to the extent that some water molecules remain coordinated until essentially all bulk solvent water content has been eliminated.[15,16] Even when very small amounts of water are added to methanolic Ni(II) solutions, species of the form $\mathrm{Ni(H_2O)_{6-\mathit{j}}(CH_3OH)_{\mathit{j}}}^{2+}$ become important.[6,9]

Shu and Rorabacher,[17] applying a spectrophotometric method similar to that of Plane and coworkers,[15] have recently affirmed that, for reasonably low nickel ion concentrations, only the nickel ion species containing zero, one, and two methanol molecules need to be considered in methanol–water solvent mixtures up to 95% methanol or greater. The solvation-sphere equilibrium reactions are given in eq 13 and 14

$$\mathrm{Ni(H_2O)_6}^{2+} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{Ni(H_2O)_5(CH_3OH)}^{2+} + \mathrm{H_2O} \quad (13)$$

$$\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{Ni(H_2O)_4(CH_3OH)_2}^{2+} + \mathrm{H_2O} \quad (14)$$

for which the following equilibrium expression can be defined.

$$K_1' = [\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}][\mathrm{H_2O}]/[\mathrm{Ni(H_2O)_6}^{2+}][\mathrm{CH_3OH}] \quad (15)$$

$$K_2' = [\mathrm{Ni(H_2O)_4(CH_3OH)_2}^{2+}][\mathrm{H_2O}]/[\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}][\mathrm{CH_3OH}] \quad (16)$$

The concentration values for K_1' and K_2' reported by Shu and Rorabacher are 0.66 and 0.067, respectively, with relative standard deviations of about 20 and 50%, respectively. (Although both concentration and activity values for K_1' and K_2' were calculated by Shu and Rorabacher, the concentration values yielded a closer statistical fit to the experimental data, indicating that the available activity corrections for the two solvent components may be invalidated by salt effects under the prevailing conditions.[17]) These values indicate that the $\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}$ species exhibits a maximum mole fractional contribution of 0.6 in the region of 85–90% methanol, as noted in Figure 3. Therefore, species with more than one methanol in the inner coordination sphere do not predominate until above 90% methanol.

The striking correlation between nickel–monoammine complex formation rate constant and the $\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}$ concentration maxima at nearly identical solvent compositions, as noted from a comparison of Figures 2 and 3, suggests that this species has an enhanced lability. Furthermore, the marked decrease in the observed formation rate constants past 90% methanol strongly indicates that all solvated nickel ion species containing more than one methanol must be considerably less reactive, which is consistent with previous observations on highly methanolated species.[6,9]

Based on the above-mentioned assumptions, an attempt was made to resolve the observed nickel–solvent bond dissociation rate constant, $k^{\mathrm{M-S}}$, defined by eq 1, into the individual rate constants for the three solvated nickel ion species present in significant concentrations at the various methanol–water solvent compositions studied. The expansion of eq 2 is as follows

$$k_{\mathrm{Ni}}^{\mathrm{NH_3}}[\mathrm{NiS_6}]_{\mathrm{T}} = k_{6:0}^{\mathrm{M-S}}[\mathrm{Ni(H_2O)_6}^{2+}] + k_{5:1}^{\mathrm{M-S}}[\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}] + k_{4:2}^{\mathrm{M-S}}[\mathrm{Ni(H_2O)_4(CH_3OH)_2}^{2+}] \quad (17)$$

where the subscript notation on the $k^{\mathrm{M-S}}$ constants indicates the number of water and methanol molecules, respectively, bound in the inner coordination sphere. From material balance considerations, the total concentration of solvated nickel ion, $[\mathrm{NiS_6}]_{\mathrm{T}}$, can be represented as

$$[\mathrm{NiS_6}]_{\mathrm{T}} = [\mathrm{Ni(H_2O)_6}^{2+}] + [\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}] + [\mathrm{Ni(H_2O)_4(CH_3OH)_2}^{2+}] \quad (18)$$

the more methanolic species of nickel being considered relatively negligible for solvent compositions below about 99% methanol. Upon substitution of eq 15 and 16 into eq 18 with subsequent rearrangements, the various solvated nickel ion species concentrations can be expressed in terms of experimentally accessible variables and parameters as follows

$$[\mathrm{Ni(H_2O)_6}^{2+}] = [\mathrm{H_2O}]^2[\mathrm{NiS_6}]_{\mathrm{T}}/\Phi \quad (19)$$

$$[\mathrm{Ni(H_2O)_5(CH_3OH)}^{2+}] = K_1'[\mathrm{H_2O}][\mathrm{CH_3OH}][\mathrm{NiS_6}]_{\mathrm{T}}/\Phi \quad (20)$$

$$[\mathrm{Ni(H_2O)_4(CH_3OH)_2}^{2+}] = K_1'K_2'[\mathrm{CH_3OH}]^2[\mathrm{NiS_6}]_{\mathrm{T}}/\Phi \quad (21)$$

where

$$\Phi = [\mathrm{H_2O}]^2 + K_1'[\mathrm{H_2O}][\mathrm{CH_3OH}] + K_1'K_2'[\mathrm{CH_3OH}]^2 \quad (22)$$

When eq 19–21 are substituted into eq 18, upon rearrangement the following expression is obtained.

$$\frac{k_{\mathrm{Ni}}^{\mathrm{NH_3}}\Phi}{K_{\mathrm{os}}[\mathrm{H_2O}]^2} = k_{6:0}^{\mathrm{M-S}} + k_{5:1}^{\mathrm{M-S}}K_1'\frac{[\mathrm{CH_3OH}]}{[\mathrm{H_2O}]} + k_{4:2}^{\mathrm{M-S}}K_1'K_2'\frac{[\mathrm{CH_3OH}]^2}{[\mathrm{H_2O}]^2} \quad (23)$$

---

[16] N. J. Friedman and R. A. Plane, *Inorg. Chem.*, **2**, 11 (1963) *cf.*; J. Bjerrum and C. K. Jorgensen, *Acta Chem. Scand.*, 7, 951 (1953); C. C. Mills and E. L. King, *J. Amer. Chem. Soc.*, **92**, 3017 (1970).

[17] F. R. Shu and D. B. Rorabacher, submitted for publication.

A linear plot should result when $k_{Ni}^{NH_3}\Phi/K_{os}[H_2O]^2$ is plotted *vs.* $K_1'[CH_3OH]/[H_2O]$ up to the point where the contribution of the $k_{4:2}^{M-S}K_1'K_2'[CH_3OH]^2$ term becomes appreciable. Such a plot exhibits linear behavior for the solvent range of 0–80%. (A value of 4 Å was selected for the reactive distance term, this value having been shown to yield excellent agreement between the theoretically predicted and experimental rate constants in water;[4] the resulting K_{os} value of 0.16 was used in performing the above and following calculations.) The value for $k_{5:1}^{M-S}$, as determined from the slope, is 1.26 × 10^5 sec^{-1} and the intercept, corresponding to $k_{6:0}^{M-S}$, is equal to 2.8 × 10^4 sec^{-1}, the latter value being in excellent agreement with previously reported values in aqueous medium.[2,4,18]

It is to be noted that these values are obtained from a line based on the 0, 25, 65, and 80% methanol points only, the plotted points for 50 and 90% being notably low. The 50% value is acknowledged to be inconsistent with the other data. A reexamination of the experimental conditions used in obtaining this point indicates that the temperature attained following the temperature jump was, in fact, approximately 24° (instead of 25°) and the reaction conditions were otherwise somewhat different from those used in obtaining all other points.

On the other hand, there is no basis for assuming that the observed rate constant for 90% methanol involves any experimental error. Of the points included in the plot, this point is most subject to influence from higher methanolated species. However, the fact that this point falls below the line cannot be attributed to the failure to include the last term in eq 23, since any significant contribution by this term would cause this point to fall above the established line. Therefore, it is suggested that the inconsistency arises from a faulty value for K_2'. Since the K_2' value was acknowledged to be questionable, an iterative method was applied to the K_1' and K_2' values using eq 23. If the assumption made earlier, that solvated nickel ion species containing more than two inner-coordination-sphere methanol molecules may be neglected, is correct, then $k_{4:2}^{M-S}$ must be a much smaller value than $k_{5:1}^{M-S}$. Consequently, as an upper limit on $k_{4:2}^{M-S}$, a value equal to $k_{Ni}^{NH_3}/K_{os}$ for the 99% data point was supplied for the iterative calculation (1 × 10^4 sec^{-1}). The results based on the $k_{Ni}^{NH_3}$ values for 0, 25, 65, and 80% methanol yielded values of 0.62 and 0.14 for K_1' and K_2', respectively. The former value is essentially unchanged from that obtained by Shu and Rorabacher. The latter value is now larger by a factor of 2, a correction which is consistent with the fact that species containing more than two methanol ligands were not included in resolving the spectrophotometric solvation data.

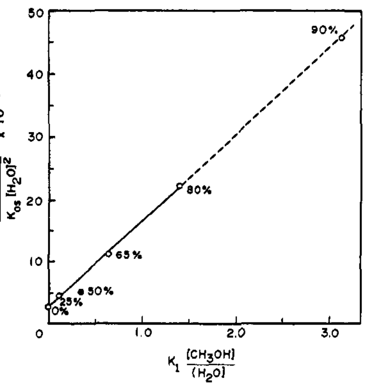


Figure 4. Resolution of the rate constants for the 6:0 and 5:1 solvated nickel ion species using eq 23 and the iterated solvation constants $K_1' = 0.62, K_2' = 0.14$.

Applying these new constants to the kinetic data, the 90% point is now seen to fall exactly on the line established by the 0, 25, 65, and 80% points, as shown in Figure 4. Thus the assumption that the kinetic contribution of $k_{4:2}^{M-S}$ does not become important until after 90% methanol appears reasonable. The value for $k_{5:1}^{M-S}$ obtained in this manner is 1.38 × 10^5 sec^{-1}. Despite the approximations required, the K_1' solvation constant and the rate constant value for $k_{5:1}^{M-S}$ are essentially unchanged. Thus the reported value for $k_{5:1}^{M-S}$ is presumed to be reasonably accurate within the limitations of the solvation constants (*i.e.*, K_1', K_2') used.

In view of the evidence cited earlier that solvent exchange in $Ni(CH_3OH)_6^{2+}$ is a dissociative process[14] and the additional evidence that the incorporation of H_2O molecules into the inner coordination sphere enhances the rate of methanol exchange,[6,9] the specific rate of methanol exchange between the bulk solvent and the inner coordination sphere of $Ni(CH_3OH)_6^{2+}$ can be used to establish a lower limit for $k_{4:2}^{M-S}$. Thus $k_{4:2}^{M-S}$ is presumed to exceed 1.0 × 10^3 sec^{-1} for Ni(II) at 25°.[6]

Since all of the rate constant parameters in eq 17 are either known or have been estimated, the overall nickel–solvent bond dissociation rate constant, k^{M-S}, may be calculated, where $k^{M-S} = k_{Ni}^{NH_3}/K_{os}$, according to eq 2. Upon substitution of eq 19–22 into eq 17 the following equation is obtained

$$k^{M-S} = (k_{6:0}^{M-S}[H_2O]^2 + k_{5:1}^{M-S}K_1'[H_2O][CH_3OH] + k_{4:2}^{M-S}K_1'K_2'[CH_3OH]^2) \quad (24)$$

whereby the k^{M-S} value can be estimated at any methanol–water solvent composition and, by implication, a value for $k_{Ni}^{NH_3}$ as well. Figure 2 gives a comparison of the calculated curves for k_{Ni}^{NH} using eq 2, applying lower limits for $k_{4:2}^{M-S}$ for both the spectrophotometric and iterated solvation constant values to the k^{M-S} values as calculated from eq 24, and a value of 4 Å for the reactive distance in all solvents.

In corroboration of the foregoing interpretation, it has been found that cobalt(II)–monoammine formation[19] behaves in a similar manner to that observed for nickel–monoammine formation when solvation constant values are estimated from the work of Pasternack and Plane[15] in ethanol–water mixtures. However, when the same treatment is applied to the combined data of Pearson and Ellgen[7] and Caldin and coworkers[8] for nickel–2,2′-bipyridyl complex formation, linearity is not observed for eq 23, indicating that the simple form of the dissociative mechanism as depicted by eq 1 does not apply. On the basis of an examination of molecular models, it is suggested that a steric effect and/or a change in the rate-determining step from the first to the second nickel–nitrogen bond formation is involved with this ligand. The applicability of the dissociative

---

[18] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

[19] D. B. Rorabacher and R. W. Taylor, unpublished results.

mechanism to a reaction involving such effects will be examined in a separate study.[20]

Estimation of Rate Constants for Ni-H_2O and Ni-CH_3OH Bond Dissociation. From statistical considerations, metal-solvent bond rupture in the $Ni(H_2O)_5(CH_3OH)^{2+}$ species is weighted 5 to 1 toward the occurrence of a nickel-water bond rupture. Thus, the overall nickel-solvent bond dissociation rate constant, $k_{5:1}{}^{M-S}$, for the $Ni(H_2O)_5(CH_3OH)^{2+}$ species may be resolved into its component parts as depicted in eq 25, *if it can be assumed that all of the nickel-water bonds are equivalent.* The two component rate constants are

$$k_{5:1}{}^{M-S} = (k_{5:1}{}^{Ni-CH_3OH} + 5k_{5:1}{}^{Ni-H_2O})/6 \qquad (25)$$

superscripted to denote specifically the bond type undergoing rupture.

From eq 25 and the value of $k_{5:1}{}^{M-S}$ reported in the previous section, it is possible to place the magnitude of $k_{5:1}{}^{Ni-CH_3OH}$ and $k_{5:1}{}^{Ni-H_2O}$ within close approximate limits. A maximum value for each constant is obtained if the other is assumed to equal zero. Maximum values thus obtained for $k_{5:1}{}^{Ni-CH_3OH}$ and $k_{5:1}{}^{Ni-H_2O}$ are 8.3×10^5 and 1.7×10^5 sec^{-1}, respectively. It is obvious that neither rate constant can be smaller than zero; therefore, the maximum range for each constant is established.

The question arises as to which type of bond is more labile. The solvation study by Shu and Rorabacher[17] indicates that the nickel-water bond is more stable than the nickel-methanol bond (*i.e.*, the numerical value for the equilibrium constant of eq 15 is less than five). Based on the assumption that one methanol molecule in the nickel ion inner coordination sphere does not greatly affect the rupture rate of the five nickel-water bonds, it is concluded that a fair approximation for $k_{5:1}{}^{Ni-CH_3OH}$ may be made based on the assumption that $k_{5:1}{}^{Ni-H_2O} \approx k_{6:0}{}^{Ni-H_2O}$. The value for $k_{5:1}{}^{Ni-CH_3OH}$ obtained in this manner is 6.9×10^5 sec^{-1}. To be consistent with the conclusions of this paper, however, it is anticipated that $k_{5:1}{}^{Ni-H_2O} < k_{6:0}{}^{Ni-H_2O}$, which would increase the calculated value of $k_{5:1}{}^{Ni-CH_3OH}$ to a value not exceeding the upper limit previously estimated. Thus the limits are closely established: $6.9 \times 10^5 < k_{5:1}{}^{Ni-CH_3OH} < 8.3 \times 10^5$ sec^{-1}.

A value of 8×10^5 sec^{-1} was estimated by Rorabacher and coworkers for nickel-alcoholic oxygen bond rupture in aqueous solution as determined from kinetic studies on Ni(II) reactions with poly(amino alcohols).[21] The remarkably good agreement between that value and the values estimated for $k_{5:1}{}^{Ni-CH_3OH}$ in this work give strong support to the above interpretation accorded to the nonaqueous data.

Inner-Solvation-Sphere Effects. If, in fact, the nickel-methanol bond is more labile than the nickel-water bond, as is indicated by both kinetic and equilibrium studies, it remains to explain the slower solvent exchange rate of $Ni(CH_3OH)_6{}^{2+}$ relative to $Ni(H_2O)_6{}^{2+}$. To gain perspective on this problem, we have listed in Table IV a series of normalized single bond-rupture rate constants in logarithmic form. In this table three different metal-ligand bond types are considered for two metal ions (*i.e.*, methanol, water, and ammonia ligands with the Ni(II) and Co(II) ions). From the comparison of various bond-rupture rate constants in the pure solvents listed (*i.e.*, methanol, water, and liquid ammonia) several features are apparent: (a) the Co(II) rate constants for the species indicated parallel those observed for Ni(II) except that they are one or two orders of magnitude greater; (b) in each given solvent the available data indicate that the metal-ligand bond-rupture rate constants follow the order $k^{M-CH_3OH} > k^{M-H_2O} > k^{M-NH_3}$, which is consistent with the general trend in bond strength; (c) a series of comparative values can be distinguished for *solvent exchange* in the pure methanol, water, and ammonia solvents: $k_{(NH_3)}{}^{M-NH_3} > k_{(H_2O)}{}^{M-H_2O} > k_{(CH_3OH)}{}^{M-CH_3OH}$ (where the parenthetical subscripts represent the pure solvents in which the measurements were made); and (d) the observed trend for a specific bond-rupture rate constant in the various pure solvents parallels the strength of the solvent species as a ligand, *e.g.*, $k_{(NH_3)}{}^{M-NH_3} > k_{(H_2O)}{}^{M-NH_3} > k_{(CH_3OH)}{}^{M-NH_3}$. (Identical behavior has been reported for nickel acetate, nickel chloride, and nickel thiocyanate in these solvents.[22]) These observations are consistent with the proposal that *a pure solvent of a strong coordinating nature results in a more stable five-coordinated metal ion transition state relative to its six-coordinated ground state than does a pure solvent of weaker coordinating ability.*

Table IV. Logarithmic Values for Single Bond-Rupture Rate Constants (sec^{-1}) in Various Solvents at 25°

M–L bond	Pure solvents CH_3OH	 H_2O	 NH_3
Ni–CH_3OH	3.0[a,b]	5.9[c,d]	
Ni–H_2O		4.5[a,e,f]	
Ni–NH_3	−1.7 (est)[c]	0.6[f]	5.0[a,g,h]
Co–CH_3OH	4.3[a,b]	6.8[i]	
Co–H_2O		5.9[a,e,f]	
Co–NH_3	0.3 (est)[j]	3.2[f]	7.0[a,g]

[a] Corrected for statistical factor of 6. [b] Reference 6. [c] This work. [d] Reference 21. [e] Reference 18. [f] Reference 4. [g] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965). [h] T. J. Swift and H. H. Lo, *J. Amer. Chem. Soc.*, **88**, 2294 (1966). [i] D. B. Rorabacher and D. B. Moss, *Inorg. Chem.*, **9**, 1314 (1970). [j] Reference 19.

Assuming the applicability of the dissociative mechanism in all three solvents, these trends lead to the prediction that, relative to aqueous conditions, complex formation will proceed more rapidly in ammonia, and less rapidly in methanol, provided the dielectric effect on K_{os} is not sufficient to overcome this trend in the case of charged ligands. The nickel-monoammine complex formation behavior reported in this work affirms this prediction, as does the work of Pearson and Ellgen[7] and of Hoffmann and coworkers.[14,22]

As discussed earlier, the nickel-monoammine formation data permit a quantitative resolution of the rate contribution of the mixed-solvated species, $Ni(H_2O)_5(CH_3OH)^{2+}$, which is found to be about five times as reactive as the $Ni(H_2O)_6{}^{2+}$ species. The same study also reveals that the $Ni(H_2O)_4(CH_3OH)_2{}^{2+}$ species reacts at least ten times more slowly than $Ni(H_2O)_5(CH_3OH)^{2+}$. A further decrease in rate is indicated for

---

(20) W. J. MacKellar and D. B. Rorabacher, manuscript in preparation; *cf.* Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR-38.

(21) D. B. Rorabacher, T. S. Turan, J. A. Defever, and W. G. Nickels, *Inorg. Chem.*, 8, 1498 (1969).

(22) F. Dickert, H. Hoffmann, and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, 72, 1096 (1968); H. Hoffmann, personal communication.

higher methanolated species. This is consistent with the trend in reactivities of the more methanolated species, $M(H_2O)_2(CH_3OH)_4^{2+}$ > $M(H_2O)(CH_3OH)_5^{2+}$ > $M(CH_3OH)_6^{2+}$, which was observed quantitatively for cobalt ion, and qualitatively for nickel ion by Luz and Meiboom.[6]

In light of these data, the relative reactivities are viewed as an extension of the inner-sphere effects previously observed by Margerum and coworkers[23] involving the influence of coordinated ligands upon subsequent metal–water bond rupture in aqueous solution, where a strongly bonded ligand in a coordination complex accelerates the metal–solvent bond rupture rate of the solvated central metal ion.

In terms of the metal ion species with mixed solvation, the corollary to the evidence presented by Margerum is that the substitution of weaker coordinating ligands in the inner solvation sphere decelerates the metal bond rupture rate for all other ligands in the inner sphere. In keeping with the previous suggestion for pure solvated species, it is proposed that this effect results from a greater destabilization of the five-coordinate transition state relative to the six-coordinate ground state. This is depicted graphically in Figure 5 in terms of activation enthalpy for the three solvated Ni(II) species discussed in this work.

Available data to support this theory are limited at present, but it is to be noted that the activation enthalpy for rupturing the nickel–ammonia bond decreases on going from aqueous solution ($\Delta H^{\ddagger}$ = 13–14 kcal/mol[4]) to ammonia ($\Delta H^{\ddagger}$ = 10–11 kcal/mol[24]). To obtain quantitative evidence to corroborate the proposed activation enthalpy trends for the metal ion species with mixed solvation, involved in reactions similar to that reported in this work, would require the determination of protonation, stability, solvation, and kinetic constants for a series of temperatures over the entire range of solvent compositions. Such work is now under way.

In summary, kinetic solvent effects can be formulated as follows. Barring overriding steric effects, the reactivity of any solvated metal ion (which adheres to the dissociative ion-pair mechanism) directly reflects the rupture rate of the weakest metal–solvent bond in the inner coordination sphere. However, this rate is modified greatly by the donor strengths of the other solvent ligands present within the inner sphere. In mixtures of two coordinating solvents, the solvated species with the greatest lability is that species which contains one molecule of the weaker bonding solvent in the inner coordination sphere, with the remaining sites occupied by molecules of the stronger bonding solvent (*e.g.*, $Ni(H_2O)_5(CH_3OH)^{2+}$). As additional molecules of the weaker solvent ligand enter the inner coordination sphere, the dissociation rates of all metal–solvent bonds decrease. Therefore, the solvated metal ion species saturated with the weaker ligand (*e.g.*, $Ni(CH_3OH)_6^{2+}$) becomes the least labile species for reactions dependent upon dissociative behavior.

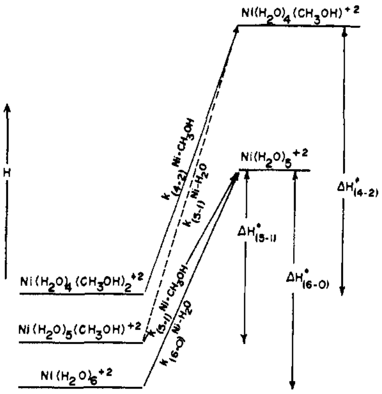


Figure 5. Schematic diagram illustrating the postulated inner-sphere solvation effects wherein the substitution of weaker ligands (methanol) in place of stronger ligands (water) is presumed to affect the relative stability of the five-coordinate transition-state more than the six-coordinate ground-state complex. Note that for mixed solvated species two types of bond rupture are possible, resulting in two possible transition states. Thus for the 5:1 species, $Ni(H_2O)_5(CH_3OH)^{2+}$, the energetically less favorable—but statistically more probable—process designated by the rate constant $k_{5:1}^{Ni-H_2O}$ contributes to the observed rate, which should yield a slightly larger value for $\Delta H^{\ddagger}_{5:1}$ (and a slightly smaller value for $\Delta S^{\ddagger}_{5:1}$ than that represented here.

Acknowledgment. The authors wish to thank the National Institute of General Medical Sciences for support of this research under Grant No. GM-12596.

---

[23] D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1088 (1967); J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **92**, 1875 (1970).

[24] H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).