

product. The sodium complex $\text{Na}_2[\text{Co}(\text{CN})_5\text{H}_2\text{O}]$ undergoes spontaneous polymerization in aqueous solution and in the solid state³⁴ and the infrared spectrum of the polymer shows bands at 2202 (m) and 2135 cm^{-1} (s),³⁵ very similar to the cyano bands for the DMF-insoluble product and also for the soluble product after drying *in vacuo*. When dehydrated the sodium salt shown above changes from yellow to green, a property also possessed by both products obtained in this work.

$\text{K}_2[\text{Ni}(\text{CN})_4]$ and $\text{K}_4[\text{Ni}_2(\text{CN})_6]$.—The green precipitate formed in each case on reaction with nitrosyl chloride was identified as $\text{Ni}(\text{CN})_2 \cdot x\text{DMF}$ by means of infrared spectroscopy. The spectrum of the material obtained from the nickel(II) complex showed cyano bands at 2170 (vs, sp) and 2129 cm^{-1} (w), as well as bands characteristic of DMF. For the product isolated from the nickel(I) complex, bands were found at

(34) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

(35) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

2166 (vs, sp) and 2132 cm^{-1} (w). The infrared spectrum of $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ (taken for comparison) exhibits absorption bands at 2166 (vs, sp) and 2130 cm^{-1} (w) in the cyano region, as well as bands attributable to water at 3710, 3500, and 1620 cm^{-1} .

The $\text{K}_2[\text{Ni}(\text{CN})_4]$ -NOCl system is the only one in which reaction occurs and it is not the metal which is oxidized by the nitrosyl chloride. It would appear that oxidation of the cyanide ligand takes place. This hypothesis is supported by electrochemical data²⁴ obtained for the tetracyanonickelate(II) complex. Polarography at a rotating platinum electrode in DMF with 0.1 *M* tetraethylammonium perchlorate as supporting electrolyte showed that oxidation of the complex occurred at $E_{1/2}$ (vs. sce) = +0.89 V. Cyclic voltammetry at a stationary platinum electrode indicated that the oxidation wave obtained from polarography was irreversible and corresponded to a two-electron change. Oxidation of cyanide ion to cyanogen would account for the electrochemical information.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK 11201

Pressure-Jump Relaxation Kinetics of Magnesium(II), Manganese(II), Nickel(II), Cobalt(II), Copper(II), and Zinc(II) *m*-Benzenedisulfonates in Anhydrous Methanol at 25°

BY G. MACRI¹ AND S. PETRUCCI

Received August 15, 1969

The kinetics of ion association of the *m*-benzenedisulfonates of Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , and Zn^{2+} have been studied by the pressure-jump relaxation technique. Through the support of results by electrical conductance these data have been interpreted by the Eigen multistep theory of ionic association. The observed relaxation times are interpreted as due to the process of penetration of the inner sphere of the metals by the ligand, this process being coupled to a much faster outer-sphere equilibration. The rates of complexation were found to be much slower than the nmr rates of solvent exchange. This is discussed in terms of alternate mechanisms.

Introduction

Relaxation kinetics, nmr kinetics, and other more conventional tools like thermodynamics and mass transport, when applied to the process of complexation and ligand exchanges, have given a rather complete picture of the dynamics of short-range interactions in dilute aqueous ionic solutions,²

In particular for divalent transition metal ions the process of ionic association and complexation appears to be multistep³ starting from a diffusion-controlled approach between solvated ions to form an outer-sphere ion pair. Whether this diffusion process is

always a single discrete one as in the original Von Smoluchowsky-Debye^{4a} and Eigen^{4b} calculations or sometimes characterized by a spectrum of relaxation times due to the many possible configurations of the outer-sphere complexes (as possibly suggested by recent ultrasonic measurements by Plass and Kehl⁵ on metal sulfates) remains to be established.

In any case this diffusion-controlled process is followed by a slower cation desolvation with the ligand entering the first coordination sphere of the metal. The mechanism⁶ of this process differs depending on the metal and the ligand, varying from the limits of an association type (with the formation of a seven-

(1) This work is part of the thesis of G. Macri in partial fulfillment for the requirements of the degree of Doctor in Philosophy, Polytechnic Institute of Brooklyn, 1970.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

(3) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII part II, A. Weissberger, Ed., John Wiley and Sons, New York, N. Y., 1963.

(4) (a) M. Von Smoluchowsky, *Physik. Z.*, **17**, 557 (1916); P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); (b) M. Eigen, *Z. Physik. Chem. (Frankfurt)*, **1**, 176 (1954).

(5) K. G. Plass and A. Kehl, *Acustica*, **20**, 360 (1968).

(6) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York, N. Y., 1967.

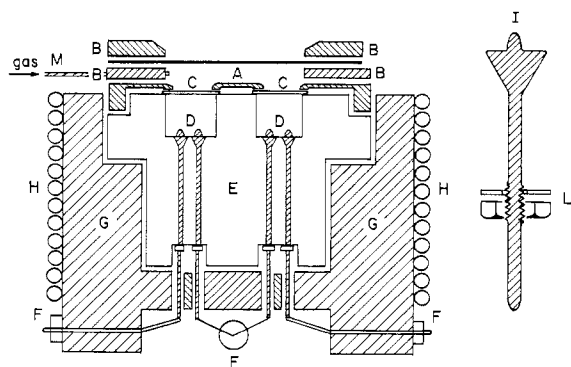


Figure 1.—Scheme of the pressure-jump cell: A, brass disk; B, stainless steel ring holding the piezoelectric transducer; C, Teflon diaphragms; D, conductance cells with electrodes; E, polystyrene case; F, UHF connector posts; G, stainless steel holder; H, thermostat coils; I, enlargement of a stainless steel electrode with conical fitting to avoid glue; L, $1/8$ -in. 40 threads with washer and bolt to fasten the electrodes; M, nitrogen inlet.

coordinated intermediate) and of a dissociative type (with the formation of a five-coordinated intermediate) to the intermediate cases of a ligand-interchange mechanism. The monograph by Langford and Gray² gives an exhaustive treatment of these cases including the possibility suggested by Eigen⁷ of an internal hydrolysis of the outer-sphere ion pair for Al^{3+} and Fe^{3+} followed by attack by the protonated ligand.

In nonaqueous solvents knowledge of the mechanism of ionic association is in a far less sophisticated state mainly due to a paucity of experimental data available. Recent nmr data on rates of solvent exchange in polar solvents have been furnished by the work of Babiec, *et al.*,⁸ Matwiyoff,⁹ Pearson,¹⁰ and Meiboom^{11a} and recently reviewed.^{11b}

Metal complexation studies of Ni^{2+} have been done by Pearson¹² by flow techniques in methanol. The process was interpreted by an interchange mechanism (where, however, the rates of solvent substitution agreed within a factor of 2 with the rates of solvent exchange). Tobe¹³ studied the rate of ligand exchange of complexes of $\text{Co}(\text{en})_2\text{Cl}_2^+$ with Cl^- in methanol, dimethylformamide, and dimethylacetamide. He concluded that subsequent to outer-sphere ion pairing the mechanism is analogous to acid hydrolysis.²

We have decided to study the ionic complexation kinetics of the cations Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , and Zn^{2+} with the *m*-benzenedisulfonate ions (BDS) in anhydrous methanol at 25°. The choice of Zn^{2+} , Mg^{2+} , and first-row transition metals has been dictated by the existence of nmr data of solvent-exchange rates,^{8,10,11}

information of fundamental importance in devising a mechanism of complexation from results of ligand-substitution relaxation kinetics.

Measurements of electrical conductance for the above systems have been performed in this laboratory¹⁴ in order to obtain information on thermodynamic association constants, minimum distances of association, and hydrodynamic radii.¹⁵

The kinetic study on these systems presented here has been done by the pressure-jump technique.³

Experimental Section

Materials.—Methanol (Baker reagents ACS) was distilled over aluminum amalgam using a 36-in. Pyrex column packed with glass beads in an all-glass apparatus. Only the middle portion boiling at 64.5° was collected and stored in a drybox under N_2 atmosphere. Karl Fischer and vpc analyses performed just before the runs indicated less than 0.01% water content in the methanol.

The anhydrous benzenedisulfonate salts were prepared by metathesis of solutions of BaBDS and the metal sulfates adding solutions of the latter to the former until no further precipitation of BaSO_4 occurred. After filtration and check for absence of SO_4^{2-} the *m*-benzenedisulfonate solutions were recrystallized twice from a 1:10 mixture of water-acetone and dried under moderate vacuum (10^{-2} mm) in an oven at various temperatures below 150° for a period of at least 1 week. Metal cation analysis by standard procedures, anion analysis by acidimetry (after having converted the salt to the corresponding acid), and Karl Fischer water content analysis proved the salts to be anhydrous.

The BaBDS used in these syntheses was prepared by neutralizing a solution of benzenedisulfonic acid (K & K Chemical Co.) with BaCO_3 . The solution was decolorized with charcoal and filtered, and the BaBDS was precipitated by volume reduction and addition of acetone. The salt was recrystallized from 1:10 water-acetone mixtures.

Equipment.—The pressure-jump apparatus used in this work was similar to that described by Hoffmann, Stuehr, and Yeager.¹⁶ The only modification was in the pressure-jump cell. This is a dual conductance cell (Figure 1) constructed of polystyrene. One cell contains the solution under investigation and the other an electrolyte of approximately the same conductivity but exhibiting no relaxation effects slower than 20 μsec . The standard chosen for this study was tetrabutylammonium bromide in methanol.

In order to avoid glueing the electrodes, these were constructed with a conical stem (Figure 1) so that an increase of pressure would favor their adherence to the cell itself. No leakage was noticed up to a pressure of 30 atm.

The following electronic system was used in this work. A General Radio sine wave generator, Model 1210C, was used to feed the dual-arm conductance bridge (Figure 2). The frequency used was 100 kc. General Radio shielded transformers, Model 578-c, were used at the entrance and the exit of the bridge to the detector system. The bridge was constructed of General Radio resistors (Type 510) variable from 0.01 ohm to 10 kilohms and were connected parallel with variable capacitors from 15 pF to 0.01 μF . Special care was taken in the shielding of all the elements.

The detector system consisted of a General Radio amplifier (Model 1232 A) and of a rectifier system similar to that described by Hoffmann, *et al.*¹⁶ In particular HP 2900 silicon diodes were used. These had a linear response only above 300 mV. It was necessary then to insert a preamplifier stage to reach this level of voltage. The detector system included also an *R-C* network

(14) G. Macri and S. Petrucci, unpublished data.

(15) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, New York, N. Y., 1959.

(16) H. Hoffmann, J. Stuehr, and E. Yeager in "Chemical Physics of Ionic Solutions," B. E. Conway and R. G. Barradas, Ed., John Wiley and Sons, New York, N. Y., 1966.

(7) M. Eigen, "Coordination Chemistry: Seventh International Conference," Butterworth and Co. Ltd., London, 1963, p 97.

(8) J. S. Babiec, C. H. Langford, and T. R. Stengle, *Inorg. Chem.*, **5**, 1363 (1966).

(9) N. Matwiyoff, *ibid.*, **5**, 788 (1966).

(10) R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *Z. Elektrochem.*, **68**, 110 (1960).

(11) (a) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058, 1066 (1964); (b) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967); C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **19**, 193 (1968).

(12) R. Pearson and P. Elgen, *Inorg. Chem.*, **6**, 1379 (1967).

(13) M. L. Tobe in "Mechanism of Inorganic Reactions," Summer Symposium of the Division of Inorganic Chemistry, American Chemical Society, Lawrence, Kans., 1964.

($R = 10$ kilohms fixed, $C = 0.1$ – $0.001 \mu F$ in 12 steps) to provide filtering of the unwanted frequency noise. The time constant was generally set at $470 \mu\text{sec}$ during this work.

Both the ac signal and the rectified signal were displayed on a Tektronix (Model 502A) dual-beam oscilloscope. The scope was externally triggered by a piezoelectric transducer, Model LD-2J (Atlantic Research Co.), at the instant of the pressure release. A 40-db gain charge amplifier, Model LG-1004 (Atlantic Research Co.), was used to bring the output level of the transducer pulse to the one necessary to trigger the scope. This system was used for processes having a relaxation time longer than about 1 msec. For faster times down to 0.2 msec a Tektronix carrier amplifier (Type 3C66) plug-in unit connected to a Tektronix RM564 oscilloscope was used. This self-contained unit eliminated the need of any electronics except the transducer triggering circuit. However, to increase sensitivity to small voltage displacements from null, an external voltage divider network was inserted between the cell and the amplifier (Figure 3) in parallel with the carrier amplifier input. This reduced the effective input resistance and increased the sensitivity. This arrangement was found to be 5–10 times less sensitive than the conductivity bridge arrangement. The temperature of the pressure bomb was kept at $25 \pm 0.2^\circ$ by circulating oil from a thermostat through a copper tubing spiraled around the cell. The temperature was measured with a YSI No. 44003 precision thermistor. The pressure-jump instrument was calibrated with nickel malonate in water reproducing the data of Hoffmann, *et al.*,¹⁶ within experimental error ($\pm 10\%$).

Solutions.—A stock solution of approximately $10^{-2} M$ concentration of the metal BDS salt in anhydrous methanol was prepared under N_2 atmosphere. All dilutions of this stock were made volumetrically and stored in a drybox under N_2 . The stock solutions were standardized by cation exchange and titration of H_2BDS by THAM.¹⁷

Filling the pressure-jump cell took no more than 10 sec. This operation performed both in the open air and in a drybox demonstrated that no difference was detectable in the pressure-jump results. The room in which all the conductance and pressure-jump experiments were carried out was maintained at $21 \pm 1^\circ$ at 19% relative humidity.

Results and Calculations

Results from electrical conductance data on the same systems¹⁴ in the form of association constants, $K(\Lambda)$, collision diameters between free ions, a_J , and hydrodynamic radii at infinite dilution, R_+^0 and R_-^0 , have been obtained by analyzing the conductance data by the Fuoss–Onsager equation¹⁵ for associated electrolytes. The hydrodynamic radii¹⁵ have been calculated by the formula

$$R_{\pm}^0 = \frac{Fe|z_{\pm}|}{1800\pi\lambda_{\pm}^0\eta} \quad (1)$$

where F is the Faraday constant, e is the electron charge, and η is the viscosity of the solvent. λ_{+}^0 and λ_{-}^0 were obtained from the determined limiting conductances Λ_0 and the transference numbers in methanol¹⁸ of K^+ (the conductance of K_2BDS has been separately measured).¹⁴ The association constants $K(\Lambda)$ are in the range $34,000$ – $40,000 M^{-1}$, the collision diameters a_J are in the range 10 – 12×10^{-8} cm, the hydrodynamic radii R_+^0 vary between 5.1 and 5.3×10^{-8} cm, while $R_-^0 = 5.4 \times 10^{-8}$ cm. Details of this work¹⁴ will be published at a later time,

With the three parameters $K(\Lambda)$, a_J , and Λ_0 the

(17) L. Meites in "Handbook of Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 334.

(18) J. P. Butler, H. I. Schiff, and A. R. Gordon, *J. Chem. Phys.*, **19**, 752 (1951).

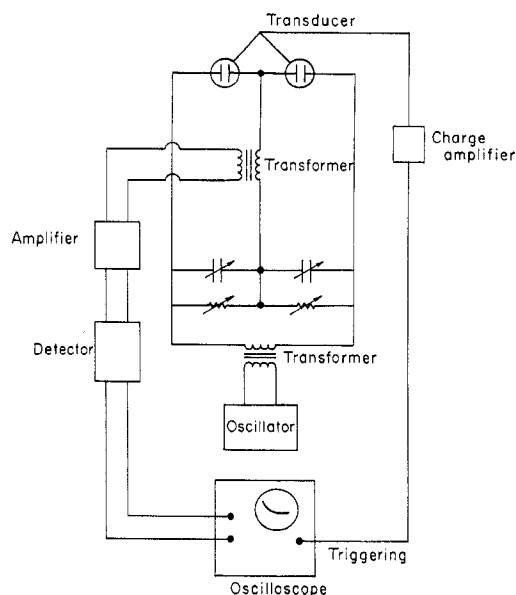


Figure 2.—Scheme of electrical circuit.

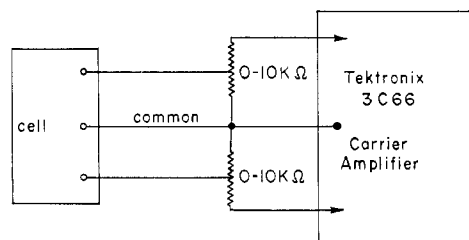


Figure 3.—Scheme of electrical connections to the 3C-66 carrier amplifier.

Fuoss–Onsager equation fit the data, proving that the only species present besides free ions are the 1:1 species M^+BDS . Had any other charged species been present, such a fit would not have been observed. The pressure-jump results are given in Table I which

TABLE I
STOICHIOMETRIC CONCENTRATION AND RECIPROCAL OF RELAXATION TIMES FOR THE VARIOUS ELECTROLYTES INVESTIGATED IN METHANOL AT 25°

| $10^4 c_0, M$ | $\tau^{-1}, \text{sec}^{-1}$ | $10^4 c_0, M$ | $\tau^{-1}, \text{sec}^{-1}$ |
|---------------|------------------------------|---------------|------------------------------|
| MgBDS | | NiBDS | |
| 263 | 41.25 | 275 | 31.3 |
| 110 | 37.0 | 127 | 30.3 |
| 65.8 | 34.4 | 68.9 | 28.7 |
| 26.3 | 31.0 | 27.5 | 26.5 |
| 5.15 | 24.3 | 5.50 | 19.6 |
| 0.52 | 15.5 | 0.55 | 9.30 |
| MnBDS | | CuBDS | |
| 254 | 47.0 | 262 | 65.1 |
| 109 | 44.1 | 117 | 62.5 |
| 63.5 | 43.0 | 55.8 | 59.0 |
| 25.4 | 36.9 | 11.2 | 47.2 |
| 5.08 | 29.0 | 2.24 | 33.7 |
| 0.51 | 14.3 | 0.22 | 14.9 |
| CoBDS | | ZnBDS | |
| 233 | 44.1 | 213 | 47.6 |
| 105 | 43.0 | 102 | 45.1 |
| 58.0 | 41.5 | 53.3 | 41.9 |
| 23.3 | 37.9 | 21.3 | 38.0 |
| 4.66 | 26.6 | 4.26 | 26.6 |
| 0.33 | 12.4 | 0.43 | 13.4 |

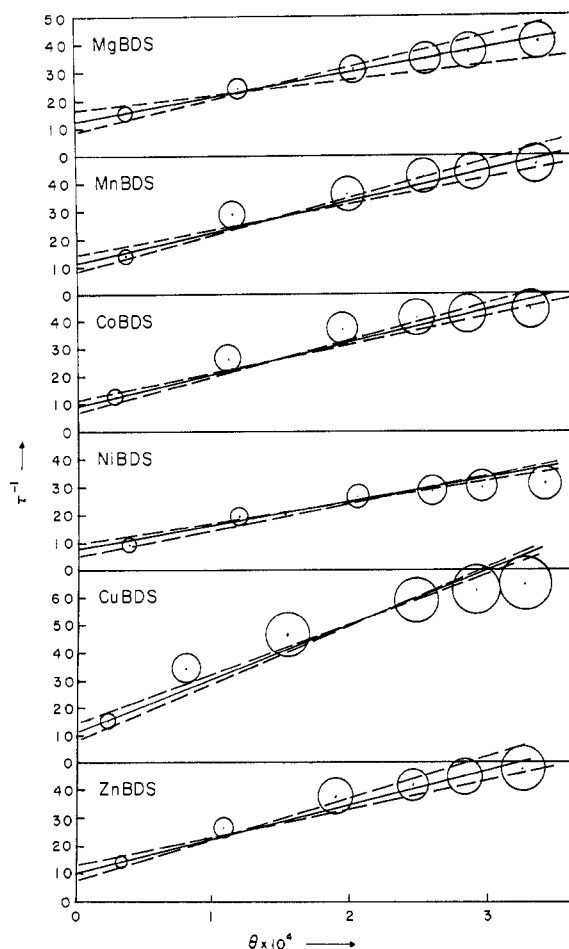
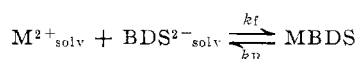


Figure 4.—Plot of τ^{-1} vs. θ for the various electrolytes in methanol at 25°.

reports the stoichiometric concentrations and the relaxation times (expressed as τ^{-1}) for the various electrolytes investigated. The average precision for the relaxation times τ was $\pm 15\%$ as determined from at least five photograph recordings. Semilog plots of vertical displacements vs. time were constructed obtaining τ^{-1} as the slope of the graphs. The plots were always linear demonstrating that the process observed had only a single relaxation in this time range. Blank experiments with solutions of $\text{Ni}(\text{ClO}_4)_2$ and $\text{Mn}(\text{ClO}_4)_2$ in methanol showed no relaxation effects.

The data have been interpreted in terms of ionic association. According to Eigen³ the overall process of ionic association



corresponds to the relation

$$\tau^{-1} = k_f\theta + k_R \quad (2)$$

where k_f is the second-order forward rate constant, k_R is the first-order reverse rate constant, θ is equal to the relation (see the method of calculation below)

$$\theta = \alpha c_0 \gamma_{\pm}^2 \left(2 + \frac{d \ln \gamma_{\pm}^2}{d \ln \alpha} \right) \quad (3)$$

with α the degree of ionization, c_0 the stoichiometric concentration, and γ_{\pm} the mean activity coefficient. Figure 4 reports the plots of τ^{-1} vs. θ . The size of the circles corresponds to the average precision of τ^{-1} . Table II reports the values of k_f and k_R cal-

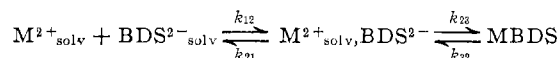
TABLE II

OVERALL RATE CONSTANTS k_f , AND k_R , OVERALL ASSOCIATION CONSTANT $\bar{K}_A = k_f/k_R$, AND CALCULATED k_{23} AND k_{32} FOR THE VARIOUS ELECTROLYTES INVESTIGATED IN METHANOL AT 25°

| Electrolytes | $10^4 k_f, M^{-1} \text{sec}^{-1}$ | k_R, sec^{-1} | \bar{K}_A, M^{-1} | k_{23}, sec^{-1} | k_{32}, sec^{-1} |
|--------------|------------------------------------|------------------------|---------------------|---------------------------|---------------------------|
| MgBDS | 9 ± 3 | 12 ± 3 | 7,500 | 80 ± 30 | 11 ± 4 |
| MnBDS | 11 ± 2 | 11 ± 2 | 10,000 | 110 ± 25 | 8 ± 4 |
| CoBDS | 12 ± 2 | 9 ± 2 | 13,300 | 107 ± 20 | 8 ± 3 |
| NiBDS | 9 ± 2 | 8 ± 2 | 11,200 | 77 ± 16 | 5 ± 3 |
| CuBDS | 19 ± 2 | 11 ± 2 | 17,300 | 160 ± 25 | 10 ± 3 |
| ZnBDS | 13 ± 2 | 10 ± 2 | 13,000 | 100 ± 30 | 9 ± 4 |

culated as slope and intercepts from Figure 4. Notice that the ratio $k_f/k_R = \bar{K}_A$ is of the same order of magnitude as the conductance $K(\Lambda)$ thus giving faith in the reliability of the interpretation of the relaxation spectra as due to ionic association. The calculated k_f and k_R are several orders of magnitude slower than those of a diffusion-controlled process of ionic recombination (and *vice versa*).³ Therefore it is conceivable that the association process is multistep.

In order to probe into this mechanism a two-step Eigen scheme has been assumed. The results have therefore been interpreted as due to the penetration of the ligand in the first coordination sphere of the metal cations, this process being coupled to a much faster diffusion-controlled one according to



In the hypothesis that $k_{12}, k_{21} \gg k_{23}, k_{32}$, Eigen has shown the following relation to be valid³

$$\tau^{-1} = k_{32} + k_{23} \frac{k_{12}\theta}{k_{12}\theta + k_{21}} = k_{32} + k_{23} \frac{\theta}{\theta + K_{12}} = k_{32} + k_{23}\Phi \quad (4)$$

with $K_{12} = k_{21}/k_{12}$.

The calculations have been performed as follows. The quantity θ has been calculated from α and γ_{\pm} by combining the two expressions

$$K(\Lambda) = \frac{1 - \alpha}{\alpha^2 c_0 \gamma_{\pm}^2} \quad (5)$$

$$-\log \gamma_{\pm} = \frac{S_f \sqrt{c\alpha}}{1 + A r_D \sqrt{c\alpha}} \quad (6)$$

where $K(\Lambda)$ is the experimentally determined formation constant by conductance,¹⁴ S and A are Debye-Hückel coefficients, and r_D is the minimum distance between free ions set equal to a_J from the conductance results.¹⁴ This assumption implies that all the ions at distance less than r_D are associated.

The outer-sphere association constant $K_{21} = k_{12}/k_{21} = K_{12}^{-1}$ has been calculated from¹⁹ the Fuoss expression

(19) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

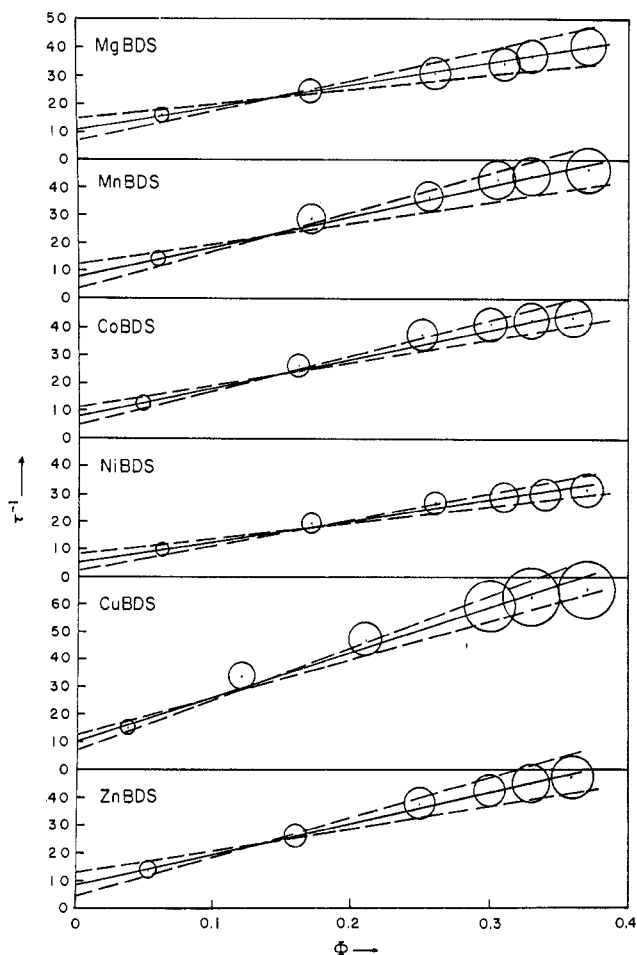


Figure 5.—Plot of τ^{-1} vs. Φ for the various electrolytes in methanol at 25°.

$$K_{21} = K_F = \frac{4\pi N r_D^3}{3000} e^\beta \quad (7)$$

$$\beta = \frac{|z_+ z_-| e^2}{r_D D k T}$$

where N is the Avogadro number, β is the Bjerrum parameter, z_+ and z_- are the ionic charges, e is the electronic charge, D is the dielectric constant of the solvent, k is the Boltzmann constant, and T is the absolute temperature.

In Figure 5 the plots of τ^{-1} vs. Φ are reported and in Table II the calculated slopes and intercepts, namely, the quantities k_{23} and k_{32} , are also reported.

Discussion

In Figure 6 the rate constants k_{23} are plotted for the various metal cations investigated (in the form of $\log k_{23}$) together with the rates of exchange in methanol as determined by nmr, taken from the literature.^{10,11a} The corresponding values for the solvent water^{11b} are also reported on the same graph.

One can see that the values of k_{23} are somewhat smaller in water and far smaller in methanol than the rate constants of solvent exchange as determined by nmr. While in the case of the aqueous solutions k_{23} is on the average $0.2k_{\text{exch}}$ (Figure 6), for the meth-

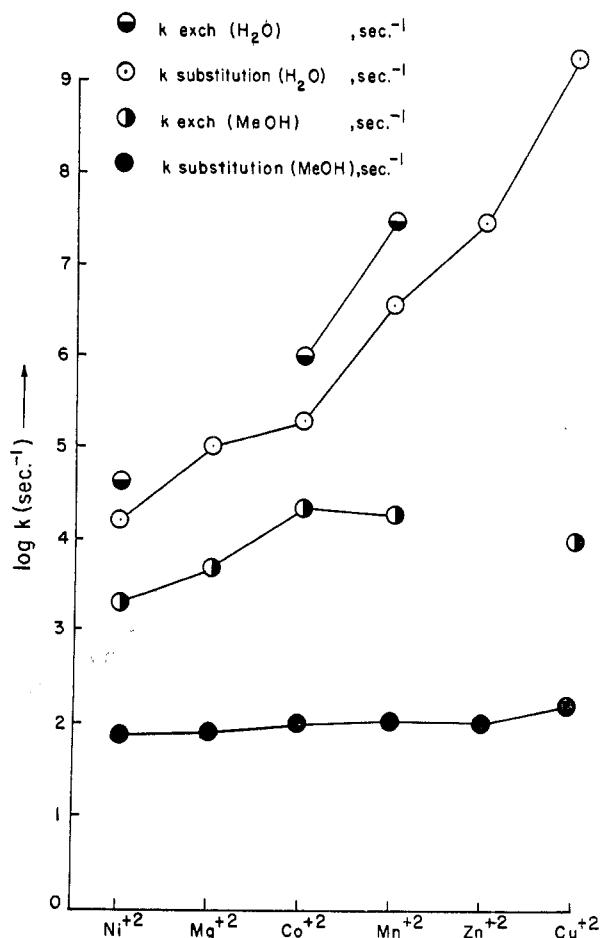


Figure 6.—Plot of first-order rates of ligand exchange for various metal cations in water and methanol at 25°.

anolic solutions k_{23} is between $0.07k_{\text{exch}}$ and $0.01k_{\text{exch}}$. This larger difference between the two systems either could be attributed to a different mechanism of solvent substitution or could be rationalized in terms of qualitative differences of the same mechanism in the substitution process. In the following these two alternate possibilities are discussed.

The result $k_{23} \ll k_{\text{exch}}$ may first suggest an associative mechanism (SN2) of solvent substitution with the formation of an intermediate of higher coordination. A peculiarity of the ligand BDS^{2-} in this respect could also be suggested by some recent work¹² by flow technique in methanol of the complexation of Ni^{2+} with SCN^- , SeCN^- , dithiooxalate, and maleonitriledithiolate anions. For all these ligands k_{23} has been found to be in substantial agreement with k_{exch} (within a factor of 2) as already mentioned.

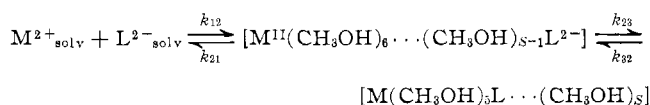
There are however some experimental facts in the present work that elude such a straightforward interpretation. From Figure 6 one may notice a parallelism between k_{23} and k_{exch} for the various metal cations both in water and in methanol. If an associative mechanism were responsible for the reported differences between k_{23} and k_{exch} in methanol, one would not expect such a parallelism given the different electrophilic character of the metal cations (ranging from d^0 to d^{10}).

An alternate interpretation of the finding $k_{23} \ll k_{\text{exch}}$ for M^{II} BDS could be based on a dissociative mechanism (interchange). The differences between k_{23} and k_{exch} could then be rationalized on statistical grounds. In favor of this possibility the following experimental findings may be put in evidence.

First it can be noticed that the hydrodynamic radii calculated from conductance data result in rather high values of R_{+}^{0} . Indeed in methanol Λ_0 is around $115 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ while the methanol viscosity is $\eta = 5.5 \times 10^{-3} \text{ P}$. In water $\Lambda_0 \approx 110 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ while the water viscosity is $\eta = 8.9 \times 10^{-3} \text{ P}$ at 25° . It is clear from eq 1 that in methanol the cations are moving as larger kinetic entities than in water. The distance $R_{+}^{0} + R_{-}^{0}$ (of the order of 10 \AA) may represent the collision distance for the beginning of association of the two ions. Second, it can be noticed that the calculated $K(A)$ from conductance indicate that these electrolytes in methanol exist to a large degree as associated species. Indeed the overall association constant is around $34,000\text{--}40,000 \text{ M}^{-1}$. At $c = 10^{-2} \text{ M}$ this corresponds to an average degree of ionization $\alpha \simeq (1/\sqrt{Kc}) \simeq 0.05$. Therefore, 95% of the electrolyte is either paired or complexed. Because of the extent of ion-pair association, one can assume that a fraction of the nonfree ions are in the second coordination sphere of the cations.

In the interchange I_d mechanism an interchange of ligands from the inner sphere to the outer sphere around the metal cations occurs. It has been suggested^{11b} that because of statistical considerations $k_{23} < k_{\text{exch}}$.

Indeed after the ion pair has been formed an interchange of ligands occurs according to the second part of the scheme



where $M^{II}(\text{CH}_3\text{OH})_6$ represents the metal cation surrounded by the first octahedrally coordinated solvation shell, S is the solvation number in the second coordination shell, and L^{2-} is the ligand.

Suppose that one of the S outer-sphere ligand sites in the ion pair is occupied by the ligand L^{2-} , while

the remaining outer sphere sites ($S - 1$) are occupied by solvent molecules. When a "dissociative event" occurs, a solvent molecule from the inner sphere is expelled into the outer sphere. The chance that the outer-sphere ligand L^{2-} is in a favorable position for the entry is $(1/S)$. Therefore $(S - 1)/S$ "dissociative events" lead to solvent exchange so that the rate k_{23} should be roughly $1/S$ times the rate of solvent exchange k_{exch} from nmr measurements.

The above considerations applied to our case keeping in mind the rather large hydrodynamic radius of the ions (and consequently large values of S), the existence of a large population of outer-sphere ion pairs, and the measured $k_{23} \ll k_{\text{exch}}$ might suggest an I_d mechanism. The same mechanism has been suggested^{11b} also in water for the metal sulfates, k_{23} being $0.2k_{\text{exch}}$ (Figure 6). Examples where $k_{23} \simeq 0.05k_{\text{exch}}$ have appeared in the literature²⁰ and are attributed to an I_d mechanism.

A possible objection to the above rationalizations is that if the described I_d mechanism is really responsible for the discrepancies between k_{23} and k_{exch} , then the rate of penetration k_{23} should be a property of the metal cation, or in other words a consequence of its layer solvation shell in our case. Therefore k_{23} should be smaller than k_{exch} but equal for all the ligands.

The above objection fails, however, to recognize the importance of the individual mutual affinity of metal cation and ligand. If the ligand sitting in the outer sphere of solvation around the cation is strongly preferred as an inner-sphere partner over the solvent, then the statistical considerations leading for an I_d mechanism to the prediction $k_{23} < k_{\text{exch}}$ are invalid.^{11b} This could explain the differences between the present and previous works.¹²

An unequivocal choice between an I_d or an A mechanism is not possible from the present data alone unless a study of the dependence of the rate constant k_{23} on the nucleophilic nature of the ligand (with concurrent equilibrium studies of the association constants) is performed.

Acknowledgments.—The authors wish to express their gratitude to Professor John Stuehr of Case Western Reserve University for valuable suggestions for the experimental setup of the pressure-jump apparatus.

(20) N. V. Duffy and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 816 (1967).