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Kinetics of Association of Nickel(II), Copper(II), and Zinc(II) Perchlorates in Acetonitrile[1a]

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Ultrasonic absorption data for $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ in acetonitrile at temperatures ranging from +25 to −30° reveal the presence of relaxation processes which are interpreted in terms of ionic association. For $Ni(ClO_4)_2$ the rate constants are in accordance with values predicted by diffusion-controlled rate theories. For $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$, the two-step Eigen mechanism is used to interpret the data. Visible absorption spectra at −30° for $Ni(ClO_4)_2$ show no change with respect to existing data at 25°. These spectra suggest that for Ni^{2+} the association is mainly of outer-sphere type. The rate constants at 25° for substitution of acetonitrile from the first coordination shell of Cu^{2+} and Zn^{2+} (as determined by ultrasonics) and for exchange of acetonitrile from the first coordination shell of Ni^{2+}, Co^{2+}, and Mn^{2+} (as determined by nmr) relate linearly with the corresponding rate constants in water. In particular, when arranged in order of increasing rate constants, the cations seem to follow roughly the same sequence in the two solvents. The enthalpies of activation for acetonitrile exchange and substitution follow the same trend as for water in accordance with crystal field predictions for d^8 and d^9 configurations. Supporting conductance data for the interpretation based on ionic association were obtained for $Zn(ClO_4)_2$ and $Cu(ClO_4)_2$ at 25°, −15°, and −30°. Data at 25° for all three electrolytes were taken from the literature. Analysis of the conductance data by the Fuoss–Edelson technique reveals that the electrolytes are slightly associated.

Introduction

The study of the mechanism of ionic association and complexation of transition metals in nonaqueous solvents has not received the extensive analysis as the counterpart aqueous systems.[2] In particular it is of interest to establish whether the multistep Eigen mechanism is applicable to these systems and whether for octahedrally coordinated metal cations the mechanism is mainly SN1 (or I_d) with a dissociative activation mode.[3]

If one wants to study the inner-sphere–outer-sphere equilibrium between contact species and solvent-separated outer-sphere complexes, the choice of the ligand is of fundamental importance. For a given coordinating metal cation if the ligand is strongly preferred over the solvent as an inner-sphere partner, forming mainly a covalent bond, it is to be expected that the relative outer-sphere population will be small. The kinetic study reduces itself to the usual inner-sphere formation study alone. The preequilibration step corresponding to formation of the solvent-separated ion-pair intermediate[4] can only be accounted for by theoretically calculated association constants based on electrostatic models of approximate nature.[5] On the other hand, if the ligand is a poor competitor with the solvent and the bonding with the metal is mainly electrostatic, it may be expected that if association exists at all, the species will be more uniformly distributed between inner- and outer-sphere complexes. For the same ligand the situation in terms of the outer-sphere–inner-sphere distribution may change with the nature of the metal cation. For instance,[6] it is known that in water at 25°, for the sulfates of the metals of the first transition series $NiSO_4$ exists mainly as an outer-sphere species, the ratio between the concentration of the two species being about 10. For $ZnSO_4$ the ratio is reduced to 4 whereas for $CuSO_4$ a roughly equimolar distribution between the two species exists.

Because of the above considerations, and mainly in the hope that if association were observable, both inner-sphere and outer-sphere species existed, a ligand like ClO_4^- was chosen. One could indeed have expected the weakest possible interaction for ClO_4^- among the ligands. One additional reason for the choice of ClO_4^- as ligand was to show that although ClO_4^- acts as a completely inert ionic partner in water, it may participate in ionic association processes in nonaqueous solvents of lower dielectric constants than water.

Existence of rate constants of solvent exchange for transition metal cations in acetonitrile as measured by nmr[7] favored the choice of this solvent for the present study.

Ultrasonic relaxation by the pulse technique proved to be the appropriate tool to study the outer-sphere–inner-sphere processes for copper(II) and zinc(II) perchlorates in acetonitrile. As expected, only the outer-sphere formation could be studied for nickel(II) perchlorates by ultrasonics. If inner-sphere species exist at all, the relatively slow rate of solvent exchange[7] precludes the study of the inner-sphere formation by pulse ultrasonics.

Electrical conductance data support the ultrasonic study, indicating weak association for the above systems as shown in the second part of this work.

Experimental Part

The instrumentation and procedure used in the ultrasonic work[8a] and for the conductance measurements[8b] have been described elsewhere.[8c] The perchlorate salts were prepared[9] in the anhydrous state in acetonitrile by mixing stoichiometric portions of $AgClO_4$ (Alfa Inorganics) with anhydrous $M^{II}Cl_2$ (Baker). Small excesses of either ClO_4^- or Cl^- were found by spot turbidity tests and corrected by adding either $M^{II}Cl_2$ or $AgClO_4$ by a trial and error procedure.

After vacuum filtration through a hyperfine glass fritted disk, the solutions were analyzed for ClO_4^- by cation exchange (after dilution with water) and acidimetry and for the metal cations by standard

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(1) This work is part of the thesis of A. Diamond in partial fulfillment for the requirements of the degree of Master of Sciences, Polytechnic Institute of Brooklyn.

(2) M. Eigen and L. DeMaeyer in "Investigation of Rates and Mechanism of Reaction," Vol. 8, A. Weissberger, Ed., Wiley, New York, N. Y., 1963, part II; S. Petrucci in "Ionic Interactions," Vol. II, Academic Press, New York, N. Y., 1971.

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

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(5) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5058 (1958).

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(8) (a) S. Petrucci, *J. Phys. Chem.*, **71**, 1174 (1967); S. Petrucci and M. Battistini, *ibid.*, **71**, 1181 (1967); G. S. Darbari, M. R. Richelson, and S. Petrucci, *J. Chem. Phys.*, **53**, 859 (1970); (b) S. Petrucci, P. Hemmes, and M. Battistini, *J. Amer. Chem. Soc.*, **89**, 5552 (1967); R. Lovas, G. Macri, and S. Petrucci, *ibid.*, **92**, 6502 (1970); (c) A. Fanelli and S. Petrucci, *J. Phys. Chem.*, **75**, 2649 (1971).

(9) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 137 (1967).

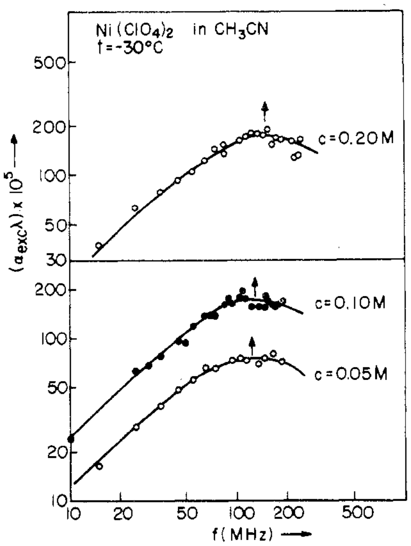

Figure 1. $\alpha_{exc}\lambda$ *vs.* the frequency f for $Ni(ClO_4)_2$ 0.20, 0.10, and 0.05 M in CH_3CN at −30°.

techniques. For the conductance runs, in order to gain the necessary accuracy, analysis of the stock solutions was performed by potentiometric acidimetric titration of a weighed amount of solution after passage through an ion-exchange column.[8c]

Another procedure[10] used for the solutions for conductance measurements was to dissolve recrystallized $M^{II}(ClO_4)_2 \cdot 6H_2O$ salts in the approximate desired amount of predistilled acetonitrile and refluxing the solutions over molecular sieves. Water was analyzed by vapor-phase chromatography and found to be less than 0.05%. In order to have an assessment of the reliability of the data it was of interest to ascertain the effect of small quantities of water in the sound absorption measurements. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ 0.05 M in acetonitrile gave the same results within experimental error as anhydrous $Cu(ClO_4)_2$ solutions of the same concentration. That the water had no effect on the sound absorption or relaxation frequency was rechecked by comparing a solution 0.047 M $Cu(ClO_4)_2$ prepared by the refluxing procedure[10] with the same solution to which had been added 6 mol of water per mole of $Cu(ClO_4)_2$. Identical results were obtained. This also ensured that preparation of anhydrous $Cu(ClO_4)_2$ by either metathesis or refluxing procedure gave comparable results. Similarly, for $Zn(ClO_4)_2$ a solution of 0.0375 M anhydrous salt or hexahydrated salt gave identical ultrasonic results within experimental error.

The spectra of the $Ni(ClO_4)_2$ solutions at −30° were obtained with a Cary 14 spectrophotometer, using a specially designed quartz cell having vacuum jackets facing the optical path to avoid moisture condensation on the quartz windows. Viscosities were measured with an Ubbelhode suspended-level viscometer using liquids of known viscosity for calibration.

Dielectric constants were measured with a Bontoom Q-meter resonator in the frequency range 0.1-10 MHz using a two-terminal cylindrical cell[11] having a capacity of 5.35 pF. The cell was calibrated with *n*-hexane in the temperature range where permittivities of acetonitrile are reported. No detectable temperature dependence of the empty-cell capacitance was observable.

For measurements at low temperature the cell was cooled by circulation of chilled *n*-hexane through an aluminum block surrounding the cell. The *n*-hexane in the reservoir was maintained at constant temperature with a Cryo-cool C-60 cold finger and a Bayley Model 30 proportional thermoregulator. To avoid moisture condensation the cell assembly was enclosed in a Plexiglas drybox maintained at a positive pressure of prepurified dry N_2 (Matheson Coleman and Bell).

Temperatures were measured with a Pt resistance thermometer connected to a Mueller bridge. The thermometer, calibrated by the National Bureau of Standards, permitted temperature measurements to within 0.001°. The average precisions in the reported temperatures of the various measured quantities were as follows: ultrasonic absorption, ±0.05°; electrical conductance, ±0.005° at 25° and ±0.01° at −15 and −30°; viscosity and dielectric constants, ±0.1°.

Results

Figure 1 reports ultrasonic excess absorption coefficient (α_{exc}) times the wavelength λ *vs.* the frequency for $Ni(ClO_4)_2$ at −30° and the various concentrations investigated.

Figure 2 similarly reports the ultrasonic representative results for $Cu(ClO_4)_2$ at 25, −15, and −30° at three concentrations. Ultrasonic results for $Zn(ClO_4)_2$ at 35 and 25° for three concentrations are shown in Figure 3. Figure 3 also reports the same quantity, namely, $\alpha_{exc}\lambda$ *vs.* f for 0.15 M $Zn(ClO_4)_2$ at 0, −15, and −30°.

In the above the excess absorption coefficient $\alpha_{exc} = \alpha - \alpha_0$ (neper cm^{-1}). α and α_0 are the measured absorption coefficients for the solution and the solvent, respectively. λ is the wavelength of sound equal to the sound velocity V divided by the frequency f. The sound velocity has been assumed equal to that of the solvent and independent of frequency.

A brief statement may be useful at this point to support the last approximation. From classical relaxation theory of liquids[12] applied to a Newtonian fluid subjected to a single relaxation process, one has

$$M' = \rho V^2 = K' = K_0 + K_R \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} = \rho V_0^2 + \rho(V_\infty^2 - V_0^2)\frac{\omega^2\tau^2}{1 + \omega^2\tau^2}$$

$$M'' = \frac{2\alpha_{exc}\rho V^3}{\omega} = K'' = K_R \frac{\omega\tau}{1 + \omega^2\tau^2} = \rho(V_\infty^2 - V_0^2) \times \frac{\omega\tau}{1 + \omega^2\tau^2}$$

where ρ is the density and M', M'', K', and K'' are the real and imaginary parts of the longitudinal and compressional moduli, respectively. V_0 and V_∞ are the low- and high-frequency values of the longitudinal velocity. Then

$$\alpha_{exc}\lambda = \frac{V_\infty^2 - V_0^2}{V^2} \pi \frac{\omega\tau}{1 + \omega^2\tau^2}$$

At the relaxation frequency $\omega\tau = 1$ and

$$(\alpha_{exc}\lambda)_{max} = \frac{V_\infty^2 - V_0^2}{V_\infty^2 + V_0^2} \pi$$

since for $f = f_R$

$$V^2 = V_0^2 + \frac{1}{2}V_\infty^2 - \frac{1}{2}V_0^2 = \frac{1}{2}(V_\infty^2 + V_0^2)$$

If $(\alpha_{exc}\lambda)_{max} = 314 \times 10^{-5}$ and $V_0 = 1300$ m/sec then $V_\infty = 1301$ m/sec; therefore, a change of 0.1% in velocity results whereas the experimental precision of V is about 1%.

Table I reports all the physical properties of the solvent (either taken from the literature or measured in this laboratory as indicated) pertinent to this work.

Table II reports the equivalent conductance data at the temperatures and concentrations investigated for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$. As already mentioned, the temperature was checked to be within ±0.005° at 25° and ±0.01° at lower temperature, during the runs by means of a Mueller bridge connected to a calibrated Pt thermometer.

Calculations and Discussion

For the sake of clarity this section will be divided into two parts according to the major methods of attack.

Part I. Kinetic Measurements. The relaxation phenomenon for $Ni(ClO_4)_2$ at −30° will be analyzed first. The solid

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[10] P. Arthur, W. M. Haynes, and P. Varga, *Anal. Chem.*, 38, 1630 (1966).

[11] Rutherford Research Co., Inc., Rutherford, N. J.

[12] T. A. Litovitz and C. M. Davis in "Physical Acoustics," Vol. 2, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965, part A.

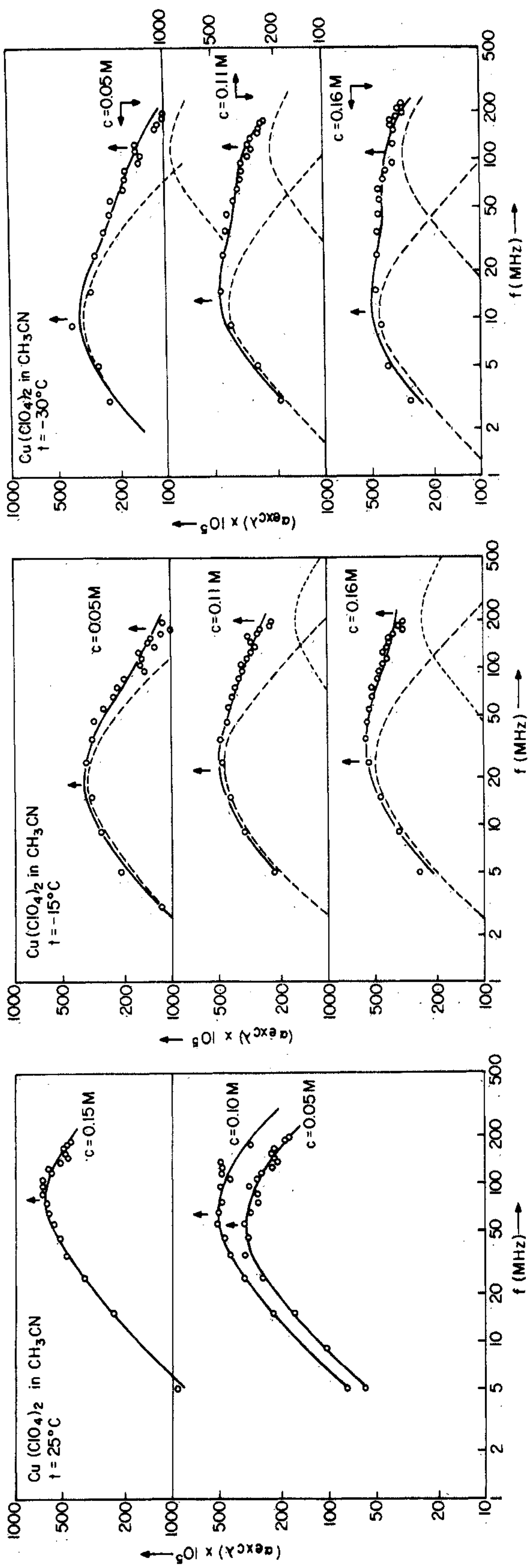

Figure 2. $\alpha_{exc}\lambda$ *vs.* the frequency *f* for $Cu(ClO_4)_2$ 0.15, 0.10, and 0.05 *M* in CH_3CN at 25, -15, and -30°.

Table I. Physical Constants of Acetonitrile Pertinent to This Work (Density and Viscosity from "International Critical Tables"; Otherwise Indicated)

Temp, °C	*D*	ρ, g/cm^3	η, P	$10^{17}(\alpha_0/f^2)$,[a] cm^{-1} sec^2	*V*,[b] m/sec
35	34.2	0.7665	(0.00313)[d]	70.5	1228
25	36.0	0.7767	0.00345	63.5	1290
15	37.9	0.7877	0.00375	57.5	1330
0	40.6	0.8035	0.00442	49.2	1370
−15	43.0	0.8193	0.00531[c]	40.2	1412
−30	45.4	0.8352	0.00685[c]	34.2	1485

[a] Average precision ±2%. [b] Average precision ±1%. [c] Figures determined in this laboratory. [d] Value extrapolated from data from the "International Critical Tables."

Table II.[a] Equivalent Conductances (Ω^{-1} cm^2 equiv^{-1}) and Concentrations (*M*) for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ in Acetonitrile

25°		−15°		−30°	
10^4C	Λ	10^4C	Λ	10^4C	Λ
		$Cu(ClO_4)_2$			
1.8555	186.439	1.9568	118.174	1.9947	95.235
3.1446	180.935	3.3162	115.038	3.3806	92.796
5.0128	175.822	5.2864	112.055	5.3889	90.225
7.7181	170.067	12.8464	103.943	8.2972	87.321
12.1816	162.789	15.7466	101.708	13.0957	83.625
14.9317	159.212	19.3970	99.391	16.0522	81.794
18.3932	155.729	22.2069	97.605	19.7734	79.945
21.0577	153.023	26.0084	96.131	22.6379	78.747
		30.4766	94.369	31.0680	75.868
		$Zn(ClO_4)_2$			
2.1787	183.877	2.2976	117.278	2.3422	94.615
5.6995	172.615	6.0100	110.304	6.1274	89.065
8.2694	166.777	8.7207	106.898	8.8901	86.086
10.7243	162.517	11.3095	104.280	11.5291	83.990
12.7527	160.072	13.4487	102.640	13.7099	82.755
16.7968	156.410	15.5445	101.091	15.8465	81.374
		17.7135	100.374	18.0576	80.875

[a] To avoid round-off error in the conductance calculations, one extra figure with respect to the sensitivity of the method has been included in the data.

lines in Figure 1 for $Ni(ClO_4)_2$ at −30° are calculated in accordance with the function for a single relaxation[2]

$$\alpha_{exc}\lambda = 2(\mu_{exc})_{max}\frac{\omega\tau}{1+\omega^2\tau^2} = 2(\mu_{exc})_{max} \times \frac{f/f_R}{1+(f/f_R)^2} \qquad (1)$$

where ω is the angular frequency $\omega = 2\pi f$, τ the relaxation time ($\tau^{-1} = 2\pi f_R$), f_R the relaxation frequency, and $(\mu_{exc})_{max}$ the maximum excess sound absorption at the relaxation condition $\omega\tau = 1$.

In Table III the results of function 1 applied to the data for $Ni(ClO_4)_2$ at −30° as a two-parameter equation in $(\mu_{exc})_{max}$ and f_R are reported. It may be noticed that the relaxation frequencies are concentration dependent. This and the information (given below) from conductance that Ni^{2+} and ClO_4^- are weakly associated to $Ni(ClO_4)^+$ suggest the hypothesis of ionic association as the source of the relaxation phenomenon. Then, according to Eigen[2] one may write

$$Ni^{2+} + ClO_4^- \underset{k_R}{\overset{k_f}{\rightleftharpoons}} NiClO_4^+$$

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

$$\theta = \frac{\gamma_{Ni}\gamma_{ClO_4}}{\gamma_{NiClO_4}}\left[C_{Ni} + C_{ClO_4} + C_{ClO_4} \times \frac{d\ln(\gamma_{Ni}\gamma_{ClO_4}/\gamma_{NiClO_4})}{d\ln C_{Ni}}\right]$$

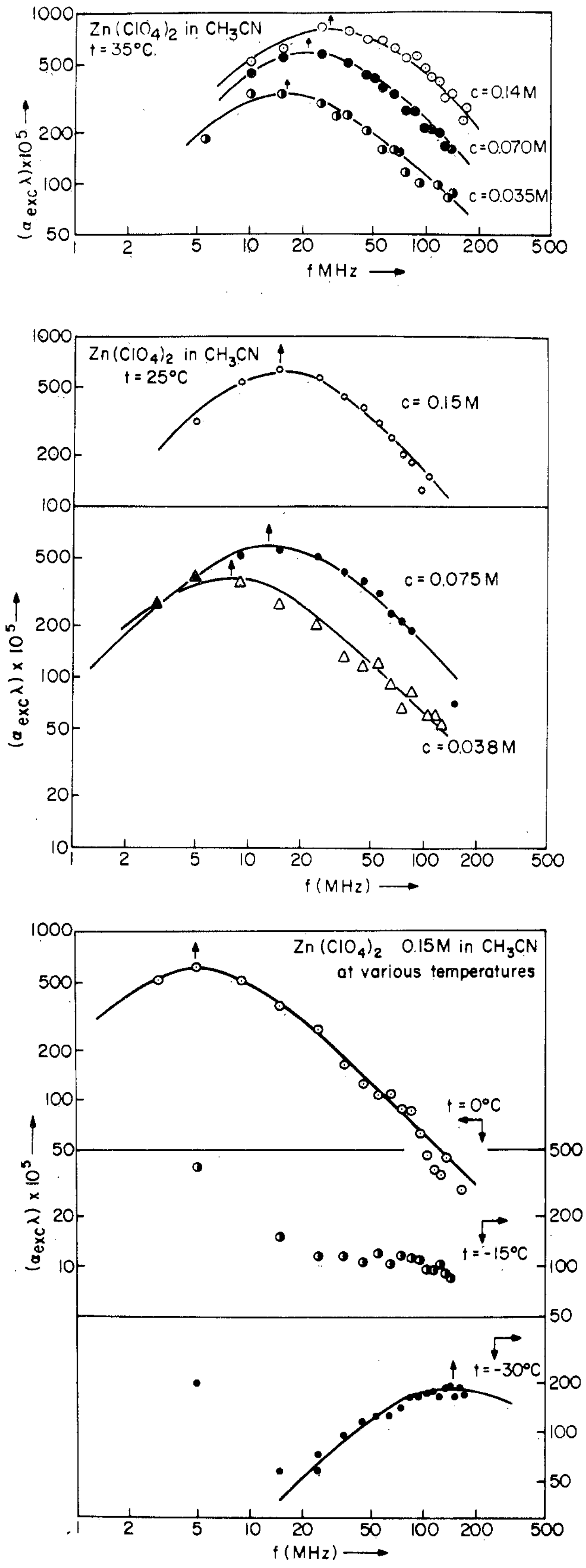

Figure 3. $\alpha_{exc}\lambda$ *vs.* the frequency f for $Zn(ClO_4)_2$ 0.15, 0.075, and 0.038 M in CH_3CN at 35 and 25°. Same quantity for $Zn(ClO_4)_2$ 0.15 M at 0, −15, and −30°.

Table III. Ultrasonic Relaxation Parameters for $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ in Acetonitrile[a]

	Temp, °C	C, M	$10^5 \cdot (\mu_{exc})_I$	f_{RI}, MHz	$10^5 \cdot (\mu_{exc})_{II}$	f_{RII}, MHz
$Ni(ClO_4)_2$	−30	0.204	170	150		
		0.097	170	130		
		0.054	75	125		
$Cu(ClO_4)_2$	25	0.150			650	80
		0.100			520	65
		0.050			340	55
	−15	0.157	250	220	500	25
		0.105	160	200	460	22
		0.052	60	180	340	18
	−30	0.161	310	110	440	11
		0.108	210	120	400	13
		0.054	90	120	350	10
$Zn(ClO_4)_2$	35	0.14			800	26
		0.07			580	21
		0.035			330	16
	25	0.150			600	15
		0.075			600	12
		0.038			380	9
	15	0.153			800	7
		0.076			550	6
		0.038			360	5
	0	0.155			600	5
		0.078			550	5
		0.039			320	4

[a] The reported μ_{exc} and f_R have been calculated by a template analysis. These figures should be considered affected by an average error of ±10%. For $Cu(ClO_4)_2$ at −15 and −30° the error in $(\mu_{exc})_I$ and f_{RI} is about ±20%. Assignment of the observed relaxations to the second step for $Cu(ClO_4)_2$ at 25° and for $Zn(ClO_4)_2$ is done only for presentation sake. The relaxation phenomenon is, in effect, the relaxation of the normal mode of oscillation of two closely coupled equilibria.

where the charge symbols have been omitted in the subscripts. If σ is the degree of dissociation, neglecting the concentration of $Ni(ClO_4)_2$, one has $C_{Ni} = C\sigma$, $C_{ClO_4} = C(1 + \sigma)$, $C_{NiClO_4} = C(1 - \sigma)$, and

$$\theta = \frac{\gamma_{2:1}{}^3}{\gamma_{1:1}{}^2}\left[(2\sigma + 1)C + (\sigma + 1)C\frac{d \ln (\gamma_{2:1}{}^3/\gamma_{1:1}{}^2)}{d \ln \sigma}\right] \quad (3)$$

where the relation $\gamma_{Ni}\gamma_{ClO_4}/\gamma_{NiClO_4} = \gamma_{2:1}{}^3/\gamma_{1:1}{}^2$ is found by considering the electrostatic interactions (not to be taken as chemical equilibria)[13]

$$Ni^{2+} + 2ClO_4^- \rightleftharpoons Ni(ClO_4)_2$$

$$\gamma_{Ni}\gamma_{ClO_4}{}^2 = \gamma_{Ni(ClO_4)_2}{}^3 = \gamma_{2:1}{}^3$$

$$Ni(ClO_4)^+ + ClO_4^- \rightleftharpoons Ni(ClO_4)ClO_4$$

$$\gamma_{NiClO_4}\gamma_{ClO_4} = \gamma_{Ni(ClO_4)ClO_4}{}^2 = \gamma_{1:1}{}^2$$

The calculation of $\gamma_{2:1}$ and $\gamma_{1:1}$ has been performed by the Debye-Huckel theory. It is understood that the use of such a theory in this range of concentrations is not justified on purely theoretical grounds.[13,14] The errors will reflect in the calculation of k_f and k_r through θ according to eq 2. However, in the following calculations the use of these approximate values of $\gamma_{2:1}$ and $\gamma_{1:1}$ should not affect the interpretation of the ultrasonic results insofar as the nature of the observed relaxation phenomenon is concerned.

Assuming the Debye-Huckel theory in the form

$$-\ln \gamma_\pm = \frac{S\Gamma^{1/2}}{1 + Aa\Gamma^{1/2}} \quad (4)$$

with Γ the ional concentration $\Gamma = \Sigma_i c_i z_i{}^2 = 2c(2\sigma + 1)$, the ratio

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(13) A. Elder and S. Petrucci, *Inorg. Chem.*, 9, 19 (1970).

(14) G. S. Darbari and S. Petrucci, *J. Phys. Chem.*, 74, 268 (1970).

$$\ln \frac{{\gamma_{2:1}}^3}{{\gamma_{1:1}}^2} = \frac{2S_{1:1}\Gamma^{1/2} - 3S_{2:1}\Gamma^{1/2}}{1 + Aa\Gamma^{1/2}}$$

then

$$\frac{\mathrm{d}\ln ({\gamma_{2:1}}^3/{\gamma_{1:1}}^2)}{\mathrm{d}\ln \sigma} = \sigma \frac{\mathrm{d}\ln ({\gamma_{2:1}}^3/{\gamma_{1:1}}^2)}{\mathrm{d}\Gamma} \frac{\mathrm{d}\Gamma}{\mathrm{d}\sigma}$$

with

$$\frac{\mathrm{d}\ln ({\gamma_{2:1}}^3/{\gamma_{1:1}}^2)}{\mathrm{d}\Gamma} = \frac{2S_{1:1} - 3S_{2:1}}{2\Gamma^{1/2}(1 + Aa\Gamma^{1/2})^2}$$

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}\sigma} = 4c$$

Therefore

$$\frac{\mathrm{d}\ln ({\gamma_{2:1}}^3/{\gamma_{1:1}}^2)}{\mathrm{d}\ln \sigma} = \frac{2c\sigma(2S_{1:1} - 3S_{2:1})}{\Gamma^{1/2}(1 + Aa\Gamma^{1/2})^2} \tag{5}$$

which must be inserted into eq 3. To solve eq 3 one needs a value of the parameter a (the minimum approach distance between free ions) and the values of σ. The parameter a has been equated to the sum of the hydrodynamic radii as calculated from conductance (see below) according to the Stokes expression

$$R_{\pm}^{0} = \frac{|Z_{\pm}| 0.82}{\lambda_{\pm}^{0}\eta} \tag{6}$$

with $a = R_+^0 + R_-^0 = 7.5 \times 10^{-8}$ cm for the present work. Values of σ at the various concentrations under study have been calculated by combining eq 4 with the expression for association

$$K_{\mathrm{A}_1} = \frac{C_{\mathrm{NiClO_4}}}{C_{\mathrm{Ni}}C_{\mathrm{ClO_4}}} \frac{\gamma_{\mathrm{NiClO_4}}}{\gamma_{\mathrm{Ni}}\gamma_{\mathrm{ClO_4}}} = \frac{1-\sigma}{c\sigma(1+\sigma)} \frac{{\gamma_{1:1}}^2}{{\gamma_{2:1}}^3} \tag{7}$$

where K_{A_1} is the equilibrium constant determined through electrical conductance (see below).

In order to examine the effect of the value of the association constants on the kinetic results, the calculation of θ has been performed with $K_{\mathrm{A}_1} = 20$ and $K_{\mathrm{A}_1} = 80\ M^{-1}$. Figure 4 shows the values of τ^{-1} *vs.* θ for $\mathrm{Ni(ClO_4)_2}$ in acetonitrile at −30°. The dashed straight line for $K_{\mathrm{A}_1} = 20\ M^{-1}$ calculated through least squares gives $k_{\mathrm{f}} = (1.5 \pm 0.7) \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ as slope and $k_{\mathrm{r}} = (6.1 \pm 1.2) \times 10^{8}\ \mathrm{sec}^{-1}$ as intercept. The average ratio between these figures is $\bar{K}_1 = 24\ M^{-1}$. For $K_{\mathrm{A}_1} = 80\ M^{-1}$ the solid straight line calculated through least squares gives $k_{\mathrm{f}} = (1.7 \pm 0.4) \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ as slope and $k_{\mathrm{r}} = (6.0 \pm 0.6) \times 10^{8}\ \mathrm{sec}^{-1}$ as intercept. The average ratio between these values is $\bar{K}_1 = 28\ M^{-1}$.

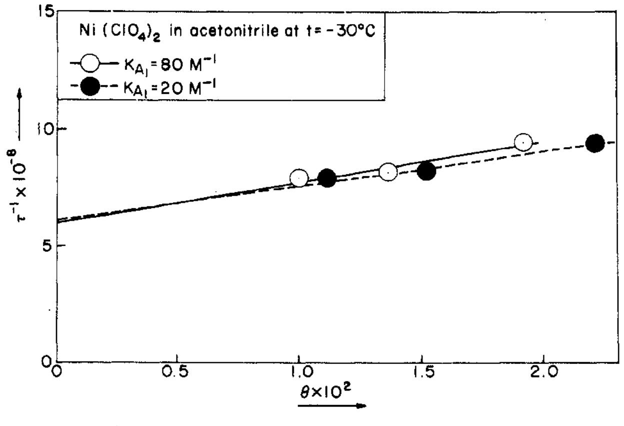

Figure 4. τ^{-1} *vs.* θ for $\mathrm{Ni(ClO_4)_2}$ in $\mathrm{CH_3CN}$ at −30°.

It may be seen that the values of k_{f} and k_{r} are rather insensitive to the retained value of K_{A_1} for the calculation of θ. Further, the calculated $\bar{K}_1$ values are of the same order of magnitude as the K_{A_1}'s calculated through conductance data.

Values of the diffusion-controlled rate constants, corresponding to the maximum rate of ionic association and dissociation when the only barrier is the one for viscous flow, may be calculated from the Smoluchowski-Debye[15] and Eigen[16] theories written in the form[8a]

$$\left.\begin{aligned} k_{\mathrm{D}} &= \frac{8NkT}{3000\eta}\left(\frac{-b}{e^{-b}-1}\right) \\ k_{-\mathrm{D}} &= \frac{2kT}{\pi a^3\eta}\left(\frac{-b}{1-e^{b}}\right) \end{aligned}\right. \tag{8}$$

and[5]

$$K_{\mathrm{Fuoss}} = \frac{k_{\mathrm{D}}}{k_{-\mathrm{D}}} = \frac{4\pi Na^3}{3000}\exp(b)$$

where $b = |Z_+Z_-|e^2/aDkT$, k is the Boltzmann constant, T the absolute temperature, N the Avogadro number, η the solvent viscosity, Z_+Z_- the ionic charges, e the electronic charge, and D the solvent permittivity.

Taking $a = 7.5 \times 10^{-8}$ cm as before gives $k_{\mathrm{D}} = 3.2 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$, $k_{-\mathrm{D}} = 5.4 \times 10^{8}\ \mathrm{sec}^{-1}$, and $K_{\mathrm{Fuoss}} = 60\ M^{-1}$ in fair agreement in order of magnitude with the experimental k_{f}, k_{r}, and $\bar{K}_1$ reported above.

It seems, therefore, that a diffusion-controlled process with the formation of an outer-sphere ion pair $\mathrm{Ni^{2+}(CH_3CN)ClO_4^-}$ is responsible for the observed relaxation. That the ion pair should be of the outer-sphere type is suggested by comparing the rate constant for solvent exchange[17] around $\mathrm{Ni^{2+}}$ ($k_{\mathrm{exch}} = 3 \times 10^{3}\ \mathrm{sec}^{-1}$ at 25°) with the position of the experimental relaxation frequency value which is several orders of magnitude too high.

Other evidence is deduced from the visible spectra obtained in this laboratory for $\mathrm{Ni(ClO_4)_2}$ at −30° in acetonitrile. The spectrum is superimposable within experimental error with the one reported by Libus[18] at 25°.

On the basis of the symmetrical nature of the absorption bands, Libus concluded that $\mathrm{ClO_4^-}$ was not present in the first coordination shell of $\mathrm{Ni^{2+}}$.

Therefore according to the spectra, if association occurs, the anion must be in the second coordination sphere of $\mathrm{Ni^{2+}}$. This is in accord with the present ultrasonic results.

The situation with $\mathrm{Cu(ClO_4)_2}$ and $\mathrm{Zn(ClO_4)_2}$ is more complex. As shown below the temperature dependence of the ultrasonic spectra was necessary to resolve these cases.

From Figures 2 and 3 it may be seen that at 25° for both $\mathrm{Cu(ClO_4)_2}$ and $\mathrm{Zn(ClO_4)_2}$ only one relaxation is present. The solid lines in Figures 2 and 3 at 25° have been calculated with the aid of eq 1 treated as a two-parameter equation in $(\mu_{\mathrm{exc}})_{\max}$ and τ. For $\mathrm{Zn(ClO_4)_2}$ at 35, 15, and 0° (Figure 3) also a single relaxation function can be fitted to the data.

At −15 and −30° the $\alpha_{\mathrm{exc}}\lambda$ *vs.* f plots for $\mathrm{Cu(ClO_4)_2}$ cannot be interpreted by a single relaxation function (Figure 2). They may be interpreted as the sum of two relaxation processes (dashed lines in Figure 2) giving as sum the solid line ac-

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[15] M. von Smoluchowski, *Z. Phys. Chem.* (*Frankfurt am Main*), 92, 179 (1917); P. Debye, *Trans. Electrochem. Soc.*, 82, 265 (1942).

[16] R. Lovas, G. Macri, and S. Petrucci, *J. Amer. Chem. Soc.*, 92, 6502 (1970).

[17] N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, 6, 1127 (1967); D. K. Ravage, *ibid.*, 6, 1127 (1967).

[18] W. Libus and H. Strzelecki, *Electrochim. Acta*, 15, 703 (1970).

cording to the function valid for two discrete relaxations

$$\alpha_{\text{exc}}\lambda = 2(\mu_{\text{exc}})_{\text{I}}\frac{\omega\tau_{\text{I}}}{1+\omega^2\tau_{\text{I}}^2} + 2(\mu_{\text{exc}})_{\text{II}}\frac{\omega\tau_{\text{II}}}{1+\omega^2\tau_{\text{II}}^2} \tag{9}$$

where $(\mu_{\text{exc}})_{\text{I}}$ and $(\mu_{\text{exc}})_{\text{II}}$ are the maximum values of the excess sound absorption per wavelength at the relaxation frequencies f_{RI} and f_{RII}. τ_{I} and τ_{II} are the corresponding relaxation times ($\tau^{-1} = 2\pi f_{\text{R}}$).

In Table III the results for the calculated μ_{exc} and f_{R} are reported. An error of ±10% is associated with these figures for the case of the single relaxation functions and for the lower relaxation of $Cu(ClO_4)_2$ at −15 and −30°. An error of about ±20% is associated with the values for the upper relaxation of $Cu(ClO_4)_2$ at −15 and −30° according to graphical template analysis. This greater error is due to the combined effects of the uncertainty of the fitting procedures using eq 9 and the larger error of the excess sound absorption per wavelength data at the highest frequencies. Indeed the difference between the total sound absorption and the solvent absorption becomes smaller with increasing frequency thereby causing greater percentage error in $\alpha_{\text{exc}}\lambda$ as pointed out elsewhere.[19]

An immediate objection to the use of a two-relaxation function to interpret the data of $Cu(ClO_4)_2$ in acetonitrile at −15 and −30° could be that at these temperatures a structural effect of the electrolyte upon the solvent may alter the sound absorption of the solvent as suggested in the case of other systems.[20] The imposed relaxation at the higher frequency could be an artifact. In other words the differences in the $\alpha_{\text{exc}}\lambda$ data at the higher frequencies with respect to the single relaxation functions (Figure 2) could be due to a change in the background sound absorption with respect to the solvent value.

That this is not the case for the present systems may be shown as follows. From Figure 3 it may be seen that the data for $Zn(ClO_4)_2$ at −15 and −30° split into more than one relaxation. Clearly at −30° only the upper relaxation is visible together with the tail of the lower one. This separation strongly suggests that the lower relaxation process has a much larger barrier of energy than the higher one. Further, the relaxation for $Zn(ClO_4)_2$ at −30° is of the same order of magnitude in the extent of the excess sound absorption and in the value of the relaxation frequency as the one analyzed for $Ni(ClO_4)_2$ at −30°. The natural question which then arises is, "Why are two relaxations clearly visible at −30° for $Cu(ClO_4)_2$ whereas for $Zn(ClO_4)_2$ the upper relaxation and only the tail of the low one are visible while for $Ni(ClO_4)_2$ only one relaxation appears?"

The question may be answered by associating the lower relaxation process with the rate of substitution of acetonitrile from the first coordination sphere of the cation by the ligand. If, as in the case of water the solvent-exchange rates follow the relative sequence[7] $Cu^{2+} > Zn^{2+} > Ni^{2+}$, then a qualitative rationalization of the above differences in the sound absorption spectra is achieved.

In other words, for $Ni(ClO_4)_2$ only one relaxation, the one corresponding to the formation of the outer-sphere complex is visible at −30°. For $Zn(ClO_4)_2$ at −30° this relaxation and the tail of the lower one (corresponding mainly to the substitution of acetonitrile in the first coordination sphere of the cation) are visible. For $Cu(ClO_4)_2$ both relaxations are well within the megahertz region because of the faster rate of exchange of acetonitrile from the axial position of Cu^{2+}. By increasing the temperature, according to this hypothesis, the lower relaxation having a larger barrier of energy (larger temperature coefficient of the relaxation frequency) coalesces with the upper relaxation in a single relaxation function which corresponds to the normal mode of vibration of two closely coupled oscillators.

The above suggests the following Eigen scheme[2] of reaction to analyze the data for $Zn(ClO_4)_2$ and $Cu(ClO_4)_2$

$$M^{2+}S_6 + L^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M^{2+}S_6,L^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} MS_5L \tag{10}$$

where $M^{2+}S_6,L^-$ is the solvent-separated ion pair; MS_5L is the contact species. k_{12} and k_{21} are the diffusion-controlled rate constants; k_{23} and k_{32} are the rate constants for the removal of a solvent molecule from the first coordination sphere of the metal cation and for the breaking of the metal-ligand bond, respectively. k_{23} should be related to the nmr rate of solvent exchange and to its barrier of energy for a dissociative mechanism.[3]

The analysis of the data has been performed as follows. For the temperatures where only one relaxation process is visible, namely, 35, 25, 15, and 0°, a steady-state approximation for the intermediate $[d(M^{2+}S_6,L^-)/dt] = 0$ applied to scheme 10 leads to the relations[21]

$$k_f = \frac{k_{12}k_{23}}{k_{21} + k_{23}} \tag{11a}$$

and

$$k_r = \frac{k_{21}k_{32}}{k_{21} + k_{23}} \tag{11b}$$

where k_f and k_r apply to the overall process

$$M^{2+}S_6 + L^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} MS_5L \tag{12}$$

Plots of τ^{-1} *vs.* θ give k_f and k_r as slope and intercept according to the relation

$$\tau^{-1} = k_f\theta + k_r \tag{13}$$

The results for k_f and k_r determined by least-squares analysis are reported in Table IV. The calculation has been reported for $K_{A_1} = 80\,M^{-1}$ and $K_{A_1} = 20\,M^{-1}$ as in the case of $Ni(ClO_4)_2$ at −30°.

In eq 11, if $k_{21} \gg k_{23}$, the expressions for k_f and k_r reduce to $k_f = K_{12}k_{23} = K_{\text{Fuoss}}k_{23}$ and $k_r = k_{32}$.[4]

This condition has been imposed on the data of $Zn(ClO_4)_2$. The K_{Fuoss} and calculated k_{23} are reported in Table IV. The results confirm the imposed condition, *i.e.*, k_{21} is always more than one order of magnitude larger than k_{23}.

For the data of $Cu(ClO_4)_2$ at 25° eq 11a and b have been solved for k_{23} and k_{32} by imposing for k_{12} and k_{21} the calculated k_{D} and $k_{-\text{D}}$ from eq 8. The results of this calculation are also reported in Table IV.

For the data of $Cu(ClO_4)_2$ at −15 and −30° where two relaxations are visible, the Eigen matrix analysis for a two-step mechanism[2] has been applied. This gives the result

$$\tau_{\text{I,II}}^{-1} = \frac{1}{2}\left[S \pm \sqrt{S^2 - 4P}\right] \tag{14}$$

with

$$S = k_{12}\theta + k_{21} + k_{23} + k_{32}$$

$$P = k_{12}\theta(k_{23} + k_{32}) + k_{21}k_{32}$$

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(20) L. G. Jackopin and E. Yeager, *J. Phys. Chem.*, 74, 3766 (1970); P. Hemmes and S. Petrucci, *ibid.*, 74, 467 (1970); F. Fittipaldi, P. Hemmes, and S. Petrucci, *Acustica*, 23, 322 (1970).

Table IV. Results of k_f, k_r, k_{23}, and k_{32} for $Zn(ClO_4)_2$ and $Cu(ClO_4)_2$ in Acetonitrile

Temp, °C	K_{A_1}, M^{-1}	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}	$k_D = k_{12}$, M^{-1} sec^{-1}	$k_{-D} = k_{21}$, sec^{-1}	K_F, M^{-1}	k_{23}, sec^{-1}	k_{32}, sec^{-1}
				$Zn(ClO_4)_2$				
35	80	$(8.73 \pm 0.80) \times 10^9$	$(3.78 \pm 0.089) \times 10^7$	9.35×10^{10}	1.29×10^9	72.7	12.01×10^7	3.78×10^7
	20	$(7.92 \pm 1.06) \times 10^9$	$(4.15 \pm 1.25) \times 10^7$	9.35×10^{10}	1.29×10^9	72.7	10.9×10^7	4.15×10^7
25	80	$(5.05 \pm 0.56) \times 10^9$	$(1.84 \pm 0.65) \times 10^7$	8.07×10^{10}	1.20×10^9	67.5	7.48×10^7	1.84×10^7
	20	$(4.17 \pm 0.52) \times 10^9$	$(2.31 \pm 0.68) \times 10^7$	8.07×10^{10}	1.20×10^9	67.5	6.18×10^7	2.31×10^7
15	80	$(1.62 \pm 0.16) \times 10^9$	$(1.82 \pm 0.20) \times 10^7$	7.06×10^{10}	1.12×10^9	62.7	2.58×10^7	1.82×10^7
	20	$(1.31 \pm 0.14) \times 10^9$	$(2.01 \pm 0.19) \times 10^7$	7.06×10^{10}	1.12×10^9	62.7	2.09×10^7	2.01×10^7
0	80	$(0.69 \pm 0.50) \times 10^9$	$(2.05 \pm 0.66) \times 10^7$	5.60×10^{10}	0.94×10^9	58.9	1.17×10^7	2.05×10^7
	20	$(0.60 \pm 0.45) \times 10^9$	$(2.06 \pm 0.68) \times 10^7$	5.60×10^{10}	0.94×10^9	58.9	1.02×10^7	2.06×10^7
				$Cu(ClO_4)_2$				
25	80	$(2.44 \pm 0.75) \times 10^{10}$	$(1.15 \pm 0.96) \times 10^8$	8.07×10^{10}	1.20×10^9	67.5	5.2×10^8	1.7×10^8
	20	$(2.00 \pm 0.54) \times 10^{10}$	$(1.43 \pm 0.75) \times 10^8$	8.07×10^{10}	1.20×10^9	67.5	4.0×10^8	1.9×10^8

Table V. k_{12}, k_{21}, k_{23}, k_{32}, and $f_{RI,II}$ for $Cu(ClO_4)_2$ in CH_3CN[a]

C, M	$10^{-10}k_{12}$, M^{-1} sec^{-1}	$10^{-8}k_{21}$, sec^{-1}	$10^{-8}k_{23}$, sec^{-1}	$10^{-8}k_{32}$, sec^{-1}	f_{RI}(calcd), MHz	f_{RI}(exptl), MHz	f_{RII}(calcd), MHz	f_{RII}(exptl), MHz
				−15°				
0.052	4.4[b]	7.5[b]	1.0	1.0	200	180	20.6	18
0.105	4.4	7.5	1.0	1.0	228	200	22	22
0.157	4.4	7.5	1.0	1.0	235	220	22	25
				−30°				
0.054	3.2[b]	5.4[b]	0.5	0.5	142	120	10.3	10
0.108	3.2	5.4	0.5	0.5	162	120	11.1	13
0.161	3.2	5.4	0.5	0.5	174	110	11.9	11
0.054	1.7[c]	6.0[c]	0.5	0.5	128	120	9.5	10
0.108	1.7	6.0	0.5	0.5	140	120	9.5	13
0.161	1.7	6.0	0.5	0.5	148	110	10.3	11

[a] Overall $K_{A_1} = 80\ M^{-1}$. [b] Calculated k_D and k_{-D}, respectively. [c] Experimental k_{12} and k_{21} respectively for $Ni(ClO_4)_2$ in CH_3CN at −30°.

The results for this calculation, using for k_{12} and k_{21} the calculated k_D and k_{-D} from eq 8, are shown in Table V. The k_{23} and k_{32} are reported together with the calculated f_R and the corresponding experimental values. It may be seen that the fit for the lower relaxation frequencies is relatively good whereas differences exist for the upper relaxation values. These differences are not too distressing if one recalls the experimental error quoted above for f_{RI} (±20%). More important it may be seen that by using the experimental k_{12} and k_{21} taken from $Ni(ClO_4)_2$ at −30° instead of k_D and k_{-D} the differences between f_{RI}(calcd) and f_{RI}(exptl) decrease. The values of f_{RII}(calcd) seem also to be rather insensitive to the values used for k_{12} and k_{21}.

The values of k_{23} may now be correlated at 25° with the existing rate constants for exchange of acetonitrile for Ni^{2+}, Co^{2+}, and Mn^{2+} taken from the literature.[7]

In particular it is of interest to correlate both k_{23} and k_{exch} with the corresponding values in water at 25°.

In Figure 5 the log k_{exch} values in water[22] are plotted *vs.* the corresponding values in acetonitrile. For Zn^{2+} and Cu^{2+} log k_{23}, the determined rate constants of solvent substitution, are also plotted for the two solvents. In water the values $k_{23}(Zn^{2+}) = 3.3 \times 10^7$ sec^{-1} [23] and $k_{23}(Cu^{2+}) = 10^9$ sec^{-1} [24] have been used.

It may be seen that the data conform to a rough linear correlation, Cu^{2+} being the fastest and Ni^{2+} the slowest ligand (or solvent) exchanging cations.

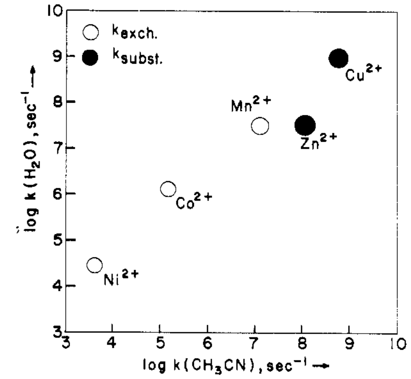

Figure 5. Log $k_{exch}(H_2O)$ *vs.* log $k_{exch}(CH_3CN)$ for Ni^{2+}, Co^{2+}, and Mn^{2+}; log $k_{23}(H_2O)$ *vs.* log $k_{23}(CH_3CN)$ for Zn^{2+} and Cu^{2+}; temperature 25°.

This is in accord[25] with the Jahn-Teller theorem for d^9 ions and with the crystal field stabilization energy having a maximum for d^8 ions as dictated by the synonymous theory. Possible differences[26] between k_{exch} and k_{subst} have been neglected in drawing the correlation of Figure 5. The above is further substantiated by the following calculations. Plots of log k_{23}/T *vs.* $1/T$ are shown in Figure 6 for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ corresponding to the calculated k_{23} value with $K_{A_1} = 80\ M^{-1}$. The slopes of the plots give $\Delta H_{23}^{\ddagger}/2.3R$, the intercept gives $\Delta S_{23}^{\ddagger}$ according to the Eyring expression

$$k_{23} = \frac{kT}{h} \exp\left(-\frac{\Delta H_{23}^{\ddagger}}{RT}\right) \exp\left(\frac{\Delta S_{23}^{\ddagger}}{R}\right) \qquad (15)$$

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

(23) F. Fittipaldi and S. Petrucci, *J. Phys. Chem.*, 71, 3414 (1967); M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49 (1965).

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(25) L. Orgel, "Introduction to Transition Metal Chemistry," Wiley, New York, N. Y., 1966.

(26) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, 2, 349 (1967).

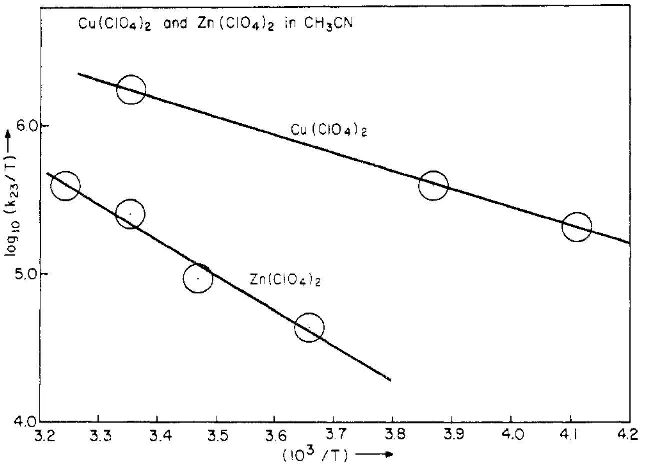

Figure 6. Log (k_{23}/T) *vs.* $(1/T)$ for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ in CH_3CN.

Least-squares analysis applied to the data give $\Delta H_{23}^{\ddagger} = 5.61 \pm 0.12$ kcal/mol and $\Delta S_{23}^{\ddagger} = 0.21 \pm 0.45$ eu for $Cu(ClO_4)_2$. For $Zn(ClO_4)_2$ $\Delta H_{23}^{\ddagger} = 11.0 \pm 1.3$ kcal/mol and $\Delta S_{23}^{\ddagger} = 14.0 \pm 4.5$ eu. Similar calculations applied to the data, assuming $K_{A_1} = 20\, M^{-1}$, give results within experimental error, namely, for $Zn(ClO_4)_2$ $\Delta H_{23}^{\ddagger} = 11.1 \pm 1.6$ kcal/mol and $\Delta S_{23}^{\ddagger} = 14.2 \pm 5.3$ eu. In Figure 7 the $\Delta H^{\ddagger}_{\text{exch}}$ for exchange of solvent (water or acetonitrile) and $\Delta H_{23}^{\ddagger}$ for substitution of acetonitrile for Cu^{2+} and Zn^{2+} are reported as a function of d^n (n is the number of electrons in the 3d orbital of the cations). The behavior of Ni^{2+} and Cu^{2+} going through a maximum and a minimum is qualitatively predicted by the crystal field theory.

In particular the values of $\Delta H^{\ddagger}$ in water and acetonitrile seem comparable and follow the same trend, an indication of the dissociative mode of activation[3] for solvent substitution in acetonitrile in conformity with the findings in water.

Recently Companion[27] has calculated crystal field activation energies for hexaaquo(transition metal) complexes for the change in symmetry on going from an octahedral structure O_h (ground state) to a square pyramid (C_{4v}) (activated state).

The calculation has been modified by the use of the many-electron method whereas previous attempts were based on the one-electron method.[28] The crystal field activation energy is computed as the difference in crystal field stabilization energy of the octahedron and the square-pyramid symmetry. Further, the ratio of the radial integrals ρ was assumed equal to or less than 1 (for compatibility between theory and experiment). Previous calculations[28] assumed $\rho = 2$. For $\rho = 1$ the CFAE (for $3d^8$ and $3d^9$ ions) are in water 4.8 kcal/mol and −5.6 kcal/mol, respectively. For the case of Ni^{2+} the result is unambiguous, the CFAE being independent of ρ. On the contrary, for Cu^{2+} the CFAE depends strongly on the value of ρ chosen (+1.1 for $\rho = 0$, −11.7 for $\rho = 2$). It is interesting to notice that if one corrects the values of $\Delta H^{\ddagger}$ for Ni^{2+} and Cu^{2+} in acetonitrile by these figures (neglecting differences in $10Dq$ for the two solvents), one gets $\Delta H^{\ddagger}_{\text{cor}} = 11.7 - 4.8 = 6.9$ kcal/mol for Ni^{2+} and $\Delta H^{\ddagger}_{\text{cor}} = 5.6 + 2.4 = 8.0$ for Cu^{2+} and $\rho = 0.5$.

Although the calculation is largely approximate, and for Cu^{2+} dependent on the chosen value of ρ, it shows that the corrected figures are more in line with a possible smooth correlation in the $\Delta H^{\ddagger}$ *vs.* d^n plot between Mn^{2+} and Zn^{2+} (for which CFSE and corrections of CFAE are necessarily zero).

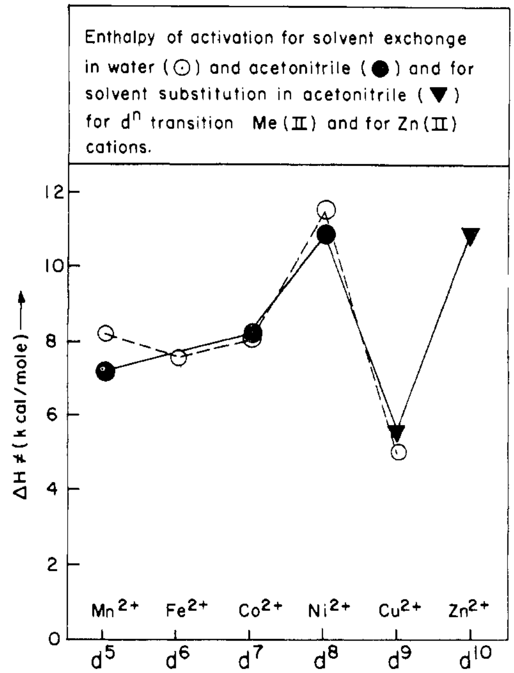

Figure 7. $\Delta H^{\ddagger}_{\text{exch}}$ and $\Delta H_{23}^{\ddagger}$ in water and acetonitrile for different $3d^n$ ions.

Part II. Conductance Measurements. The conductance data for $Ni(ClO_4)_2$ at 25° from the literature[18] and for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ at 25, −15, and −30° from this laboratory were analyzed by the Fuoss-Edelson method[29] for unsymmetrical electrolytes. This method consists of evaluating Λ_0 and K_{A_1} of an electrolyte of the type ML_2 in terms of the equilibrium

$$M^{2+} + L^- \rightleftharpoons ML^+$$

where the equilibrium leading to the neutral species ML_2 is neglected. (This approximation is probably acceptable in the case of metal(II) perchlorates.) Because of the presence of the conducting species ML^+, however, one has to consider the conductance contribution due to the charged ion pair. The approximation is made[29] that $\lambda^0_{ML^+} = 0.5\lambda^0_{M^{2+}}$. Other approximations are introduced,[29] such as the activity coefficient equality $f_{L^-} = f_{ML^+}$ and the use of the single ionic coefficient $f_{M^{2+}}$ introduced through the Debye-Huckel limiting law. As the result of these calculations the method consists of using the equation

$$\Lambda^* = \Lambda^0 - \chi \frac{K_{A_1}}{\Lambda_0} \tag{16}$$

Plotting Λ^* *vs.* χ, Λ_0 is obtained from the intercept and K_{A_1}/Λ_0 from the slope, whence K_{A_1} is obtained.

In the above $\Lambda^* = \Lambda_0\gamma_1$, where

$$\gamma_1 = \frac{\Lambda}{\Lambda_0}\left[\frac{1}{1 + \lambda^0_{M^{2+}}/2\Lambda_0}\right]\left[\frac{1}{1 - (S_{2:1}/\Lambda_0)\Gamma^{1/2}} + \frac{\lambda^0_{M^{2+}}}{2\Lambda}\right] \tag{17}$$

where $S_{2:1}$ is the Onsager conductance coefficient for a 2:1 electrolyte[30]

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[27] A. L. Companion, *J. Phys. Chem.*, 73, 739 (1969).

[28] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapters 2 and 3.

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[30] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958.

$$S_{2:1} = \frac{1.98 \times 10^6}{(DT)^{3/2}} \frac{q^*}{1 + \sqrt{q^*}} |z_1 z_2| \Lambda_0 + \frac{29.16}{\eta (DT)^{1/2}} (|z_1| + |z_2|) \qquad (18)$$

Γ is the ional concentration $\Gamma \cong 3N\gamma_1 \cong 3N$; N is the concentration in equivalents per liter. Also in the above

$$\chi = N f_{\mathrm{M}^{2+}} \Lambda^*(\Lambda^* - 0.5\Lambda_0) \qquad (19)$$

In order to calculate $S_{2:1}$ an estimate of the quantity q^* is necessary

$$q^* = \frac{2\Lambda^0}{3(2\lambda^0_- + \lambda^0_{\mathrm{M}^{2+}})} \qquad (20)$$

The following calculation has been performed in our case. At 25° taking $\Lambda_0 = 198.5$ as reported[18] for $Ni(ClO_4)_2$, $Zn(ClO_4)_2$, and $Cu(ClO_4)_2$ and $\lambda^0_- = 103.4$, q^* is readily calculated. At the other temperatures, for instance −30° for $Zn(ClO_4)_2$, one can calculate q^* as follows. The Walden product at 25° from the determined $\Lambda_0 = 201.2$ (Table VI) is $(\Lambda_0\eta)_{25} = 0.6941$ and $(\lambda^0_{\mathrm{Zn}^{2+}}\eta)_{25} = 0.3374$. At −30° one may start from an approximate value of Λ_0 from a free-hand extrapolation of a Λ *vs.* $c^{1/2}$ plot. If $\Lambda_0 = 102\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1}$, $(\Lambda_0\eta)_{-30} = 0.6987$. Assuming the same trend of the Walden product for the whole electrolyte as well as for the single ion

$$(\lambda^0_{\mathrm{Zn}^{2+}}\eta)_{-30} = \frac{0.6987}{0.6941} \frac{0.3374}{0.00685} = 49.6\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1}$$

(The viscosity of acetonitrile at −30° is 0.00685 P.) The above approximation is equivalent to assuming constancy of the transference number with temperature. Fortunately q^* is not too sensitive to changes in $\lambda^0_\pm$. Further it enters into $S_{2:1}$ with such a functional form that trial variations of the numerical values of $\lambda^0_\pm$ (keeping in mind $\lambda^0_+ + \lambda^0_- = \Lambda_0$) prove $S_{2:1}$ to be a rather insensitive function of q^*. $S_{2:1}$ having been calculated, γ and Λ^* are calculated. With the expression for the activity coefficient

$$-\log f_{\mathrm{M}^{2+}} = 128.94 \times 10^4 \frac{(Z_{\mathrm{M}^{2+}})^2}{(DT)^{3/2}} \sqrt{3N} \qquad (21)$$

one may calculate χ. The final plots of Λ^* *vs.* χ are shown in Figure 8 for $Ni(ClO_4)_2$ at 25°[18] and $Zn(ClO_4)_2$ at the temperatures investigated. They are the result of several cycles with successive values of Λ_0 until convergence was achieved. The final figures for Λ_0 and K_{A_1} are reported in Table VI.

It may be seen from Figure 8 that the plots become nonlinear as the concentration increases, an effect noticed earlier.[8b] This is because of the failure of the approximations involved in the theory and of the neglect of the $Ec \log c$, J_1c, and $J_2c^{3/2}$ terms[31] in the conductance equation used in the Fuoss-Edelson method. The figures reported for K_{A_1} (Table VI) have been obtained as a tangent at low concentrations of a function which rapidly diverges from a straight line (Figure 8). They should therefore be considered as orders of magnitude of the actual values of the association constants. However, since the more complete conductance equations[31] are correct only for symmetrical electrolytes, further calculations of K_{A_1} do not seem warranted at this time.

Table VI. Conductance Results for Λ_0 and K_{A_1} According to the Fuoss–Edelson Method

Electrolyte	Temp, °C	Λ_0, Ω^{-1} cm^2 equiv^{-1}	K_{A_1}, M^{-1}	Ref
$Ni(ClO_4)_2$	25	202.9	42	18
$Zn(ClO)_2$	25	201.2	48	This work
	−15	128.1	35	This work
	−30	103.3	34	This work
$Cu(ClO_4)_2$	25	203.2	75	This work
	−15	128.2	30	This work
	−30	103.0	26	This work

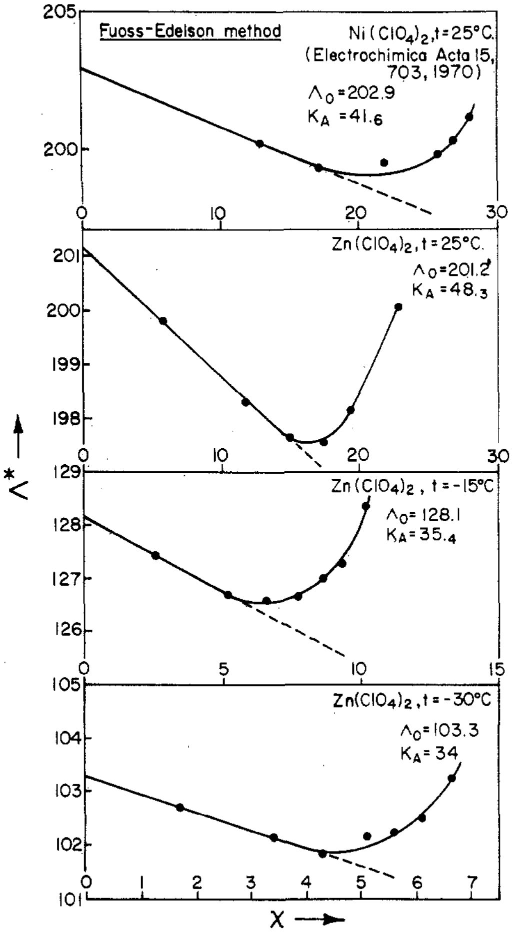

Figure 8. Fuoss–Edelson analysis of the conductance data for $Ni(ClO_4)_2$ in CH_3CN at 25°[18] and for $Zn(ClO_4)_2$ in CH_3CN at 25, −15, and −30°.

A final comment may be made regarding hydrodynamic radii. From the determinent Λ_0, assuming as mentioned above constancy of transference number with temperature, one may estimate $\lambda^0_\pm$ and the hydrodynamic radii through the Stokes expression (6). The average results are $R^0_\pm = 5 \times 10^{-8}$ cm and $R^0_- = 2.4 \times 10^{-8}$ cm giving as the sum of the hydrodynamic radii 7.4 Å. The cation radius is in agreement with a model visualizing the solvation shell constituted by six molecules of acetonitrile arranged in an octahedral symmetry moving with the cation. Indeed, taking[18] the N-C distance in the acetonitrile molecule equal to 1.16 Å, the C-C distance 1.46 Å, and the van der Waal radius of the CH_3 group ~2 Å gives as the diameter of the acetonitrile molecule 4.6 Å. This, added to the Pauling radius of Ni^{2+}, 0.8 Å, gives a calculated solvated radius for $Ni(CH_3CN)_6{}^{2+}$ of 5.4 Å in surprisingly good agreement with the calculated R^0_+.

Registry No. $Ni(ClO_4)_2$, 13637-71-3; $Cu(ClO_4)_2$, 13770-18-8; $Zn(ClO_4)_2$, 13637-61-1; CH_3CN, 75-05-8.

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(31) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959; R. Fernandez-Prini, *Trans. Faraday Soc.*, 65, 3311 (1969); C. DeRossi, B. Sesta, M. Battistini, and S. Petrucci, *J. Amer. Chem. Soc.*, 94, 2961 (1972).