wave at −0.44 V. In 50% aqueous acetonitrile each of the organoarsonate complexes showed a single irreversible wave (dropping mercury electrode) or cathodic peak (cyclic voltammetry, wax-impregnated graphite electrode) at −0.5 to −0.6 V. Electrolysis on a mercury pool cathode at −0.65 V involved the addition of at least 12 electrons per anion and led to amber-colored solutions that have not been examined further.

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Registry No. $[(p\text{-}H_3NC_6H_4As)_4Mo_{12}O_{46}]\cdot10CH_3CN\cdot6H_2O$, 78571-54-7; $(p\text{-}H_3NC_6H_4As)_4Mo_{12}O_{46}$, 78571-53-6; $[(CH_3As)_4Mo_{12}O_{46}](NH_4)_4$, 78656-72-1; $[(CH_3As)_4Mo_{12}O_{46}][N(C_4H_9)_4]_4$, 78549-89-0; $[(PhAs)_4Mo_{12}O_{46}](NH_4)_4$, 78549-87-8; $[(PhAs)_4Mo_{12}O_{46}][N(C_4H_9)_4]_4$, 78571-56-9; $[(HOCH_2CH_2As)_4Mo_{12}O_{46}][N(C_4H_9)_4]_4$, 78571-52-5; $(NH_4)_4H_4As_4Mo_{12}O_{50}$, 78609-75-3; $[N(C_4H_9)_4]_4H_4As_4Mo_{12}O_{50}$, 78624-40-5.

Supplementary Material Available: Listing of structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

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Structural Rearrangements Accompanying Zinc(II) Complexation Reactions in Aqueous Dimethyl Sulfoxide

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Ultrasonic absorption measurements on $Zn(NO_3)_2$ and $ZnCl_2$ solutions in Me_2SO demonstrate that a conformation change from octahedral to tetrahedral coordination accompanies the addition of the third bound chloride but is absent in the nitrate system. At 25 °C and a water mole fraction of 0.59, the $ZnNO_3^+$ complexation rate constant equals $2.2 \times 10^8\ s^{-1}$. At 25 °C and a water mole fraction of 0.039 and 0.904, the chloride complexation rates are 4.1×10^7 and $3.3 \times 10^7\ s^{-1}$, respectively.

Introduction

Despite its importance in inorganic and biochemical systems, relatively few kinetic investigations of Zn(II) complexation studies have been carried out. Many of the complexation investigations utilized the temperature-jump method, and the relaxation times are near the experimental limit of the equipment, thereby requiring lower temperatures for the measurements. Second-order Zn(II) complexation rates are $4 \times 10^6\ M^{-1}\ s^{-1}$ for pyridine-2-azo-*p*-dimethylaniline (15 °C),[2a] $8.0 \times 10^6\ M^{-1}\ s^{-1}$ for murexide (15.5 °C),[2b] greater than $3 \times 10^6\ M^{-1}\ s^{-1}$ for 1,10-phenanthroline (25 °C),[3] $8.3 \times 10^5\ M^{-1}\ s^{-1}$ for 2,2′-bipyridine (20 °C),[3] and between 5.9×10^7 and $3.9 \times 10^8\ M^{-1}\ s^{-1}$ for glycine and the glycine zwitterions depending upon ionic strengths (25 °C).[4,5] In order to convert second-order complex formation rate constants into ligand penetration rates, the outer-sphere association constants must be measured or calculated. Values of the first-order ligand penetration rates, corresponding to cation solvent-exchange rates, are $3 \times 10^7\ s^{-1}$ for pyridine-2-azo-*p*-dimethylaniline (15 °C),[2a] between 3×10^7 and $1 \times 10^8\ s^{-1}$ for acetate and sulfate (25 °C),[6] $2 \times 10^7\ s^{-1}$ for ammonia (11 °C),[7] and $7 \times 10^8\ s^{-1}$ for glycine (25 °C).[4] In addition, Swift investigated $Zn(NO_3)_2$ complexation in water and found a concentration-independent relaxation with a relaxation time of approximately 0.13 s, attributed to a structural rearrangement involving tetrahedral $Zn(H_2O)_4^{2+}$ and another conformation.[8] In concentrated glycine, Miceli and Stuehr observed the formation of the bis(glycinato) complex with a relaxation time of the order of 10^{-8} s, coupled to the rate-determining unimolecular rearrangement from a tetrahedral to an octahedral species with a rate constant of 93 s^{-1}.[4]

In principle, ultrasonic relaxation measurements can separate the relaxations corresponding to outer- and inner-sphere complexation via the multistep mechanism

$$M^{m+}(S) + L^{n-}(S) \underset{\substack{k_{21} \\ \text{step 12}}}{\overset{k_{12}}{\rightleftharpoons}} M^{m+}(S)_xL^{n-} \underset{\substack{k_{43} \\ \text{step III}}}{\overset{k_{34}}{\rightleftharpoons}} ML^{m-n}(S) \qquad (1)$$

Step 12 involves the diffusion-controlled formation of an outer-sphere ion pair coupled to solvent loss from the inner solvation shell of the ligand. Step III is the loss of solvent from the cation solvation shell followed by cation–ligand bond formation, i.e., the ligand penetration rate. In ultrasonic relaxation measurements, step 12 occurs at high frequency and step III at lower frequency. Darbari, Richelson, and Petrucci studied aqueous $ZnCl_2$ association reactions using ultrasonics, obtaining only a single relaxation even at high salt concentrations.[9] Because a single relaxation is inconsistent both with a multistep reaction and with the expected multiple complexation reactions involving Zn^{2+}, $ZnCl^+$, $ZnCl_2$, $ZnCl_3^-$, and $ZnCl_4^{2-}$, the observed relaxation could not be explained in chemical terms. Recently, Tamura has carried out ultrasonic investigations on $ZnCl_2$, $ZnBr_2$, and $Zn(NO_3)_2$ in water, obtaining single relaxations with the halides and no relaxations for the nitrate.[10] Tamura postulates a mechanism involving bis, tris, and tetrakis complexes with the halides coupled to structural changes involving species of coordination numbers 4, 5, and 6. Tamura's model was based upon earlier com-

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(2) (a) R. G. Wilkens, *Inorg. Chem.*, 3, 520 (1964); (b) A. Bewick and P. M. Robertson, *Trans. Faraday Soc.*, **63**, 678 (1967).

(3) R. Holyer, C. Hubbard, S. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).

(4) J. A. Miceli and J. E. Stuehr, *Inorg. Chem.*, **11**, 2763 (1972).

(5) S. Harada, Y. Uchida, M. Hiraishi, H. L. Kuo, and T. Yasuraga, *Inorg. Chem.*, **17**, 3371 (1978).

(6) G. Mass, *Z. Phys. Chem.* (*Wiesbaden*), **60**, 138 (1968).

(7) D. Rorabacher, *Inorg. Chem.* **5**, 1891 (1966).

(8) T. J. Swift, *Inorg. Chem.*, 3, 526 (1964).

(9) G. S. Darbari, M. R. Richelson, and S. Petrucci, *J. Chem. Phys.*, **53**, 859 (1970).

(10) K. Tamura, *J. Phys. Chem.*, **81**, 820 (1977).

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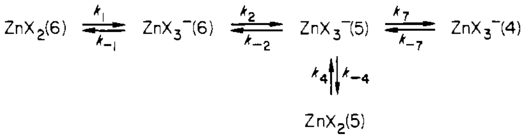
plexation data for zinc chloride systems including all complexes up to $ZnCl_4^-$.[11]

Evidence for $ZnCl_4^{2-}$ is found in infrared and Raman spectral studies in concentrated aqueous solutions and anhydrous melts. Irish contrasts the cationic transference numbers for aqueous $ZnCl_2$ at 25 °C from the literature and notes that the slopes of the curve change at 0.5 M and 1.88 M, with the negative values of the transference number above 1.88 M indicating the existence of an anionic zinc species.[12] Irish has reported the existence of an octahedral $ZnCl_4(H_2O)_2^{2-}$ species in concentrated $ZnCl_2$ aqueous solution.[13] Gilbert found $ZnCl_4^{2-}$ present above a 1 M $ZnCl_2$ concentration, measuring the equilibrium constants[14]

$$ZnCl_2 + 2Cl^- = ZnCl_4^{2-} \qquad K = 0.040\ M^{-2} \tag{2}$$

$$ZnCl_4^{2-} + Zn^{2+} = 2ZnCl_2 \qquad K = 0.72 \tag{3}$$

Quicksall and Spiro studied the spectra of 2.88 M $ZnCl_2$ containing 9.35 M HCl, obtaining a tetrahedral $ZnCl_4^{2-}$ species.[15] Thus, $ZnCl_4^{2-}$ is a known species in concentrated $ZnCl_2$ solutions. Gaizer and Silber have utilized a potentiometric method to investigate the complexation constants for 0.01 M $ZnCl_2$ in aqueous Me_2SO at an ionic strength of 0.5, obtaining evidence for the absence of $ZnCl_4^{2-}$ at all solvent compositions except a water mole fraction of 0.63.[16] In the aqueous region the complexation constant is too small to be detected in these experiments. At $ZnCl_2$ concentrations significantly below 1 M, Tamura's mechanism can be simplified:



$$\begin{tikzcd}
ZnX_2(6) \arrow[r, shift left, "k_1"] & ZnX_3^-(6) \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & ZnX_3^-(5) \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_7"] \arrow[d, shift left, "k_{-4}"] & ZnX_3^-(4) \arrow[l, shift left, "k_{-7}"] \\
 & & ZnX_2(5) \arrow[u, shift left, "k_4"] &
\end{tikzcd} \tag{4}$$

The numbers in parentheses are the coordination numbers of each species. Tamura considered several species to be reactive intermediates, including $ZnX_2(5)$. If this species is eliminated by using the steady-state hypothesis, the bulk of the reactions can be represented as

$$ZnX_2(6) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ZnX_3^-(6) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} ZnX_3^-(5) \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} ZnX_3^-(4) \tag{5}$$

Reaction 5 predicts three separate relaxations corresponding to the three different forms of the tris complex. Either if $ZnX_3^-(5)$ is present in vanishing small concentrations or if the loss of both solvent molecules is a concerted process, then only two relaxations should be observable. If the solvation change for the halides is similar to those observed by Swift for the nitrate at about 0.13 s, then only a single relaxation in the ultrasonic range above 1 MHz would be observable, consistent with all of the experimental observations.

In addition to providing kinetic information about metal ion complexation reactions, ultrasonic absorption measurements in mixed solvents can be utilized to determine changes in coordination number. For those complexation reactions where the ΔH of complexation is small, the amplitude of the excess absorption maximum is proportional to the square of the reaction volume change. If solutions of constant salt concentration are monitored as a function of solvent composition in mixed solvents, then the excess absorption maximum, μ_{max}, should decrease as the solvent dielectric constant increases due to a decreasing complexation equilibrium constant. However, if complexation is accompanied by a coordination number change, then μ_{max} has an anomalous increase as the dielectric constant increases.[17] The lanthanide(III) series is one in which a coordination number change has often been postulated in water. Using Er(III) as a test cation in aqueous methanol, we have developed this technique to demonstrate the existence of a coordination number change caused by steric crowding in the inner coordination shell with the bulky ligands nitrate,[17] perchlorate,[18] bromide,[19] and iodide,[19] but not with the smaller chloride.[20] Lanthanide coordination changes can also be induced with chloride by changing the cation[21] or the solvent system.[22] If an alkaline earth ion, Na^+, is used, no structural change accompanies complexation chloride in either aqueous methanol or aqueous Me_2SO.[23]

We have initiated this kinetic and ultrasonic absorption structural investigation of $Zn(NO_3)_2$ and $ZnCl_2$ in aqueous Me_2SO in order to determine whether or not a structural change occurs within the zinc systems. Furthermore, the data will demonstrate that if the structural change occurs, then from the absorption frequency range it can be determined if the structural change is rapid or slow. By studying $Zn(NO_3)_2$ in aqueous Me_2SO it should be possible to increase the association constant over that present in water so as to be able to study the complexation reaction, even though the association constant is too small to detect by complexometric titration.[16]

Experimental Section

Chemicals. Reagent grade $ZnCl_2$, $Zn(NO_3)_2$, and Me_2SO (Fisher Scientific) were used without further purification. The stoichiometric amount of water in the solid zinc salts was determined with use of ion exchange.[23] Stock solutions were made by weight in water or Me_2SO. The zinc solutions used in the absorption as a function solvent composition studies were 0.400 M in Zn(II).

Ultrasonic Equipment. The ultrasonic absorption techniques are similar to those described previously.[19] New Matec equipment utilized for this study consisted of a 6600 main frame, a 666B RF pulse comparitor, a 1204B master synchronizer and exponential generators and RF plug-ins 755 (1–20 MHz), 760 (10–90 MHz), and 765 (90–30 MHz). The greater power available significantly improves the accuracy of absorption data at both high and low frequencies. The experimental frequency range was from 5 to 250 MHz with use of X-cut quartz 1-, 4-, 5-, and 10-MHz piezoelectric crystals.[24]

Analysis of Ultrasonic Data. The experimental data of absorption coefficient α, as a function of frequency, f, can be fit to either a single- or double-relaxation expression depending upon the system, given by

$$\alpha/f^2 = A_{12}/[1 + (f/f_{12})^2] + A_{III}/[1 + (f/f_{III})^2] + B \tag{6}$$

where B is the absorption due to solvent, A_{12} and A_{III} are the absorption amplitudes of the chemical relaxation processes, and f_{12} and f_{III} are the respective relaxation frequencies. The excess absorption, μ, is given by

$$\mu = (\alpha/f^2 - B)fc \tag{7}$$

where c is the solution sound velocity. The excess absorption maximum, μ_{max}, is calculated from the characteristic parameters by

$$2\mu_{max} = A_i f_i c \tag{8}$$

and at constant salt concentration μ_{max} is approximately proportional to the square of the reaction volume change, thereby serving as a sensitive probe of coordination number changes as the solvent com-

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(11) L. G. Sillen and A. E. Martell, Eds., "Stability Constants of Metal Ion Complexes", 2nd ed., Chemical Society, London, 1964.

(12) D. E. Irish in "Ionic Interactions from Dilute Solutions to Fused Salts", Vol. II, S. Petrucci, Ed., Academic Press, New York, 1971, pp 187–258.

(13) D. E. Irish, R. McCarroll, and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).

(14) B. Gilbert, *Bull. Soc. Chim. Belg.*, **76**, 493 (1967).

(15) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **5**, 2232 (1966).

(16) F. Gaizer and H. B. Silber, *J. Inorg. Nucl. Chem.*, **42**, 1217 (1980).

(17) J. Reidler and H. B. Silber, *J. Inorg. Nucl. Chem.*, **36**, 175 (1974).

(18) H. B. Silber, *J. Phys. Chem.*, **78**, 1940 (1974).

(19) H. B. Silber and G. Bordano, *J. Inorg. Nucl. Chem.*, **41**, 1169 (1979).

(20) J. Reidler and H. B. Silber, *J. Phys. Chem.*, **78**, 424 (1974).

(21) H. B. Silber, D. Bouler, and T. White, *J. Phys. Chem.*, **82**, 775 (1978).

(22) H. B. Silber in "The Rare Earths in Modern Science and Technology", Vol. II, G. J. McCarthy, J. J. Rhyne, and H. B. Silber, Eds., Plenum Press, New York, 1980, pp 93–98.

(23) H. B. Silber, *J. Chem. Educ.*, **49**, 586 (1972).

(24) L. U. Kromer, M.S. Thesis, The University of Texas at San Antonio, San Antonio, TX, 1979.

Table I. Ultrasonic Relaxation Results for 0.400 M Zn(II) Solutions at 25.0 °C

X_{H_2O}	$10^{17}A_{12}$, Np cm^{-1} s^2	f_{12}, MHz	$10^4\mu_{max}(12)$, Np	$10^{17}A_{III}$, Np cm^{-1} s^2	f_{III}, MHz	$10^4\mu_{max}(III)$, Np	$10^{17}B$, Np cm^{-1} s^2
$Zn(NO_3)_2$							
0.020	23.15 ± 3.71	499.3 ± 503.0	86.3 ± 100.8	671.54 ± 11.16	11.50 ± 0.27	57.63 ± 2.32	35.0
0.10	27.72 ± 16.32	254.5 ± 292.9	53.0 ± 92.2	542.56 ± 18.75	14.45 ± 0.98	58.91 ± 6.02	33.3
0.10	36.57 ± 11.96	178.06 ± 91.64	48.94 ± 41.19	537.07 ± 48.00	13.33 ± 1.55	53.81 ± 5.50	33.3
0.15	35.22 ± 10.85	156.50 ± 64.28	41.76 ± 30.01	467.01 ± 22.99	15.82 ± 1.40	55.95 ± 7.72	33.3
0.17	30.21 ± 7.56	246.46 ± 173.30	56.51 ± 53.88	538.39 ± 11.14	13.30 ± 0.53	54.37 ± 3.33	32.7
0.22	40.07 ± 8.58	156.94 ± 46.45	48.17 ± 24.57	487.59 ± 8.44	15.50 ± 0.51	57.87 ± 2.90	32.3
0.23	59.18 ± 6.75	104.14 ± 15.18	47.23 ± 12.28	496.13 ± 9.18	12.82 ± 0.47	48.74 ± 2.68	32.3
0.40	73.28 ± 15.75	128.79 ± 37.76	78.99 ± 40.14	364.77 ± 17.41	13.61 ± 1.32	41.55 ± 6.02	32.2
0.55	95.73 ± 6.51	87.10 ± 8.73	68.28 ± 6.84	367.78 ± 30.17	6.08 ± 0.60	18.31 ± 3.32	32.3
0.59	55.79 ± 11.50	129.25 ± 26.63	58.91 ± 24.28	136.42 ± 9.30	19.20 ± 3.71	21.40 ± 5.59	31.8
0.66	48.05 ± 4.38	104.90 ± 15.61	42.59 ± 10.22	154.04 ± 16.84	6.90 ± 0.96	8.98 ± 2.23	31.6
0.81				13.14 ± 2.22	20.11 ± 5.27	2.24 ± 0.97	32.4 ± 0.6
0.95				30.46 ± 5.05	12.57 ± 1.97	3.07 ± 0.98	23.8 ± 0.3
1.00						0	21.9 ± 2.7
$ZnCl_2$							
0.039	9.28 ± 1.82	101.02 ± 28.93	6.93 ± 3.34	115.72 ± 22.57	6.16 ± 1.04	5.27 ± 1.92	35.4
0.12	10.53 ± 2.24	120.51 ± 44.96	9.56 ± 5.60	406.49 ± 126.50	3.09 ± 0.66	9.47 ± 4.95	33.4
0.33	6.45 ± 1.80	321.1 ± 275.9	16.18 ± 18.41	455.83 ± 36.03	4.55 ± 0.30	16.21 ± 2.35	32.1
0.52	9.53 ± 1.58	396.9 ± 256.4	30.71 ± 24.92	785.36 ± 136.20	4.03 ± 0.44	25.70 ± 7.27	32.4
0.64				3281.6 ± 306.2	3.23 ± 0.20	89.01 ± 13.76	35.7 ± 3.4
0.76				21014 ± 776	2.25 ± 0.06	404.3 ± 25.7	50.0 ± 10.3
0.80				18895 ± 2025	3.02 ± 0.18	484.2 ± 81.4	36.8 ± 5.3
0.85				20627 ± 194	3.72 ± 0.03	645.7 ± 11.3	23.0
0.90				14751 ± 212	4.82 ± 0.07	588.0 ± 17.0	63.6 ± 14.9
0.90				13917 ± 151	5.16 ± 0.05	592.2 ± 11.7	33.4 ± 6.6
0.99				4317 ± 63	8.46 ± 0.16	275.7 ± 9.2	70.2 ± 13.9
1.00				2626 ± 86	11.74 ± 0.43	230.7 ± 16.0	41.8 ± 10.8

Table II. Ultrasonic Relaxation Results for the Zn(II) Kinetic Studies at 25.0 °C

salt concn, M	X_{H_2O}	$\theta(c)$, M	$10^{17}A_{12}$, Np cm^{-1} s^2	f_{12}, MHz	$10^{17}A_{III}$, Np cm^{-1} s^2	f_{III}, MHz	$10^{17}B$, Np cm^{-1} s^2
0.258 $Zn(NO_3)_2$	0.59	0.602	35.27 ± 4.47	131.64 ± 16.20	57.89 ± 4.14	20.20 ± 3.35	32.2
0.515 $Zn(NO_3)_2$	0.59	1.055	94.11 ± 14.15	121.60 ± 15.08	203.25 ± 11.72	25.32 ± 2.31	32.2
0.696 $Zn(NO_3)_2$	0.59	1.337	116.70 ± 16.91	150.92 ± 21.85	385.31 ± 14.60	26.49 ± 1.63	32.2
0.400 $ZnCl_2$	0.039		6.67 ± 3.37	80.04 ± 52.40	117.69 ± 30.40	6.42 ± 1.55	35.4
0.600 $ZnCl_2$	0.039		9.33 ± 2.39	122.98 ± 46.32	97.53 ± 27.72	6.56 ± 1.67	35.4
0.800 $ZnCl_2$	0.039		10.84 ± 2.14	194.87 ± 83.95	195.04 ± 13.34	6.65 ± 0.50	35.4
0.200 $ZnCl_2$[a]	0.90		1.18 ± 0.74	534.1 ± 1755	5608 ± 276	5.60 ± 0.20	22.9
0.400 $ZnCl_2$[a]	0.90		150.99 ± 176.00	20.83 ± 13.40	14305 ± 256	4.94 ± 0.17	22.9
0.500 $ZnCl_2$[a]	0.90		102.70 ± 423.90	31.44 ± 84.03	12057 ± 1246	6.08 ± 0.85	22.9
0.600 $ZnCl_2$[a]	0.90		87.42 ± 80.27	50.50 ± 43.95	13908 ± 349	6.64 ± 0.20	22.9

[a] The errors associated with the high-frequency relaxation suggest that only a single relaxation is present.

position changes. Figures 1 and 2 show the variation in excess absorption with frequency for several solvent compositions for the $Zn(NO_3)_2$ and $ZnCl_2$ systems, respectively.[25] The calculated relaxation parameters are summarized in Tables I and II. For those solutions in which only a single relaxation is present, the chemical background is allowed to vary, whereas it is fixed to the experimental value of the solvent for the double-relaxation systems.

Results and Discussion

$Zn(NO_3)_2$ Results. In water, 0.400 M $Zn(NO_3)_2$ has no measurable excess absorption, consistent with Tamura's data on more concentrated solutions.[10] As Me_2SO is added, a small excess absorption is measured for the 0.400 M $Zn(NO_3)_2$ solutions. The magnitudes of the absorption amplitudes indicate a small complexation constant, consistent with the potentiometric measurements.[16] In aqueous Me_2SO above a water mole fraction, X_{H_2O}, of 0.66 only a single relaxation is observed. At lower water mole fractions a high-frequency relaxation appears. This is similar to the results for lanthanide nitrate complexation where the low-frequency relaxation is identified with inner-sphere complexation and the high-frequency relaxation with outer-sphere complexation, consistent with reaction 1.[17] If this assignment is correct, then the kinetic data should give reasonable rate constants for both steps of reaction 1. For a two-step coupled system, the calculated

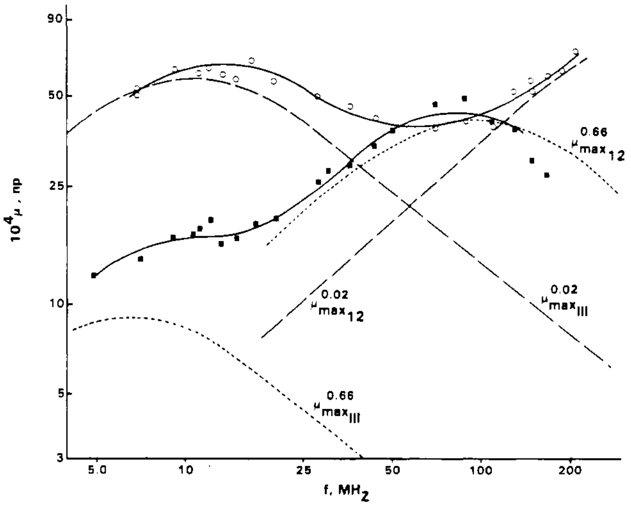

Figure 1. Excess absorption for 0.400 M $Zn(NO_3)_2$ solutions at 25 °C and water mole fractions 0.02 and 0.66. The dashed lines are the computer-calculated high- and low-frequency relaxations.

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[25] Experimental absorption data are available from H. B. Silber.

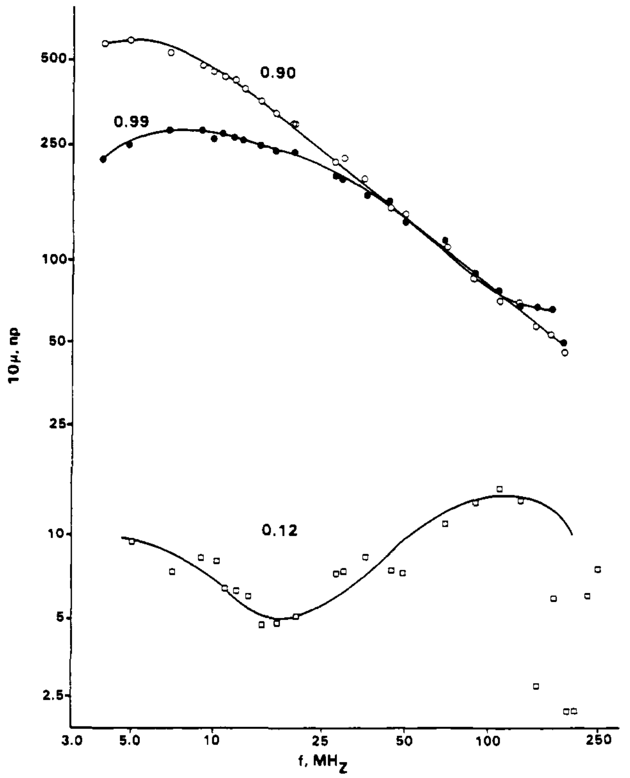

Figure 2. Excess absorption for 0.400 M $ZnCl_2$ solutions at 25 °C and water mole fractions 0.12, 0.90, and 0.99. At low water mole fractions there is a low-amplitude absorption, which contains two relaxations. At high frequencies only a single relaxation appears to be present. The relaxation amplitudes reach a maximum near water mole fraction 0.85. The deviations in the $X_{H_2O} = 0.12$ solution are a reflection of the low absorption amplitude.

relaxation times are related to the concentrations of Zn^{2+} and NO_3^- by

$$\Sigma k = 2\pi(f_{12} + f_{III}) = k_{12}(\theta(c)) + k_{21} + k_{34} + k_{43} \quad (9)$$

$$\pi k = 4\pi^2 f_{12} f_{III} = k_{12}(\theta(c))(k_{34} + k_{43}) + k_{21} + k_{43} \quad (10)$$

$$\theta(c) = [Zn^{2+}] + [NO_3^-] \quad (11)$$

If the complexation constant is known for $ZnNO_3^+$ complexation, plots of Σk and of πk as a function of $\theta(c)$ should be two straight lines. The four rate constants can then be calculated from the two slopes and two intercepts. In the absence of a measurable association constant, an iterative procedure is utilized in which K is assumed and $\theta(c)$ and the four rate constants are calculated, and then a new equilibrium constant is obtained via

$$K = K_{12}(1 + K_{III}) = k_{12}/k_{21}(1 + k_{34}/k_{43}) \quad (12)$$

This process is continued until K no longer changes. With use of this procedure, at $X_{H_2O} = 0.59$ and 25 °C the constants were determined to be the following: $k_{12} = 1.9 \times 10^8$ M^{-1} s^{-1}; $k_{21} = 4.5 \times 10^8$ s^{-1}; $k_{34} = 2.2 \times 10^8$ s^{-1}; $k_{43} = 1.3 \times 10^8$ s^{-1}; $K_{12} = 0.43$; $K_{III} = 1.7$; $K = 1.2$.

An alternate procedure to calculate the rate constants assumes that the two reaction steps are far enough apart so as to decouple the relaxations. This calculation was also carried out, and K was calculated to be 1.1 under the same conditions. However, this second procedure requires that the step 12 rate constants be an order of magnitude greater than those for step III, a feature inconsistent with the experimental data. No other Zn(II) outer-sphere rate constants have been reported in mixed solvents in the literature. The observed outer-sphere complexation rate is less than that for a diffusion-controlled process, but step 12 is a coupled reaction including the loss of solvent from the NO_3^- solvation shell, which undoubtedly is slower. In aqueous Me_2SO at $X_{H_2O} = 0.163$ and 25 °C, $k_{12} = 2.2 \times 10^8$ M^{-1} s^{-1} for the loss of solvent from the outer-sphere $ErNO_3^{2+}$ ion pair.[26] The closeness of the two values suggests that the loss of solvent from the anion solvation shell is essentially independent of the cation, a feature that is predicted by the postulated mechanism. The ligand penetration rate constant, k_{34}, is larger than those estimated at lower temperatures for the reaction of Zn(II) with simple ligands,[1,3,5] but lower than that calculated in water at 25 °C for glycine complexation.[7] Thus, the $ZnNO_3^+$ inner-sphere complexation rate constant is within the range calculated for other zinc systems in water. Insufficient data are available on the rate constants for other zinc systems in mixed solvents to determine the effect of solvent composition upon the rate. The close similarity between these experimental rate constants and those for similar systems lends credence to the postulated mechanism being the correct one for zinc nitrate complexation in aqueous Me_2SO.

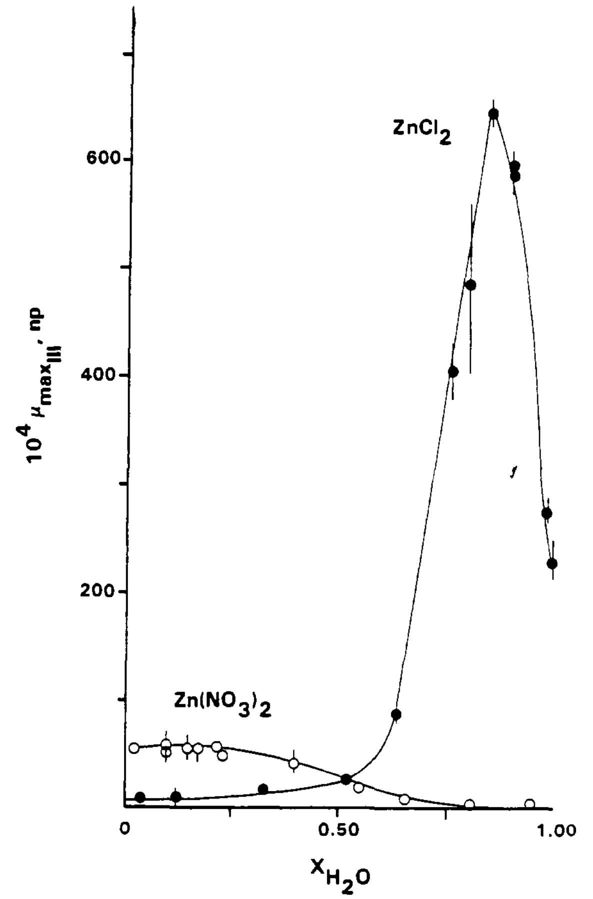

Figure 3. Variation in excess absorption maxima with water mole fraction for 0.400 M $Zn(NO_3)_2$ and 0.400 M $ZnCl_2$ at 25 °C. The existence of a maximum in the excess absorption maxima for $ZnCl_2$ indicates the existence of a coordination number change as the solvent composition varies.

Figure 3 is a graph of $\mu_{max}(III)$ as a function of solvent composition for 0.400 M $Zn(NO_3)_2$ solutions at 25 °C. The major feature of the graph is the decrease in $\mu_{max}(III)$ as the solvent dielectric constant increases, a feature consistent with decreased complexation. No evidence exists for any rapid coordination number change in the zinc nitrate system, but no information can be gleaned from these experiments about the possibility of a long-lived structural change.[8]

Sze and Irish have carried out vibrational spectroscopic studies of $Zn(NO_3)_2$ complexation in water,[27] aqueous diox-

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(26) H. B. Silber and L. U. Kromer, *J. Inorg. Nucl. Chem.*, **42**, 103 (1980).
(27) Y.-K. Sze and D. E. Irish, *J. Solution Chem.*, **7**, 395 (1978).

ane,[28] and aqueous acetonitrile.[29] In water, the $ZnNO_3^+$ complexation constant is 0.02; below 3.5 M $Zn(NO_3)_2$, octahedral $Zn(H_2O)_6^{2+}$ and nitrate ion are the primary species; when the ratio of water plus nitrate ion is less than 6:1 compared to Zn^{2+}, a tetrahedral Zn^{2+} species exists.[27] In our study in water, the $Zn(NO_3)_2$ concentration is 0.400 M, and on the basis of Sze and Irish's results, no inner-sphere nitrate complexes should be detected, consistent with the absence of an excess absorption in water. In addition, the ratio of water plus nitrate compared to Zn^{2+} exceeds 6:1, and no octahedral–tetrahedral conversion is therefore expected. Our kinetic association constant of 1.2 at an X_{H_2O} of 0.59 is within the range of those reported in methanol (2.6),[30] in aqueous dioxane at an X_{H_2O} of 0.67 (0.21–0.22),[28] in aqueous dioxane at an X_{H_2O} of 0.80 (0.071),[28] and in aqueous acetonitrile at an X_{H_2O} of 0.80 (0.090).[29] Sze and Irish find no direct relationship between the association constant and the solvent dielectric constant. Thus, our ultrasonic absorption results are consistent with those for $Zn(NO_3)_2$ in other solvent systems determined by infrared and Raman absorption.

$ZnCl_2$ Results. The $ZnCl_2$ results are very different from those for the same concentration of nitrate. Figures 2 and 3 represent the excess absorption as a function of water mole fraction. In the region of low water content, the excess absorption is very low, but at high water mole fractions, μ_{max} increases dramatically and then drops again near $X_{H_2O} = 1.0$. In the region of low water content, the complexation equilibrium constant is between 10^7 and 10^9, whereas in the aqueous region it is of the order of unity.[16,31] If the excess absorption is due primarily to the effect of changes in complex concentrations, then the opposite order should be observed for μ_{max}. The kinetic data at X_{H_2O} equal to 0.039 and 0.904 are almost identical, consisting of a concentration-independent low-frequency absorption. At low water mole fractions there is a high-frequency relaxation that appears to disappear at high water mole fractions. The high-frequency relaxation is attributed to small concentrations of outer-sphere complexes, and at high water mole fractions the amplitude fades into the solvent background. A high-frequency relaxation can be calculated at an X_{H_2O} of 0.904, but the experimental errors associated with this relaxation exceed 100%, and therefore the existence of this high-frequency relaxation cannot be experimentally verified. At both water mole fractions the major species that can react further with chloride is Zn^{2+} to form $ZnCl_2$, which then forms $ZnCl_3^-$. Because of the immeasurably low concentration of $ZnCl^+$, the concentration dependence for the complexation with regard to chloride should be different depending upon which step is observed. However, the lack of any concentration dependence prevents the mechanism being determined from this data alone. In water, Tamura has investigated the chloride association with Zn(II) and has utilized the chloride dependence to establish that the observed relaxation corresponds to the addition of a third chloride to the bis complex.[10] The similarity between Tamura's data and the present study is consistent with this observation. Therefore, the observed relaxation corresponds to that represented in eq 4 and simplified in eq 5.

The nondependence of the low-frequency relaxation on concentration would suggest that the rate-determining step in the complexation process is the rate of solvent exchange for $ZnCl_2$. In this case

$$\tau_{III}^{-1} = k_f + k_b = 2\pi f_{III} \qquad (13)$$

where k_f, the complexation rate constant, and k_b, the dissociation rate constant, can be related to the six rate constants of reaction 3 and are represented by

$$ZnCl_2(6) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ZnCl_3^-(4) \qquad (14)$$

Extrapolation of the equilibrium data yields $\log \beta_2 = 6.0_5$, $\log \beta_3 = 8.7_0$ and $K_3 = 450$ at $X_{H_2O} = 0.039$ and $\log \beta_2 = 0.3_0$, $\log \beta_3 = 1.0_3$, and $k_3 = 10$ at $X_{H_2O} = 0.904$. Since $K_3 = k_f/k_b$, we can calculate the two rate constants at each solvent composition. At $X_{H_2O} = 0.039$, the average $\tau_{III}^{-1} = 4.11 \times 10^7$ s^{-1}, $k_f = 4.1 \times 10^7$ s^{-1}, and $k_b = 9.1 \times 10^4$ s^{-1}. At $X_{H_2O} = 0.904$, $\tau_{III}^{-1} = 3.65 \times 10^7$ s^{-1}, $k_f = 3.3 \times 10^7$ s^{-1}, and $k_b = 3.3 \times 10^6$ s^{-1}. Both complexation rate constants are within experimental error of each other and are within the range of Zn(II) water-exchange rates measured in aqueous solution.

Examination of Figure 3 reveals the large increase in μ_{max} at high water content is absent for the same concentration of nitrate salt and is not reflected in the evaluation of the complex stability constants.[16] Since the concentration of $ZnCl_2$ is less in this region, either the complexation mechanism totally changes or a major increase in the reaction volume change occurs. A much smaller increase in μ_{max} within the lanthanide systems has been attributed to a coordination number change, probably corresponding to one solvent molecule.[17-22] The much greater increase in μ_{max} observed in the $ZnCl_2$ system suggests a larger coordination number change is coupled to the complexation step. This coordination number change is attributed to reaction 12, involving an octahedral–tetrahedral conversion accompanying the addition of the third chloride ion. Support for this mode comes from stability constant measurements of Ahrland,[31] from Tamura's ultrasonic data,[10] and from the work of Irish.[12,13] Mechanistically this means that when the bound solvent molecues are the bulky Me_2SO ones, the addition of the third chloride does not require a structural conversion. In the aqueous region where most of the bound solvent molecules are small water molecules, the addition of a third chloride allows the complex to rearrange to the stable tetrahedral structure. Thus, no mechanistic discontinuity is required to cause the μ_{max} dependence, which now results from a change in the distribution of bound solvent molecules.

The observed chloride complexation rates are within experimental error of each other, despite the observation that one is measured in the region where no structural change occurs and one is coupled to the octrahedral–tetrahedral conversion. In addition, the rate is a factor of 5 slower than for the nitrate. Both observations suggest that significant steric hindrance exists in the octahedral complexes, independent of whether the bound solvent consists of Me_2SO, water, or a mixture of the two.

In summary, the analysis of the ultrasonic absorption measurements for 0.400 M zinc salt solutions in aqueous Me_2SO is consistent with the hypothesis of the existence of a structural rearrangement from octahedral to tetrahedral coordination for the chloride, but not the nitrate. The data indicate the existence of $ZnNO_3^+$ complexes in aqueous Me_2SO having a ligand penetration rate of 2.2×10^8 s^{-1} at 25 °C, whereas that for the formation of $ZnCl_3^-$ is between 3.3×10^7 and 4.1×10^7 s^{-1}. In the $ZnCl_2$ system, the coordination number change is a very rapid process. Although no evidence appears for a coordination number change for the nitrate in a rapid step, the predicted change cannot be eliminated from this study.

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Registry No. $ZnCl_2$, 7646-85-7; $Zn(NO_3)_2$, 7779-88-6; Me_2SO, 67-68-5.

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(28) Y.-K. Sze and D. E. Irish, *J. Solution Chem.*, **7**, 417 (1978).

(29) Y.-K. Sze and D. E. Irish, *J. Solution Chem.*, **8**, 395 (1979).

(30) S. A. Al-Baldawi, M. H. Brooker, T. E. Gough, and D. E. Irish, *Can. J. Chem.*, **48**, 1202 (1970).

(31) S. Ahrland and N. O. Björk, *Acta Chem. Scand., Ser. A*, **A30**, 265 (1976).