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Are the Pre-Lanthanides Similar to the Lanthanide Ions in Aqueous Methanol?

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Ultrasonic absorption measurements were carried out at 25 °C on 0.200 M salt solutions of $ScCl_3$, YCl_3, and $LaCl_3$ as a function of solvent composition in aqueous methanol. In methanol, lanthanum chloride exists as the bis complex, with some indication that yttrium chloride also exists in a similar form. The destabilization of the bis complex is accompanied by a coordination number change in both salt systems. $ScCl_3$ behaves as a normal d-type transition metal under the same reaction conditions.

Introduction

As the utility of lanthanide substitution techniques in biochemical systems increases, the need for basic structural information about the lanthanide ions in water and mixed solvents becomes greater. In water, different groups have obtained significantly different results by using the same or different techniques.

It has been reported that in aqueous solutions the coordination numbers are 9 in the La–Pm range and 8 in the Tb–Lu range.[1-3] X-ray studies in concentrated rare-earth chloride solutions by several groups give different results. In an early study, Brady determined that in concentrated erbium chloride solutions, the cation is surrounded by eight species, six water molecules and two chloride ions.[4] Starting with anhydrous rare-earth chlorides and adding them to water and to methanol, Wertz obtained coordination numbers of 8 for the chlorides of La, Nd, and Gd in water and in 10 M HCl.[5-9] Within the series, differences were observed, with the predominant species predicted to be $[La(H_2O)_8]^{3+}$, $[NdCl(H_2O)_7]^{2+}$, and $[GdCl(H_2O)_7]^{2+}$.[6-8] Spedding's group reports somewhat different results for the chlorides in water using X-ray measurements, including major differences in the X-ray scattering curves.[10,11] In 3.4–3.8 M rare-earth chloride solutions in water, Spedding found the light rare earths to have a coordination number of 9, the heavies to have a coordination number of 8, and those in the middle of the rare-earth series to have a number between 8 and 9 A recent neutron diffraction study of $NdCl_3$ in water by Narten and Hahn detects no inner-sphere chloride binding and an average coordination number of 8.5, in agreement with Spedding's rather than Wertz's results.[12]

The controsversy about whether or not the ligand is in the inner coordination shell of the lanthanide has been attacked by using other techniques. Choppin has utilized spectroscopic methods to determine that lanthanide complexes of chloride, nitrate, and thiocyanate contain predominantly outer-sphere complexes, whereas ligands such as acetate and sulfate are predominantly inner sphere.[13] Choppin has advanced the model that anions of weak acids form inner-sphere complexes in water, whereas anions of strong acids form outer-sphere complexes.[14] Alternately, both inner- and outer-sphere lanthanide complexes with nitrate have been detected with use of ultrasonic absorption.[15-17]

Using lanthanum-139 longitudinal relaxation rates, Reuben detects only outer-sphere ion pairs of concentrated lanthanum salt solutions with chloride and perchlorate ions but confirms the existence of inner-sphere nitrate complexes.[18] Kanno and Hiraishi carried out Raman spectroscopic measurements on aqueous chloride solutions of Eu and Gd as a function of salt concentration in glassy solutions.[19] Only inner-sphere waters are found (no chlorides in the inner sphere), with a coordination number of 9 for Eu and two forms of Gd, one with 9 and one with 8 waters. As the ratio of water to salt decreases, they observed the anomalous result that the 9 coordination number Gd species became more stable. Using a Eu(III) luminescence excitation technique, Horrocks detects some inner-sphere association with chloride, thiocyanate, and nitrate ligands in 0.01 M Eu(III) solutions containing large excesses of ligand (such as 5 M chloride).[20]

In water, the ultrasonic relaxation technique can easily distinguish between inner- and outer-sphere ligands. Chloride,[21] bromide,[22] iodide,[22] and perchlorate[23] are outer sphere in 0.2 M solutions, whereas nitrate[15-17] and sulfate[24,25] are inner sphere. Early ultrasonic kinetic studies were interpreted in terms of a changing solvation number within the lanthanide series,[15-17,24] but the Nd(II)–sulfate results in H_2O and D_2O indicated that cation–solvent exchange is not rate determining and, hence, the kinetic differences within the series may not be a reflection of changes in coordination number.[25] Hydration number differences within the rare-earth series have also been predicted from ultrasonic velocity measurements in water,[26] but these results combine inner- and outer-sphere effects, thereby complicating the interpretation.

Even less information is available for lanthanide complexation reactions in anhydrous or aqueous organic solvents. In methanol, Wertz obtains eight-coordinate $[La(CH_3OH)_8]^{3+}$, but after aging for 1 year $[LaCl_3(CH_3OH)_5]$ occurs in the form of $[LaCl_2(CH_3OH)_5]_2$, double entities in which adjacent $LaCl_3$ units are bonded by μ-dichloro bridges.[8,9] Concentrated

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$NdCl_3$ and $GdCl_3$ solutions in methanol were also eight-coordinate with two chlorides and six methanol molecules in the inner solvation shell.[7,8] Using the same solutions as in the X-ray study, McCain carried out a La-139 NMR study of lanthanide chloride complexation in aqueous methanol.[27] Above a water mole fraction, X_w, of 0.69, no inner-sphere chloride complexation was reported, for X_w between 0.07 and 0.69 the data were interpreted in terms of a single chloride in the inner coordination shell exchanging with another chloride ion, with some dichloride complexes also present, and in methanol both single coordinated and bridged chlorides were postulated.

Our laboratory has been investigating the behavior of lanthanide salt solutions in aqueous methanol, aqueous DMF, and aqueous Me_2SO for several years. Our results are different from those of Wertz and McCain[5-9,27] in that differences in the ultrasonic absorption behavior of constant-salt-concentration lanthanide salts are interpreted in terms of an equilibrium between two forms of lanthanide ions, postulated to involve different coordination numbers.[21-23,28-36]

Recently, Bünzli and colleqgues have applied FT IR and fluorometric techniques to determine the structures of lanthanide salts in anhydrous organic solvents.[37-39] Europium perchlorate in acetonitrile contains monodentate perchlorate ions in the inner sphere of the Eu(III) ions, but bidentate perchlorate ions exist in the outer solvation shell.[37] Since there are eight acetonitrile molecules also bound in the inner solvation shell, Bünzli reports a total coordination number of 9.1 with an error of +0.3. Me_2SO replaces acetonitrile in the inner coordination shell of Eu(III).[38] No inner-sphere perchlorates are detected in Me_2SO, and the average number of bound Me_2SO molecules is 8.7. They estimate an equilibrium constant of 10 M for the addition of an additional Me_2SO to the eight-coordinate complex to form a nine-coordinate complex.[38] The solid nitrate contains three bidentate nitrates and three Me_2SO molecules bound to the Eu(III) for a total coordination number of 9. In 0.05 M europium nitrate in Me_2SO, the ratio of inner-sphere nitrate to no inner-sphere nitrate is estimated to be 1 to 6.5. The emission spectra of 0.01 M perchlorate and nitrate solutions in Me_2SO are similar, but when the europium nitrate concentration is raised to 0.1 M, substantial intensity changes are produced, indicating the existence of mono, bis, and tris complexes.[38] In DMF the europium perchlorate salt is completely dissociated with an estimatd coordination number of 8.[39] Thus, when the solvent is changed from acetonitrile to DMF, europium perchlorate changes coordination number from 9 to 8. The intermediate value of 8.7 for the same salt in Me_2SO suggests the existence of an equilibrium between two forms of Eu(III) species in solution, differing in the total coordination number. The nitrate has the bis(nitrato) complex as the predominant species, with some mono and tris complexation also present.[39] These studies are being extended to other lanthanides salt solutions by Bünzli.

This investigation of the solution chemistry of the early or pre-lanthanides Sc(III), Y(III), and La(III) was initiated in order to contrast the chemical behavior of these similar ions with the lanthanide chlorides in aqueous methanol. Significant differences were anticipated compared to our earlier studies, since the ionic radii vary from 0.68 Å (Sc) to 0.88 Å (Y) to 1.061 Å (La). Consequently the ionic potential and the charge density at the surface of the rare-earth ions decreases substantially on going from Sc(III) to La(III). In addition, all pre-lanthanide triad ions can polymerize in solution,[40] with the degree of polymerization decreasing from Sc(III) through La(III). Also, the apparently nomadic behavior of Y(III) with respect to the lanthanides in different systems is of interest. Although the polymerization of Y(III) may influence to some extent the nomadic behavior, covalent interactions of the lanthanides involving the 4f electrons may be more important.[41] In other words, it may not be Y(III) that migrates, but rather the lanthanide ions themselves due to varying amounts of covalency from system to system.

No previous ultrasonic investigations exist involving any of the three salts in aqueous methanol, but $Y(NO_3)_3$ has been investigated in water with mononitrate inner-sphere complexes present.[42] Hemmes reports the presence of only a single relaxation present in that ultrasonic investigation of Y(III) in water, a significant difference from studies on lanthanide–nitrate systems where two relaxations are present. Fratiello has utilized proton NMR to study the hydration of Sc, Y, and Th perchlorates in aqueous acetone, obtaining low hydration numbers based upon the assumption of no inner-sphere perchlorate complexation.[43] The scandium-45 NMR study of ScX_3 ($X = Cl, Br, I, ClO_4, NO_3$) and $Sc_2(SO_4)_3$ and their hydrates in aqueous and tetrahydrofuran solutions demonstrates the strong hydration of the Sc(III) ions.[44]

Experimental Section

Preparation of the Solutions. La_2O_3 (99.99%, low Ca content, Alfa Products), Y_2O_3 (99.99%, Alfa), and Sc_2O_3 (99.9%, Alfa) were used as starting materials. The oxides were calcinated prior to use at 1100 °C for 5 h to remove CO_2 and other volatile impurities present (in the case of old La_2O_3, the weight loss was above 5%). A 0.1-mol sample of the rare-earth oxide was weighed in a 200-mL beaker, and 50 mL of water was added (in the case of the basic freshly calcinated La_2O_3 the reaction was so exothermic that the water boiled). Then, concentrated HCl (Fisher) was added dropwise, with magnetic stirring and heating employed until the oxide was completely dissolved (approximately 50 mL of the HCl was added). The solutions were then evaporated until the pH reached about 2. The solutions were quantitatively transferred to weighed 100-mL volumetric flasks. Weighed 1.00-mL samples of 2 M rare-earth chloride stock solutions were titrated with 0.100 M $Na_2H_2(EDTA)\cdot 2H_2O$ (Merck) solution by using freshly prepared xylenol orange indicator and ammonium acetate buffer at a pH slightly over 5. Weighed amounts of the standardized 2 M stock solutions were added to 50-mL volumetric flasks, and 0.200 M rare-earth chloride solutions were made in different water–methanol mixtures for the ultrasonic studies. Since a small volume contraction occurs over a period of up to 3 days, the final additions of solvent were made at the end of that time. When methanol stock solutions were required, the aqueous solution was heated to near dryness in a 50-mL volumetric flask; methanol (0.02% water, Merck) was added, the solution was reheated to near dryness, and the process was repeated. In some cases a drop of HCl was added to remove any possible oxychlorides formed. Karl Fischer titrations using Metrohm Automat E547 and Dosimat E535 were carried out on the solutions with the smallest water contents.

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Table I. The Ultrasonic Absorption Data for 0.200 M $LaCl_3$ in Aqueous Methanol at 25 °C[a]

f, MHz X_w =	0.0	0.0254	0.0561	0.0956	0.1925	0.2188	0.2781	0.3496	0.4153	0.5861	0.6777	0.7598	0.8294	0.8945	1.00
10.58±0.05	134.8	-	-	273.5	384.6	368.0	-	364.3	298.0	193.0	131.8	77.7	-	-	-
12.08±0.03	132.4	169.3	195.0	282.5	346.7	361.0	342.9	296.5	267.5	195.6	121.1	75.0	51.4	33.5	-
20.07±0.03	121.6	141.6	165.0	222.6	285.8	283.2	273.9	244.9	211.3	146.2	103.6	68.5	42.6	32.4	-
28.20±0.06	115.2	126.6	135.2	180.9	230.8	212.1	211.7	200.7	171.1	124.8	89.7	59.6	40.8	33.1	23.6
30.34±0.12	112.4	-	125.3	168.3	212.8	209.2	199.2	193.0	168.6	122.2	88.0	63.8	-	32.4	-
36.30±0.10	107.4	117.1	117.2	163.3	173.8	172.5	169.1	151.1	141.3	105.2	78.6	53.8	38.6	30.6	24.6
44.34±0.05	99.0	107.8	109.6	133.8	144.9	147.3	144.2	139.5	119.2	90.3	66.9	51.1	37.1	30.8	23.5
50.69±0.11	94.0	103.9	102.9	118.6	130.9	125.0	126.4	122.9	111.2	85.0	66.5	49.2	-	31.2	23.9
70.75±0.18	83.8	91.5	90.3	95.6	95.3	-	99.5	92.1	87.8	69.5	57.8	46.0	33.5	29.2	23.7
91.39±0.15	80.2	82.5	80.0	85.7	80.4	82.9	87.3	80.1	77.8	62.1	56.9	42.5	34.7	29.5	23.8
112.15±0.29	75.6	77.4	75.8	78.4	72.1	76.2	81.6	71.9	70.0	60.1	54.2	41.1	34.0	29.5	-
132.60±0.49	68.7	69.6	70.2	70.9	67.5	70.2	71.5	67.2	65.7	57.3	52.1	39.7	-	29.5	23.3
153.70±0.52	64.4	66.9	65.0	66.2	61.8	65.2	62.9	61.4	61.0	53.9	49.9	38.4	-	28.4	22.7
174.00±0.58	60.2	62.2	61.3	62.6	60.9	61.5	60.7	59.9	58.9	50.9	46.7	38.4	34.2	-	22.9
193.50±0.66	57.8	61.0	57.7	60.6	59.5	59.2	59.4	58.5	57.2	50.4	46.5	38.1	-	27.9	23.2
215.18±0.72	56.5	57.5	56.0	58.1	-	58.0	58.6	57.6	55.3	-	-	-	33.5	-	23.2

[a] Absorption units: 10^{17} Np cm^{-1} s^2.

Table II. The Ultrasonic Absorption Data for 0.200 M YCl_3 in Aqueous Methanol at 25 °C[a]

f, MHz X_w =	0.0	0.0943	0.1332	0.1605	0.1866	0.3431	0.4721	0.5796	0.6737	0.7529	0.8174	1.00
5.05±0.02	718.0	-	-	946.0	1061.0	640.0	-	-	-	-	-	-
7.16±0.19	544.0	424.0	759.0	754.3	-	-	-	-	-	-	-	-
9.10±0.02	-	-	594.0	617.5	663.0	503.0	384.8	-	-	-	-	-
11.09±0.03	321.0	-	415.0	464.4	522.0	447.6	336.5	215.0	163.6	-	-	-
12.08±0.03	261.6	316.0	356.5	379.4	-	-	-	-	-	-	58.0	-
13.11±0.05	226.4	269.0	302.6	366.5	407.0	382.0	280.9	185.0	140.8	96.9	-	-
15.11±0.06	170.6	202.0	250.4	302.2	308.7	300.5	243.0	162.5	122.2	83.0	-	-
17.05±0.02	-	-	-	-	261.1	-	-	149.5	-	74.4	-	-
20.13±0.08	148.0	161.3	175.0	185.6	176.6	196.8	170.8	133.1	98.2	67.3	48.0	-
28.16±0.05	113.2	115.7	117.8	129.2	130.1	137.8	126.0	105.8	81.7	61.2	45.0	23.8
30.63±0.04	-	103.0	-	131.1	125.4	116.9	123.7	103.3	80.7	59.7	44.6	23.4
36.27±0.05	101.3	93.0	102.9	105.6	103.4	109.9	102.5	91.5	71.2	55.5	43.8	23.4
44.28±0.06	88.0	81.9	84.5	94.52	85.4	88.9	90.0	84.0	64.3	50.0	40.4	23.1
50.91±0.08	85.8	75.1	81.7	84.7	-	83.4	85.9	79.2	63.0	48.0	39.0	22.8
71.01±0.12	74.0	68.8	65.9	68.6	71.2	70.6	70.4	74.1	57.9	44.3	38.2	22.9
91.38±0.32	65.2	65.3	58.5	62.3	65.7	67.0	65.5	67.1	51.0	43.3	36.8	23.6
111.76±0.41	62.2	64.7	55.9	59.0	62.5	65.1	63.9	62.8	48.8	42.5	36.5	23.3
132.07±0.72	60.2	60.1	54.2	57.8	60.6	62.6	61.6	56.8	44.7	41.2	35.7	23.1
154.54±0.53	59.8	56.2	-	56.9	-	57.8	58.0	55.8	43.5	39.5	-	22.6
174.07±1.22	57.5	54.3	50.5	55.2	58.7	57.1	55.6	55.4	42.4	38.0	-	22.8
192.61±0.71	57.6	-	-	54.3	58.4	57.7	54.8	-	-	-	-	22.5
215.08±0.68	56.0	54.2	52.6	53.0	56.1	57.2	54.9	-	-	-	-	24.1
237.65	-	-	-	50.4	-	-	-	-	-	-	-	

[a] Absorption units: 10^{17} Np cm^{-1} s^2.

Ultrasonic Equipment. The Matec ultrasonic apparatus consists of a Model 6600 main-frame with three rf plug-ins to generate the experimental frequencies: Model 755 (5–17 HHz), 760V (12–70 MHz), and 765 (90–215 MHz). X-Cut quartz piezoelectric transducers with 1-, 4-, and 10-MHz fundamental frequencies (Valpy Corp., Hopkinton, MA) were used to generate the experimental data. The sending crystal was a gold-plated $^1/_2$-in.-diameter crystal with a quartz delay rod. It is connected to a micrometer (Starret Tool Co.) that is raised or lowered into the test solutions to vary the path length between the sending and the receiving crystal, a 1-in.-diameter gold-plated crystal in fixed position at the bottom of the stainless-steel interferometer cell. A Model 666 rf pulse comparator was utilized with a 1204B master synchronizer to generate an external standard signal. Both the attenuated and external standard signals are read by using a Tektronix 5103N oscilloscope. The attenuated signal was adjusted by using the micrometer until its peak height matched the external standard. The actual experimental frequencies were measured by beating the pulsed test signal with a continuous signal generated with a Heath Model 1G-1025 rf signal generator and measuring the continuous signal with a Fluke 1910A multicounter. Each test solution was 50 mL in volume and was thermostated at 25.0 °C by using a Forma heating/cooling circulating temperature bath. The sound absorption, α/f^2, is the slope of a graph of decibels as a function of micrometer reading, with a units conversion from decibels to nepers (8.686 dB/Np). The α/f^2 values were calculated by using the least-squares method on a HP 55 calculator. All other calculations were carried out on an Apple III microcomputer. The two greatest sources of error introduced into the experimental measurements come if the two quartz crystals are not perfectly parallel and from incorrectly tuning the test frequency to the odd harmonic of the fundamental frequency. In addition, the voltages must be adjusted below the level of clipping in order to achieve a linear response between the absorption and the voltage.

Results

The ultrasonic absorption data for the three salts are summarized in Tables I–III. In water, the chlorides of Y(III) and La(III) have the same ultrasonic absorption as the solvent alone, defined as *B*, whereas the corresponding Sc(III) salt has a frequency-dependent sound absorption. Upon addition of methanol, all salts possess an ultrasonic absorption greater than *B*, and this difference is called the excess absorption. For a system consisting of one or more chemical relaxations, the absorption data are given as

$$\alpha/f^2 = B + \sum A_i/[1 + (f/f_i)^2] \tag{1}$$

where *B* is the absorption of the solvent mixture in the absence of salt,[45] A_i is the relaxation amplitude for each step, *f* is the experimental frequency, and f_i is the characteristic relaxation frequency for each step. Alternately, the data can be expressed in terms of an excess absorption, μ, which is equal to $[(\alpha/f^2) - B]fv$, where v is the sound velocity in the solution. Some solutions at high X_w could be calculated by assuming only a single relaxation, but most solutions calculated by this technique had a *B* value significantly higher than that in the solvent

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Table III. Ultrasonic Absorption Data for 0.200 M $ScCl_3$ in Aqueous Methanol at 25 °C[a]

f, MHz X_w =	0.0637	0.2049	0.3595	0.4490	0.4870	0.5586	0.5941	0.6883	0.7677	0.8377	1.000
5.03	-	-	-	-	283.0	-	-	-	-	-	-
7.04	-	241.0	-	-	-	-	-	-	-	-	-
9.09±0.02	-	204.2	198.4	-	232.5	-	-	165.5	-	-	-
10.23±0.16	-	-	-	200.0	-	-	-	164.2	-	123.3	-
11.06±0.42	-	169.2	-	-	224.2	-	-	151.1	-	-	-
12.13±0.48	74.3	149.6	186.2	189.9	196.3	171.6	177.5	159.5	144.5	112.4	83.7
13.18±0.56	-	139.0	178.4	187.8	-	-	-	144.6	135.5	-	-
15.16±0.40	65.1	123.8	169.9	153.1	171.9	-	159.4	140.6	-	-	-
20.10±0.38	56.5	102.9	146.6	148.6	159.4	144.4	147.8	136.5	121.5	102.6	76.2
28.20±0.20	53.7	85.8	121.6	127.1	135.9	131.0	139.7	126.8	109.2	93.5	71.2
30.42±0.60	52.5	-	119.8	-	133.1	124.1	136.9	119.3	108.4	95.5	70.3
36.28±0.54	51.5	78.4	109.7	118.6	125.4	121.2	131.8	-	102.5	90.7	70.1
44.25±0.40	50.7	71.8	103.0	111.7	118.1	110.8	120.8	111.4	97.2	88.2	69.1
50.50±0.38	50.5	-	100.4	-	108.7	102.7	110.8	105.6	95.2	84.4	67.0
70.93±0.62	47.8	62.6	91.5	93.5	93.8	93.9	99.5	94.7	90.3	81.5	64.7
90.84±0.66	44.2	60.3	76.2	83.3	88.0	89.5	94.4	88.8	86.8	74.1	62.5
110.84±0.68	44.2	57.5	73.2	79.0	83.5	84.5	85.4	83.2	81.1	68.6	60.3
131.22±0.62	40.6	52.2	66.2	72.6	77.5	80.5	78.3	76.7	74.5	65.1	57.0
153.93±0.67	42.2	52.1	59.4	68.1	72.9	75.0	72.0	68.3	67.0	58.4	53.0
170.85±0.82	43.3	53.1	-	68.2	65.9	70.8	-	-	65.3	56.6	51.6
191.01±0.51	44.0	-	-	58.4	-	67.5	-	-	60.3	-	-
204.88	-	-	-	-	-	-	-	-	-	53.3	-

[a] Absorption units: 10^{17} Np cm^{-1} s^2.

system alone. These solutions must be calculated with the assumption that two relaxations are present. In lanthanide complexation reactions in water or mixed solvents, the two relaxations are identified with the steps of the following mechanism:[16,17,22-25,28-36]

$$\mathrm{Ln^{3+}(S)} + \mathrm{Cl^-(S)} \overset{\text{step 12}}{=} \mathrm{Ln^{3+}(S)_X Cl^-} \overset{\text{step III}}{=} \mathrm{LnCl^{2+}(S)} \qquad (2)$$

In reaction 2 the symbol S represents bound solvent, composed of water, methanol, or a mixture of the two. The first step represents a diffusion-controlled association of the two ions to form a solvent-separated outer-sphere complex, coupled to solvent loss from the inner solvation shell of the ligand. The second step, which is slower than the first, represents solvent loss from the cation solvation shell coupled to lanthanide–ligand bond formation to form the contact, or inner-sphere ion pair. Outer-sphere complexation, when detected, occurs at high frequency (step 12) and inner-sphere complexation at low frequency (step III). The number of solvent molecules bound in the inner solvation shell is not exactly known, but is likely to be 9 or 8 for La(III) and Y(III) and 6 for the d-type transition element Sc(III). If bis or tris complexes are formed, the successive additions of ligand should follow a similar mechanism to reaction 2. In lanthanide complexation systems, the formation of the bis complex appears to occur at a faster rate than the mono complex.[28] If a coordination number change accompanies complexation, it can be coupled to any of the individual steps. The mechanism may be S_N1, or dissociative, in which the activated complex is of reduced coordination number compared to the solvated lanthanide ion; or it may be S_N2, or associative, in which the coordination number of the solvated lanthanide ion increases in the activated complex. Since both reaction types are merely limiting cases, the mechanism may be intermediate between the two.

The relaxation data for the three sets of 0.200 M $LnCl_3$ solutions are given in Table IV. For each independent relaxation, a more convenient form of the relaxation equations is in terms of the excess absorption maxima, μ_i, given by eq 3. Provided that the enthalpy changes are small (as is the case with chloride ions) and constant salt concentrations are used (as in this study), μ_i is approximately proportional to the square of the reaction volume change. If the only effect of adding water to the methanol solutions is a reduction in the extent of complexation, then μ_{III} should decrease with increasing X_w. If, on the other hand, complexation is accompanied by a geometry change involving a coordination number change, then μ_{III} shows a large increase as X_w increases. Thus, μ_{III} can serve as a reliable probe of coordination number changes in mixed solvents. In particular, because of the relatively large volume change associated with complex formation between a 3+ metal ion and a negatively charged ligand, ultrasonics not only provides a sensitive test of the differences between inner- and outer-sphere ion pairs but also easily detects coordination number changes, especially when coupled to inner-sphere complex formation. Because of the relatively large errors associated with the high-frequency relaxation (outer-sphere complexation), these results are usually less informative. The data are summarized in Figure 1 for inner-sphere complexation for the three salts.

$$\mu_i = A_i f_i v/2 \qquad (3)$$

Several questions arise when the data for the $LnCl_3$–methanol–water system are considered, especially when the data are compared as a function of metal ion radius:

(1) Which lanthanides or pre-lanthanides have inner-sphere chloride ions?

(2) As methanol is added to the aqueous solutions, where does inner-sphere complexation begin?

(3) At what X_w does methanol replace water in the inner solvation shell of the cation? Must this replacement precede inner-sphere complexation because the methanol is not expected to be as tightly bound as the water, thereby allowing chloride ion to replace methanol?

(4) What chemical species are present at the lowest X_w values, i.e., is $LnCl^{2+}$ and/or $LnCl_2^+$ formed? If bis and tris complexes exist, at what X_w do they disappear?

(5) Does the coordination number of the cation change as the solvent composition varies?

(6) Do Y(III) salts have one or two relaxations present?

Unfortunately, neither ultrasonics or any other technique in use today can totally answer all of these questions, but a good start can be made.

Table IV. Calculated Relaxation Results for 0.200 M $LnCl_3$ Solutions in Aqueous Methanol at 25 °C[a]

X_w	10^{17} A_{III}, np cm^{-1} s^2	f_{III}, MHz	10^4 μ_{III}, np	10^{17} A_{12}, np cm^{-1} s^2	f_{12}, MHz	10^4 μ_{12}, np	10^{17} B,[a] np cm^{-1} s^2	v, m s^{-1} Ref (47)
				$LaCl_3$				
0.0	60.1± 2.8	33.53± 2.50	11.1± 1.4	49.5± 3.3	206.0± 15.8	56.2± 8.0	30.37	1102.8
0.0254	101.6± 4.3	20.05± 1.80	11.4± 1.5	63.5± 3.2	168.3± 9.6	59.7± 6.4	30.59	1118.1
0.0561	151.8± 5.0	20.40± 1.34	17.3± 1.7	53.5± 3.5	188.5± 15.7	56.5± 8.4	30.62	1118.7
0.0956	244.5± 7.4	25.82± 1.69	36.6± 3.5	41.4± 7.9	247.2± 76.7	59.3±29.7	30.47	1158.9
0.1925	373.5± 6.2	26.00± 0.71	58.8± 2.6	-	-	-	52.6 ±2.2	1211.4
0.2188	373.4± 4.0	24.00± 0.55	54.9± 1.9	30.8± 3.6	376.9±129.4	71.2±32.8	29.89	1225.9
0.2781	333.2± 6.2	25.05± 1.02	52.6± 3.1	34.6± 6.0	292.3±103.4	63.7±33.6	30.40	1259.4
0.3496	331.0± 17.7	22.17± 2.81	47.8± 8.6	37.6± 17.6	217.7±150.0	53.3±61.7	31.75	1302.7
0.4153	273.3± 8.2	21.92± 1.57	40.3± 4.1	35.4± 8.0	213.3±	50.8±28.1	33.33	1345.1
0.5861	169.8± 3.9	22.95± 1.31	28.5± 2.3	21.5± 4.3	240.0±	37.7±21.3	34.83	1460.9
0.6777	93.2± 3.2	23.06± 1.81	16.3± 1.8	17.0± 3.1	268.8±101.0	34.6±19.3	34.61	1516.6
0.7598	43.5± 2.2	29.00± 3.01	9.8± 1.5	10.5± 2.3	391.7±289.7	32.1±30.8	28.41	1553.4
0.8294	28.9± 4.1	15.04± 2.30	3.4± 1.0	-	-	-	33.4 ±0.4	1568.3
0.8945	4.8± 1.1	35.02±14.87	1.3± 0.9	6.2± 1.2	373.1±222.-	17.9±14.2	23.10	1562.7
1.00	1.4± 0.5	104.4 ±97.2	1.1± 1.4	-	-	-	22.7 ±0.7	1497.0
				YCl_3				
0.0	1161.2±103.7	5.94± 0.48	38.2± 6.5	-	-	-	58.6 ±6.9	1109.2
0.0943	627.8± 46.4	9.29± 0.65	33.8± 4.9	-	-	-	55.0 ±3.6	1158.2
0.1332	1930.9±230.9	5.34± 0.46	60.9±12.5	-	-	-	51.9 ±5.6	1179.4
0.1605	1349.6± 48.2	7.16± 0.25	57.7± 4.1	-	-	-	52.8 ±4.7	1194.1
0.1866	1522.3± 50.5	7.17± 0.25	65.9± 4.4	-	-	-	48.9 ±5.2	1208.2
0.3431	722.7± 22.3	11.40± 0.47	53.5± 3.8	-	-	-	49.8 ±4.6	1298.6
0.4721	610.5± 25.6	9.75± 0.41	41.2± 3.5	27.9± 2.6	286.5± 71.5	55.2±19.0	34.51	1383.4
0.5796	367.7± 34.1	8.63± 0.65	23.1± 3.9	39.9± 1.9	152.1± 11.8	44.2± 5.6	34.91	1456.6
0.6737	421.1±100.7	6.20± 1.00	19.8± 7.9	30.8± 2.0	105.9± 8.7	24.7± 3.7	32.42	1514.4
0.7529	109.5± 24.8	12.40± 2.41	10.5± 4.4	-	-	-	40.9 ±1.3	1551.0
0.8174	34.4± 5.8	13.86±3.16	3.7± 1.5	12.5± 1.4	225.0± 68.2	22.1± 9.2	25.69	1567.1
1.00	-	-	-	-	-	-	23.1 ±0.2	1497.0
				$ScCl_3$				
0.0637	59.5± 21.7	11.57± 3.75	3.9± 2.7	-	-	-	44.5 ±1.3	1141.1
0.2049	368.4± 26.9	6.87± 0.46	15.4± 2.2	34.3± 2.5	204.6± 34.9	42.7±10.4	29.86	1218.2
0.3595	145.7± 5.8	16.08± 1.46	15.3± 2.0	59.4± 4.7	141.1± 15.3	54.9±10.3	31.98	1308.9
0.4490	173.0± 36.2	11.46± 2.97	13.6± 6.3	70.9± 7.9	140.4± 19.7	68.1±17.1	34.08	1367.7
0.4870	210.5± 9.0	10.74± 0.78	15.8± 1.8	76.2± 4.7	138.5± 14.1	73.6±12.0	34.74	1393.6
0.5941	84.4± 11.8	17.54± 5.55	10.9± 4.9	82.3± 9.2	132.4± 16.7	79.9±19.0	34.70	1466.1
0.6883	80.9± 13.6	12.51± 3.43	7.7± 3.4	80.3± 5.5	140.1±14.2	85.6±14.5	31.82	1522.3
0.7677	94.1± 17.6	11.88± 2.43	8.7± 3.4	68.5± 2.3	181.7± 9.2	96.9± 8.1	28.02	1556.0
0.8377	77.9± 33.7	9.06± 3.53	5.6± 4.6	64.1± 2.1	168.5± 8.5	85.3± 7.1	62.8 ±4.2	1568.8
1.00	46.7± 17.2	8.84± 2.54	3.1± 2.0	46.6± 0.6	226.7± 6.9	79.1± 3.5	21.7	1497.0

[a] When errors are reported, the data could only be fit by a single-relaxation procedure. Other values are taken from ref 45.

Discussion

In the absence of inner-sphere complexation such as the case of NaCl in water[45] α/f^2 follows the solvent data (B values) with only minor deviations from the solvent values. In water, Y(III), La(III), Er(III),[29] Gd(III),[32] and Nd(III)[32] contain no detectable amounts of inner-sphere complex for 0.200 M metal–chloride salt solutions. The presence of an increasing α/f^2 with decreasing experimental frequency for Sc(III) chlorides indicates that measurable quantities of inner-sphere chloride complex must be present, the first distinct difference between Sc(III) and the other lanthanide-like ions. In the absence of inner-sphere complexation, ultrasonics cannot usually detect the presence of outer-sphere complex. Thus, the absence of an absorption above that of the solvent alone does not preclude the presence of outer-sphere complexes in lanthanide chloride solutions.

At all solvent compositions where significant amounts of inner-sphere complexes are present, the amplitude of the inner-sphere μ_{III} value is significantly greater for Y(III) and La(III) than for Sc(III). We believe that the small magnitudes of the excess absorption maxima for Sc(III) reflect the fact that scandium resembles octahedral d-type transition-metal ions, whereas the other two ions have coordination numbers of 8 or greater. Thus, when an anion such as chloride enters the inner coordination shell, it reduces the effective cation charge. Because the Y and La are larger, with or without inner-sphere complex, the effect of adding the chloride is magnified. A similar small amplitude for chloride complexation occurs in the Me_2SO-rich solvent region for zinc complexation[46] even though the zinc chloride complex is known to be the 1:2 complex. Zinc nitrate only forms a 1:1 complex in the same solvent region, with the complexation constant about 10^8 smaller than the chloride, but still has a larger μ_{III} than does the same concentration chloride salt.[47] Thus, the low amplitude for $ScCl_3$ is the normal behavior for octahedral cations. It is the nonoctahedral lanthanide-like ions that have the high μ_{III} for inner-sphere chloride complexation.

Figure 1 clearly shows an increase in μ_{III} for inner-sphere complexation upon the addition of water for all three salts. Each of the three chlorides has distinct behavior prior to reaching the maximum in μ_{III}. Although an unweighted least-squares analysis of the data for Y(III) and La(III) after the maximum in the curve predicts small differences in the best fit equation through the data, within experimental error the same line can be drawn for both salts, as shown in Figure 1. The question arises if this same curve will fit all lanthanide chlorides after the structural change. In Figure 1 we have also plotted the μ_{III} values for both $NdCl_3$ and $GdCl_3$. These are both clearly different from the La(III) and the Y(III) salts, demonstrating that significant differences do occur as a function of which lanthanide ion is studied. Even greater

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(46) Silber, H. B.; Kromer, L. U.; Gaizer, F. *Inorg. Chem.* **1981**, *20*, 3323.

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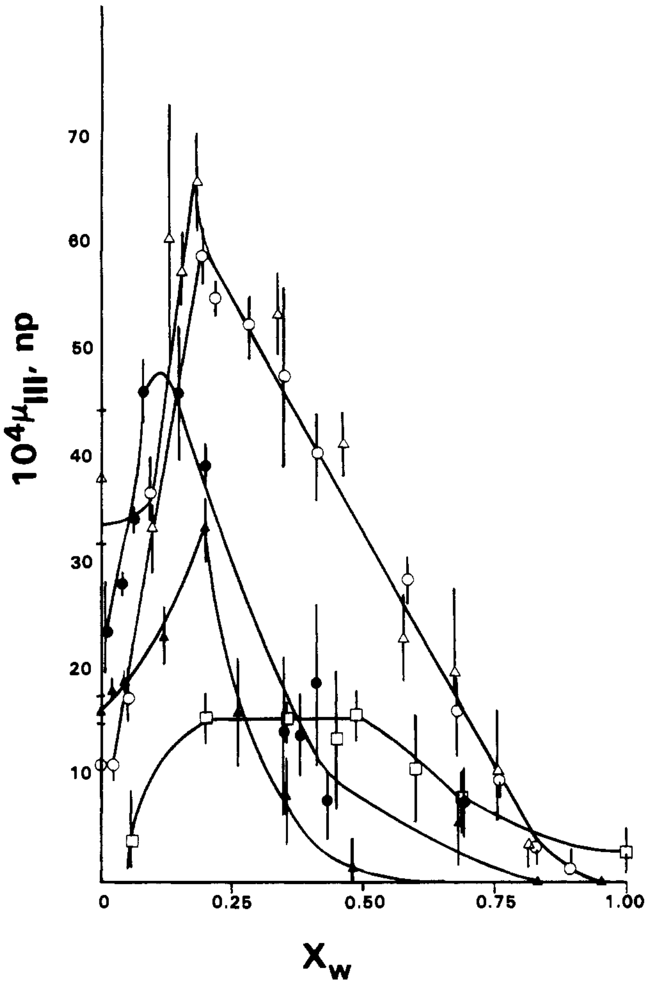

Figure 1. Excess absorption amplitudes for 0.200 M $LnCl_3$ solutions at 25 °C: △, YCl_3; ○, $LaCl_3$; □, $ScCl_3$; ●, $GdCl_3$;[32] ▲, $NdCl_3$.[32]

differences would be shown if the data for 0.200 M $ErCl_3$ were included, since at that concentration no maximum in μ_{III} is observed. However, once again, Sc(III) is different from Y(III) and La(III), in both the region and the shape of the effect. Below $X_w = 0.6$, a small increase in μ_{III} occurs for $ZnCl_2$ in aqueous Me_2SO or aqueous DMF upon the addition of water, in a solvent region where only the octahedral species is present.[46,48] At high X_w where an octahedral to tetrahedral conversion occurs, there is a dramatic increase in μ_{III}, at least 1 order of magnitude larger than that observed in any lanthanide system. On the other hand, the same salt in aqueous methanol has this large increase in μ_{III} occurring upon the first addition of water, indicating that with the relative similarity in size between water and methanol the geometry change can occur in the presence of any water.[48] Since the μ_{III} increase associated with a geometry change in octahedral systems is at least 1 order of magnitude greater than the small increase noted for Sc(III), we believe that the small increase for Sc(III) represents some other effect rather than a simple geometry change. For Y(III) and La(III) the increase in μ_{III} is similar to that occurring in other lanthanide systems, and we believe it represents a coordination number change. We will discuss the results and the chemical hypotheses for these in each region of the data.

The B value for all of the YCl_3 solutions calculated on the assumption that only one relaxation is present is significantly higher than that for the solvent alone. This is normally evidence for the existence of a second relaxation. Below $X_w = 0.47$, double-relaxation fits require a f_{III} in excess of 1000 MHz, far beyond the upper range of experimental measurement, with calculated errors in the relaxation frequency in excess of 100%. However, as water is added, the apparent high relaxation frequency decreases, and the data can be successfully resolved into double-relaxation phenomena. Therefore we conclude that Y(III) is not different from the other chloride salts. This does not disagree with Hemmes' data on the $Y(NO_3)_3$ solutions in water,[42] since there is no a priori reason why the two salts should be identical.

$0 < X < 0.2$. As water is added to the methanol solutions of Y(III) and La(III), there is a rapid increase in the ultrasonic absorption. In addition, the amplitude of μ_{III} is greater for Y(III) than for La(III). This may reflect an increased complexation constant for the smaller Y(III) cation compared to La(III), consistent with the results of the Fuoss equation for ion-pair association constants. An alternative explanation is that it may reflect differences in the possible existence of bis complexes for the two salts.

We believe this increase in μ_{III} represents a coordination number change, but is this change caused by steric crowding in the inner coordination shell of the 1:1 or the 1:2 complex? Some information can be obtained from Wertz's X-ray experiments in alcohols. Wertz notes that his X-ray spectra change with time and that after 1 year he obtains different results.[8,9] We believe that when Wertz prepares his solutions by adding anhydrous lanthanide chlorides to water or methanol, oxychlorides are actually formed, on the basis of our observation that the addition of anhydrous ErI_3 to methanol gave off a brown gas.[48] With time, the oxychlorides can become destabilized with respect to the chlorides, and hence his aged solutions may more closely resemble those of Spedding. Our experience with the ultrasonic data on lanthanide salts in water or aqueous methanol prepared by adding the inorganic acid to the lanthanide oxides indicates that the data are equivalent even 1–2 years after the solutions are made. Thus, the results obtained by Wertz on the old solutions can be utilized to understand our data.

Wertz postulates the existence of μ-dichloro bridges having the net structure of $[LaCl_2(CH_3OH)_5]_2^{2+}$, whereas the Nd(III) complex exists as a dichloro complex.[7] Thus, there can be two types of dichlorides present in solution. McCain's NMR study postulates the existence of both types of bis complexes for $LaCl_3$ in methanol.[27] Using the temperature jump relaxation technique in water, we have demonstrated tha the addition of the second ligand to lanthanide complexes results in a more rapid relaxation time.[50] Hence, if the addition of water destabilizes the bis complex relative to the 1:1 complex, then as water is added to the anhydrous salt solutions, f_{III} should decrease. In methanol, this has been observed for $ErCl_3$ in the absence of any coordination number change,[29] and for $Er(ClO_4)_3$ where the coordination number change accompanies the formation of the bis complex.[30] Where the bridged form of the complex is stable, there is no reason to expect a labilization of the bound solvent for the second ligand compared to the first. Thus, the absence of a relaxation frequency decrease with the addition of water is consistent with the presence of bridged chlorides in methanol. Table IV shows the variation in inner-sphere relaxation frequency as a function of X_w. $LaCl_3$ exhibits a decrease in f_{III} upon addition of water, consistent with the presence of unbridged bis complex, but the data for YCl_3 are not as clear. The calculated relaxation frequencies for the lanthanum solutions (double-relaxation calculations) all exceed 20 MHz, a region that is experimentally convenient

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to measure accurately. On the other hand, the yttrium solutions in the methanol-rich regions are below 10 MHz. For solutions of the absorption magnitude detected in yttrium solutions, there are real experimental errors resulting from scattered rather than absorbed sound waves, and these errors would not show up in the curve-fitting calculations. Hence, in these low-amplitude Y(III) solutions the calculated relaxation frequencies are less reliable than in the lanthanum ones. Indeed, bis complexation may be present in the Y(III) solutions of a similar nature to that in the La(III) solutions but may be buried within the experimental error. Thus, if bis complexation occurs for the Y(III) solutions, it may be the bridged type or unbridged. In both the $GdCl_3$ and the $NdCl_3$ solutions under the same conditions, no bis complexation is detected in the ultrasonic measurements. In addition, the complexation constant is expected to be greater for at least the Nd(III) salt (the behavior of the complexation constant for Gd is not as clear due to the well-known gadolinium break). Hence, we believe that the significantly higher amplitude observed for both La(III) and Y(III) over Gd(III) and Nd(III) indicates that bis complexation is present for both pre-lanthanide ions.

Below $X_w = 0.2$, the data demonstrate that a coordination number change accompanies bis complexation for $LaCl_3$ and YCl_3. The other lanthanide data demonstrate that the coordination number change need not be coupled to the destruction of bis complex. The smaller increase in μ_{III} for $ScCl_3$ may represent changes in the excess absorption when bis complex disappears in an octahedral species. On the other hand, the Sc(III) results may be caused by changes in the extent of polynuclear species, and the two explanations may be coupled together.

$0.20 < X < 0.85$. Starting with $X = 0.2$–0.25, μ_{III} decreases in the same linear manner with X_w for both $LaCl_3$ and YCl_3. We believe this essentially linear region starts at the point where only the monocomplex is present and represents decreasing complexation due to an increasing solvent dielectric constant. This is identical with the behavior observed in aqueous methanol solutions of $ErBr_3$ and ErI_3, where only a single straight line was necessary for both solutions after the structural change.[22] Each solution above $X_w = 0.2$ contains 0.010 mol of lanthanide ion and at least 0.27 mol of water. Thus, sufficient water is present to completely solvate the inner shell of the lanthanide. For X_w between 0.07 and 0.69, McCain detects inner-sphere chloride ions, and he interprets the major chemical reaction occuring in this solvent region to be the exchange of bulk chloride for bound chloride in the monochloro complex of La(III).[27] Above a water mole fraction of 0.69, McCain detects no inner-sphere chloride binding. His measurements were unable to determine if the solvation shell consists of water, methanol, or a mixture of the two in this solvent region. Our ultrasonic results are basically similar to his, with the exception that we can detect measurable amounts of inner-sphere complexation until just below $X_w = 0.9$. We believe that the coordination number change has occurred prior to this region and is not a dominant factor in the ultrasonic absorption data. In this region, both inner- and outer-sphere complexes are present, and as water is added, the outer-sphere complexes become even more dominant. The solvent shell surrounding the lanthanide ions is postulated to be preferentially that of water, as contrasted to a mixed shell of water and methanol. If significant quantities of methanol were present, then we could not expect the observed linear sound absorption values with water mole fraction due to the size differences between water and methanol molecules.

$ScCl_3$ displays behavior different from that of the other salts. The μ_{III} data are essentially constant for X_w from 0.2 to 0.55. Above this value μ_{III} decreases as water is added, due to reduced amounts of inner-sphere complex.

$0.85 < X < 1$. In this region the major components are hydrated lanthanide ions with some outer-sphere complexes, with the possible exception of the aqueous solutions where inner-sphere complexes are not present. This does not apply to $ScCl_3$ where both inner- and outer-sphere complexes are present.

All of these results are valid for 0.200 M rare-earth chloride solutions. As the concentrations significantly increase or decrease from these values, the same or different species may be the predominant ones in solution. Although often times placed with the lanthanide salts because of the similar chemistry, our results indicate that in aqueous methanol, Sc(III) behaves as a standard d-type transition-metal ion rather than as a lanthanide ion. Y(III) and La(III) do behave as lanthanide ions in aqueous methanol, including the observation that there appears to be a coordination number change occurring in aqueous methanol below water mole fractions of 0.2.

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Registry No. $LaCl_3$, 10099-58-8; $ScCl_3$, 10361-84-9; YCl_3, 10361-92-9; methanol, 67-56-1.