Inorganic Chemistry

Scandium Sulfate Complexation in Aqueous Solution by Dielectric Relaxation Spectroscopy

Simon Schrödle,[*,†,§] **Wolfgang Wachter,**[‡] **Richard Buchner,**[‡] **and Glenn Hefter**[*,†]

Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia, and Institute of Physical and Theoretical Chemistry, Universität Regensburg, D-93040 Regensburg, Germany

Received December 11, 2007

Ion association in aqueous solutions of scandium sulfate has been investigated at 25 °C and at concentrations from 0.01 to 0.8 M by broadband dielectric spectroscopy over the frequency range $0.2 \leq \nu/\mathrm{GHz} \leq 89$. Detailed analysis of the spectra reveals the presence of both inner- and outer-sphere 1:1 $[\mathrm{ScSO_4}]^+$(aq) complexes, similar to solutions of other high-valent metal sulfates. Outer–outer-sphere 1:1 complexes are probably also formed, but their contribution is swamped by the presence of higher-order inner-sphere complexes. The latter predominate in the more concentrated solutions, causing major changes to the low-frequency end of the spectrum. The data, while not definitive, are consistent with *fac*-$[\mathrm{Sc(SO_4)_3(OH_2)_3}]^{3-}$ as the major species present. The speciation is strikingly different from that recently reported for aluminum sulfate solutions and indicates that the often-postulated similarity between the aqueous chemistry of Al(III) and Sc(III) has to be treated with caution.

1. Introduction

Scandium is widely distributed in nature, with varying amounts occurring in hundreds of minerals, the major ones being nickel−cobalt−copper laterites and thortveitite associated with uranium deposits.[1] Despite the ready commercial availability of scandium as a byproduct in the production of other metals, the present industrial uses of its compounds remain limited.[1] However, various promising applications for scandium-based materials have been described in recent years, including their use as solid electrolytes in fuel cells,[2] as sintering aids,[3] in gas sensors,[4] as photonic materials,[5] and for laser technology.[6,7]

The reported coordination chemistry of Sc(III) in aqueous solution is rather limited,[8−10] and even fundamental aspects of its solution chemistry are often poorly characterized. For example, the precise nature of Sc³⁺(aq) remains controversial.[11−18] While Sc³⁺ formally belongs with the 4f³⁺ ions, it is rather smaller (for 6-coordination: $r(\mathrm{Sc}^{3+}) = 75$ pm,[19] cf. typical lanthanide ionic radii of ∼105 pm) and it is often suggested that its properties are closer to those of Al³⁺ ($r(\mathrm{Al}^{3+}) = 50$ pm)[19] than to Y³⁺ ($r(\mathrm{Y}^{3+}) = 93$ pm)[19] or the lanthanide ions.[8,9] Consistent with this view, Sc(III) functions as a typical class a (or "hard") metal ion, although its complexes with fluoride[20] and hydroxide[21] are unusually

* To whom correspondence should be addressed. E-mail: simon@schroedle.de (S.S.), g.hefter@murdoch.edu.au (G.H.).
† Murdoch University.
‡ Universität Regensburg.
§ Current address: BASF SE, Catalysis Research, D-67056 Ludwigshafen, Germany.

(1) Hedrick, J. B. *Mineral Commodity Summaries, Scandium*; U.S. Geological Survey, 2006.
(2) Badwal, S. P. S.; Ciacchi, F. T.; Milosevic, D. *Solid State Ionics* **2000**, *91*, 136–137.
(3) Cheong, D.-S.; Sanders, W. A. *J. Am. Ceram. Soc.* **1992**, *75*, 3331.
(4) Imanaka, N.; Banno, S.; Adachi, G.-Y. *Chem. Lett.* **1994**, *23*, 319.
(5) Wen, L.; Sun, X.; Xiu, Z.; Chen, S.; Tsai, C.-T. *J. Eur. Ceram. Soc.* **2004**, *24*, 2681.
(6) Rainer, F.; Lowdermilk, W. H.; Milam, D.; Hart, T. T.; Lichtenstein, T. L.; Carniglia, C. K. *Appl. Opt.* **1982**, *21*, 3685.
(7) Caird, J. A.; Shinn, M. D.; Kirchoff, T. A.; Smith, L. K.; Wilder, R. E. *Appl. Opt.* **1986**, *25*, 4294.

(8) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterwoth-Heinemann: Oxford, UK, 1997; pp 950 ff.
(9) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1997; pp 1123 ff.
(10) Cotton, S. A. *Polyhedron* **1999**, *18*, 1691.
(11) Burgess, J. *Metal Ions in Solution*; Horwood: Chichester, UK, 1978.
(12) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1988.
(13) Kanno, H.; Yamaguchi, T.; Ohtaki, H. *J. Phys. Chem.* **1989**, *93*, 1695.
(14) Smirnov, P.; Wakita, H.; Yamaguchi, T. *J. Phys. Chem. B* **1998**, *102*, 4802.
(15) Rudolph, W. W.; Pye, C. C. *J. Solution Chem.* **2000**, *29*, 955.
(16) Rudolph, W. W.; Pye, C. C. *J. Phys. Chem. A* **2000**, *104*, 1627.
(17) Rudolph, W. W. *Z. Phys. Chem.* **2000**, *214*, 221.
(18) Lindqvist-Reis, P.; Persson, I.; Sandström, M. *J. Chem. Soc., Dalton Trans.* **2006**, *2006*, 3868.
(19) Marcus, Y. *Ion Solvation*; Wiley-Interscience: Chichester, UK, 1985.
(20) Hefter, G. T. *Coord. Chem. Rev.* **1974**, *12*, 221.
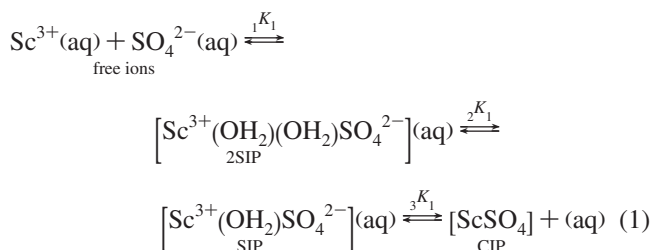(21) Baes, C. F.; Mesmer, R. E. *Hydrolysis of Cations*; Wiley: New York, 1976.

strong in relation to its charge/radius ratio. For example, log $K_1(ScF^{2+}(aq))$ lies about 3 orders of magnitude above the trend line established for other log $K_1(MF^{(n-1)+}(aq))$ values using a simple electrostatic correlation that incorporates the effects of ionic charge and radius.[20] A similar result has been reported for log $K_1(ScOH^{2+}(aq))$[21] and for log $K_1(ScSO_4^+-(aq))$,[22] although it should be noted that all these stability constants are well predicted by more sophisticated approaches.[23,24]

The higher sulfate complexes of Sc(III) are also strong,[22,25−27] which may be why sulfate ions have been employed as an additive to control morphology and particle size during the homogeneous precipitation of the Sc_2O_3 nanopowders used in the preparation of high-performance ceramic materials.[28,29] However, the nature of the species present in aqueous solutions of scandium(III) sulfate remains controversial. This is mostly because of the lack of convenient probes, both for $Sc^{3+}(aq)$ and $SO_4^{2-}(aq)$. Early investigators, employing conductivity and ion migration measurements[30−33] concluded that, in addition to 1:1 (scandium:sulfate) complexes, significant amounts of the 1:3 species, $[Sc(SO_4)_3]^{3-}$, are also present in $Sc_2(SO_4)_3(aq)$. Such measurements on highly charged asymmetric electrolytes are, however, difficult to interpret quantitatively.[34] Cation exchange studies[25−27] and a calorimetric investigation by Izatt et al.[22] have proposed 1:1, 1:2, and (sometimes) 1:3 complexes, but the reported formation constants differ by up to 2 orders of magnitude.

There is an additional problem in quantitatively characterizing the chemical speciation of the Sc(III)/SO_4^{2-} system. The extremely strong hydration of both ions ($\Delta_{hyd}G°(Sc^{3+})$ = −3801 kJ mol^{-1}; $\Delta_{hyd}G°(SO_4^{2-})$ = −1090 kJ mol^{-1})[35] favors the formation of associates in which the ions are separated by one or even two intervening solvent molecules. Such species are known, respectively, as outer-sphere and outer−outer-sphere complexes (or as they are often referred to in the physical chemistry literature: solvent-shared, SIP, and double solvent-separated, 2SIP, ion pairs). For strongly hydrated ions, such complexes may even predominate over the more familiar inner sphere complexes (or contact ion pairs, CIP), which creates difficulties in quantifying the speciation (see below).

The formation of the various ion-pair types by the successive loss of oriented water molecules from the hydration sheaths of the interacting ions, as proposed originally by Eigen and Tamm,[36,37] is represented (for the 1:1 species) in equilibrium scheme 1:

$$Sc^{3+}(aq) + \underset{\text{free ions}}{SO_4^{2-}(aq)} \overset{{}_1K_1}{\rightleftharpoons}$$

$$\left[\underset{\text{2SIP}}{Sc^{3+}(OH_2)(OH_2)SO_4^{2-}}\right](aq) \overset{{}_2K_1}{\rightleftharpoons}$$

$$\left[\underset{\text{SIP}}{Sc^{3+}(OH_2)SO_4^{2-}}\right](aq) \overset{{}_3K_1}{\rightleftharpoons} \underset{\text{CIP}}{[ScSO_4]} + (aq) \quad (1)$$

The corresponding equilibrium constants for these steps can be written (ignoring activity coefficients)

$${}_1K_1 = [2SIP]/[Sc^{3+}][SO_4^{2-}]; \quad {}_2K_1 = [SIP]/[2SIP];$$
$${}_3K_1 = [CIP]/[SIP] \quad (2)$$

where the square brackets here denote concentrations, the subscript suffix to K defines the number of anionic ligands attached to the metal ion, the subscript prefix refers to the specific ion-pair formation step, and all species are taken to be aquated. Note that the symbols adopted here for the equilibrium constants in scheme 1 differ from those used in our previous studies.[38,39] This is to avoid confusion with the symbols commonly employed in inorganic solution chemistry to represent the stepwise addition of ligands to a metal ion.

Unfortunately, there are few techniques available that can distinguish the different ion-pair types. As discussed at length elsewhere,[40] thermodynamic and transport methods measure only the overall association (they make no distinction between complexes of the same stoichiometry but differing levels of hydration). On the other hand, the most popular spectroscopic methods (UV−vis, NMR, IR, and Raman) generally detect only inner-sphere complexes and thus provide an incomplete, and sometimes seriously misleading,[39,40] view of the species present. Attempts have been made over the years to get a more detailed picture of the species present in $Sc_2(SO_4)_3(aq)$ using ^{45}Sc NMR,[41,42] ion exchange,[25,26] and ultrasonic[43] techniques. The last especially is suitable, at least in principle, for quantifying stepwise equilibria such as those in scheme 1. However, the only

(22) Izatt, R. M.; Eatough, D.; Christensen, J. J.; Bartholomew, C. H. *J. Chem. Soc. A* **1969**, 47.
(23) Brown, P. L.; Sylva, R. N. *J. Chem. Res.* **1987**, *110*, 4.
(24) Brown, P. L.; Wanner, H. *Predicted Constants using the Unified Theory of Metal Ion Complexation*; NEA Report; OECD: Paris, 1987.
(25) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*, 2nd ed.; Chemical Society: London, 1964; Special Publication No. 17.
(26) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal-Ion Complexes*, Supplement; Chemical Society: London, 1971; Special Publication No. 25.
(27) Högfeldt, E. *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*; Pergamon: Oxford, UK, 1982.
(28) Li, J.-G.; Ikegami, T.; Mori, T.; Yajima, Y. *J. Am. Ceram. Soc.* **2003**, *86*, 1493.
(29) Li, J.-G.; Ikegami, T.; Mori, T.; Yajima, Y. *J. Am. Ceram. Soc.* **2004**, *87*, 1008.
(30) Meyer, R. J.; Wassjuchnow, A.; Drapier, N.; Bodlander, E. *Z. Anorg. Chem.* **1914**, *86*, 257.
(31) Brauner, B.; Svagr, E. *Collect. Czech. Chem. Commun.* **1932**, *4*, 49.
(32) Brauner, B.; Svagr, E. *Collect. Czech. Chem. Commun.* **1932**, *4*, 239.
(33) Ivanov-Emin, B. N.; Korotaeva, L. G.; Remizov, V. G.; Ezhov, A. I. *Russ. J. Inorg. Chem.* **1966**, *11*, 278.
(34) Knoche, W.; López-Quintela, M. A. *Thermochim. Acta* **1983**, *62*, 295.
(35) Marcus, Y. *Ion Properties*; Dekker: New York, 1997.
(36) Eigen, M.; Tamm, K. *Z. Elektrochem.* **1962**, *66*, 93.
(37) Eigen, M.; Tamm, K. *Z. Elektrochem.* **1962**, *66*, 107.
(38) Buchner, R.; Capewell, S. G.; Hefter, G.; May, P. M. *J. Phys. Chem. B* **1999**, *103*, 1185.
(39) Schrödle, S.; Rudolph, W. W.; Hefter, G.; Buchner, R. *Geochim. Cosmochim. Acta* **2007**, *71*, 5287.
(40) Hefter, G. T. *Pure Appl. Chem.* **2006**, *78*, 1571.
(41) Melson, G. A.; Olszanski, D. J.; Rahimi, A. K. *Spectrochim. Acta* **1977**, *33A*, 301.
(42) Haid, E.; Köhnlein, D.; Kössler, G.; Lutz, O.; Messner, W.; Mohn, K. R.; Nothaft, G.; van Rickelen, B.; Schich, W.; Steinhauser, N. *Z. Naturforsch.* **1982**, *38a*, 317.
(43) Bonsen, A.; Knoche, W.; Berger, W.; Giese, K.; Petrucci, S. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 678.

available ultrasonic study to date on the Sc^{3+}/SO_4^{2-} system[43] was restricted to low concentrations and thus only the 1:1 complexes of the Eigen mechanism (scheme 1) were detected.

Dielectric relaxation spectroscopy (DRS), which measures the complex dielectric response of a sample to an applied oscillating electric field as a function of the field frequency, is a relatively little-utilized but powerful probe for studying the interactions between ions in solution.[39,44] In addition to its broad applicability, because it responds to the square of the dipole moment, DRS has a unique sensitivity with respect to the various ion-pair types in the order 2SIP > SIP > CIP. This makes DRS particularly useful for the investigation of the species present in $Sc_2(SO_4)_3$(aq). The only previous DRS investigation of this system to our knowledge is that of Kaatze and Giese.[45] This pioneering work was successful in identifying the presence of contact-ion pair species but the instrumentation then available did not permit a quantitative analysis of the data, which were anyway limited to a single concentration.[45]

Advances in DRS technology since the study of Kaatze and Giese have resulted in major improvements in the accuracy, sensitivity, accessible frequency range, and ease of DRS measurements. Indeed, modern DRS has been used to good effect to quantify the chemical speciation in a number of electrolyte solutions, often providing important insights into the species present.[39,40,46] Accordingly, this paper presents a detailed investigation of $Sc_2(SO_4)_3$(aq) at 25 °C over as wide a range of solute concentrations as possible, using state-of-the-art instrumentation covering the frequency range $0.2 \leq \nu/GHz \leq 89$.

2. Experimental Section

Scandium sulfate was prepared from scandium oxide (99.95% Sc_2O_3; HEFA Rare Earth Canada, Richmond, Canada) by treatment with sulfuric acid (analytical grade; Ajax, Australia) as described in the literature.[47] Fine-grained crystals were obtained and recrystallized twice from water to remove excess sulfuric acid. Crystallization was carried out at ~75 °C by evaporation because of the strong negative temperature coefficient of the solubility.[48−51] A stock solution (~1 M, M = mol L^{-1}, pH 2.5) was prepared from the final product, passed through a 0.45 μm PTFE membrane filter, and analyzed (±0.2%) by complexometric titration against EDTA (BDH, U.K., volumetric standard) using xylenol orange indicator.[52] All samples for DRS were prepared by mass from stock solutions by dilution with ~0.005 M sulfuric acid to suppress hydrolysis.[21,31] Diluted solutions so prepared had a pH of between 2.0 and 2.5 and were stored for several days prior to measurement to ensure full equilibration.[53] Approximate speciation calculations (ignoring activity coefficients but assuming a value of the protonation constant of SO_4^{2-} appropriate to the ionic strength[54] and allowing for complex formation) indicate that the concentrations of hydrolyzed species[21] and HSO_4^- in the present sulfate-containing solutions were negligible. This is consistent with the work of Tateda,[55] who reported no Sc(III) hydrolysis in sulfate solutions up to pH 2.7, and with the ^{45}Sc NMR study of Melson et al.[41]

The insignificant concentrations of HSO_4^- (<2% of the total sulfate at pH $\geq$ 2.0) calculated for the present solutions is important because gas-phase HSO_4^- has a small dipole moment (probably made smaller in aqueous solution by the exchange of the proton among the four oxygen sites and with neighboring water molecules) and might otherwise contribute to the observed DR spectra. Likewise, Sc^{3+}/HSO_4^- complexes (which would have substantial dipole moments) are likely to be extremely weak, by analogy with other M^{n+}/HSO_4^- complexes.[25,26]

Solution densities were measured with a vibrating-tube densimeter (Sodev, Canada, Model 03D) and are accurate to ~0.05 kg m^{-3}. Dielectric spectra were recorded at (25 ± 0.02) °C, with a NIST-traceable accuracy of ±0.05 °C, using a vector network analyzer (VNA) reflectometer ($0.2 \leq \nu/GHz \leq 20$; Murdoch University) and two traveling wave interferometers (A-Band, $27 \leq \nu/GHz \leq 39$, E-Band, $60 \leq \nu/GHz \leq 89$; Regensburg University) as described previously.[56,57]

3. Data Processing

Two sets of spectra were obtained by VNA reflectometry using independent calibrations, with neat water,[58] air, and mercury as the dielectric references. High-frequency data ($\nu \geq 27$ GHz) were determined for all but some of the lowest concentrations. As found in previous studies,[38,39,46] the VNA and interferometric data could be combined seamlessly. Note that only the total loss $\eta''(\nu) = \varepsilon''(\nu) + \kappa/2\pi\nu\varepsilon_0$ (solution conductivity κ, vacuum permittivity ε_0) is measurable. While the ohmic contribution $\kappa/2\pi\nu\varepsilon_0$ can be obtained by conventional conductometric measurements it was instead treated as an adjustable parameter in the data-fitting procedure for reasons discussed elsewhere.[46] The ohmic contributions so estimated were subtracted from the total loss curves to yield the complex dielectric spectra, $\hat{\varepsilon}(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, shown in Figure 1. These were decomposed into individual Debye contributions. The details of this procedure are discussed elsewhere[38,39,59] so only a brief outline is given here.

In essence, the procedure comprises a fit of the complex permittivity data to a sum of peak-shape terms, F_j (eqs 3 and 4), resulting in a set of fit parameters (relaxation times, τ_j, amplitudes, $S_j = \varepsilon_j - \varepsilon_{j+1}$, and infinite-frequency permittivity, ε_∞) up to k, the total number of processes detected

(44) Chen, T.; Hefter, G.; Buchner, R. *J. Solution Chem.* **2005**, *34*, 1045.
(45) Kaatze, U.; Giese, K. *J. Mol. Liq.* **1987**, *36*, 15.
(46) Akilan, C.; Hefter, G.; Rohman, N.; Buchner, R. *J. Phys. Chem. B* **2006**, *110*, 14961.
(47) Trousil, Z. *Collect. Czech. Chem. Commun.* **1938**, *10*, 290.
(48) Mioduski, T. J. *Radioanal. Nucl. Chem. Lett.* **1992**, *165*, 9.
(49) Komissarova, L. N.; Shatskii, V. M.; Moiseichenko, G. I. *Zh. Neorg. Khim.* **1965**, *10*, 755.
(50) Komissarova, L. N.; Bashkov, B. I.; Shatskii, V. M. *Zh. Neorg. Khim.* **1970**, *15*, 2945.
(51) Komissarova, L. N.; Chuvaev, V. F.; Statskii, V. M.; Bashkov, B. I. *Zh. Neorg. Khim.* **1971**, *16*, 1258.
(52) Vogel, A. I. *A Text-Book of Quantitative Inorganic Analysis*, 3rd ed.; Longmans: London, 1961.
(53) Koshchei, E. V.; Stryapkov, A. V.; Makarov, G. V.; Podosenov, D. E.; Razdobreev, D. A. *Russ. J. Phys. Chem.* **1998**, *72*, 1670.
(54) Kratsis, S.; Hefter, G. T.; May, P. M.; Sipos, P. *Aust. J. Chem.* **2000**, *53*, 363.
(55) Tateda, A. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 165.
(56) Barthel, J.; Bachhuber, K.; Buchner, R.; Hetzenauer, H.; Kleebauer, M. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 853.
(57) Buchner, R.; Hefter, G. T.; May, P. M. *J. Phys. Chem. A* **1999**, *103*, 1.
(58) Schrödle, S. Ph.D. Thesis, Regensburg University, Regensburg, Germany, 2005.
(59) Buchner, R.; Chen, T.; Hefter, G. *J. Phys. Chem. B* **2004**, *108*, 2365.

$$\hat{\varepsilon}(\nu) = \sum_{j=1}^{k} S_j F_j(\nu) + \varepsilon_\infty \qquad (3)$$

where, if all processes are assumed to be of the Debye type

$$F_j(\nu) = F_j^D = (1 + i2\pi\nu\tau_j)^{-1} \qquad (4)$$

The identification of individual contributions to the $Sc_2(SO_4)_3$(aq) spectra is in some ways more obvious than for the recently studied $Al_2(SO_4)_3$(aq) system,[39] because of the presence of a very distinct low-frequency process in the present spectra. Using a preliminary fit with two Debye modes (and a small high-frequency contribution from the fast water process at $\tau = 0.4$ ps,[60] which was omitted for the spectra that were limited to VNA data, $\nu \leq 20$ GHz, alone), two additional terms were found to be necessary to describe the intermediate frequency region, corresponding to $k = 5$ (or $k = 4$ for those spectra limited to 20 GHz) in eq 3. Low variances of the fits were obtained over the whole concentration and frequency range studied (Table 1). Some typical decompositions of the loss component of the spectra, $\varepsilon''(\nu)$, are shown in Figure 2, together with the individual Debye contributions (S_j, τ_j; $j = 1$ to 5).

For comparison with literature data, the conductivity values obtained from the spectral fits were corrected for the additional conductivity caused by the presence of sulfuric acid (5.02×10^{-3} M) in the sample. A constant molar conductivity of $\Lambda_{H_2SO_4} = 0.050$ S m^2 mol^{-1} was estimated from published data[61,62] which should roughly correspond to the situation in the more dilute scandium sulfate solutions. The corrected conductivities were therefore calculated as $\kappa^* = \kappa - \Lambda_{H_2SO_4} c_{H_2SO_4}$. The molar conductivities ($\Lambda_{Sc_2(SO_4)_3} = \kappa^*/c$) so obtained continue the trend in the reported low-concentration ($c \leq 5$ mM) low-frequency conductivities[30−32] quite well (Figure 3).

4. Results and Discussion

Assignment of DR spectra for aqueous electrolyte solutions is more difficult than for most other types of spectroscopy because dielectric relaxation processes typically give rise to very broad spectral features, the dominance of the solvent contribution,[59,63] and the loss of spectral information at low frequencies due to the conductivity contribution at high solute concentrations (cf. section 3). Nevertheless, by studying the effects of solute concentration on the observed spectra over as wide a range as possible and by comparing the spectra with those of related electrolyte solutions and of pure water, realistic assignments can be made.

Remembering that symmetrical ions such as Sc^{3+}(aq) (but see below) and SO_4^{2-}(aq) are not dipolar and therefore are "DRS-silent", the observed spectra reflect only the presence of dipolar ion-aggregates (complexes, ion pairs) and the

(60) Fukasawa, T.; Sato, T.; Watanabe, J.; Hama, Y.; Kunz, W.; Buchner, R. *Phys. Rev. Lett.* **2005**, *95*, 197802.
(61) Sherrill, M. S.; Noyes, A. A. *J. Am. Chem. Soc.* **1926**, *48*, 1861.
(62) Wu, Y. C.; Feng, D. *J. Solution Chem.* **1995**, *24*, 133.
(63) Buchner, R. In *Novel Approaches to the Structure and Dynamics of Liquids*, NATO Science Series II, Vol. 133; Samios, J., Durov, V. A., Eds.; Kluwer: Dordrecht, The Netherlands, 2004.
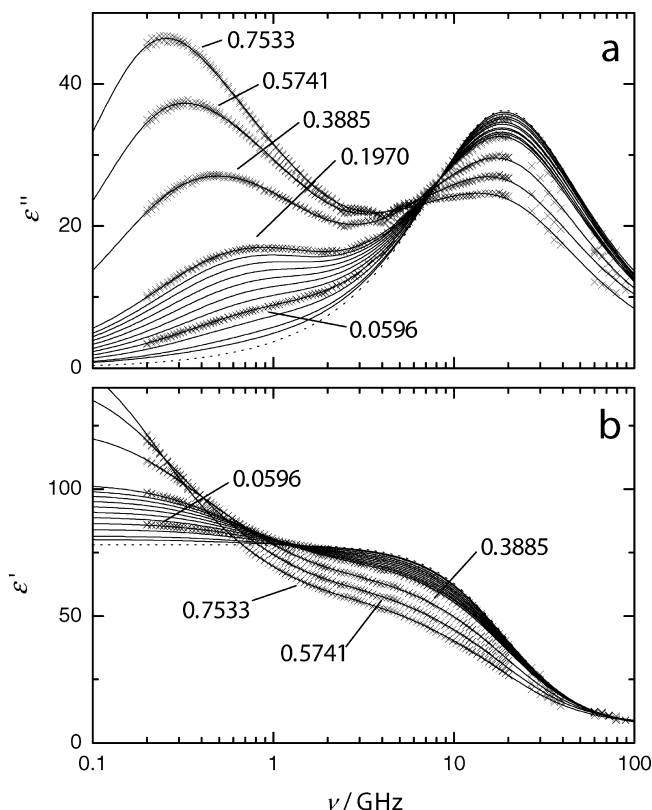
Figure 1. Dielectric loss (a, $\varepsilon''(\nu)$) and dispersion (b, $\varepsilon'(\nu)$) spectra of scandium sulfate solutions at 25 °C. The dotted line represents the spectrum of pure water.[58] Concentrations (in M) are indicated for selected spectra (see Table 1).

solvent (see also section 2 above). Providing their lifetime is longer than the DRS time scale, the former usually evidence themselves at lower frequencies, typically $\nu \lesssim 10$ GHz, in aqueous electrolyte solutions. As noted in the Introduction, the structure of Sc^{3+}(aq) is controversial. Symmetrical 6- or 8-coordinate ions will have a $\mu \approx 0$ while a 7-coordinate ion will have a dipole moment $\mu \lesssim 1.8$ D $\approx \mu(H_2O)$. This is an order of magnitude less than the dipole moments of the species detected (Table 2). Given that the intensity of DR modes is proportional to μ^2 (see eq 7) the contribution of such a species to the present spectra will therefore be negligible.

At higher frequencies, DR spectra are usually dominated by the solvent (water) contributions. Both solute and solvent relaxation processes are evident in the present spectra (Figures 1 and 2).

4.1. Solvent Response. There are two high-frequency bands in the present spectra (Table 1 and Figures 2, 4, and 5) with the major one (S_4, τ_4) centered at ~18 GHz and a minor one (S_5, τ_5) centered at ~400 GHz. On the basis of their amplitudes and relaxation times, both these modes are readily assigned to the solvent.[60] The major process corresponds to the cooperative relaxation of H-bonded bulk water molecules.[60] The minor process, which lies largely outside the range of, but still affects, the present spectra ($\nu \lesssim 90$ GHz), is generally thought to correspond to the rotation of "free" water molecules and the effects of dielectric friction.[60] Although this fast process makes only a small contribution to the present spectra (and essentially none to the spectra

Table 1. Concentrations, c, Densities, ρ, Conductivities, κ, Limiting Permittivities, ε_j, Relaxation Times, τ_j, and Variance of the Fits, σ^2, Obtained for $Sc_2(SO_4)_3$(aq) at 25 °C[a]

c	ρ	κ	ε_1	τ_1	ε_2	τ_2	ε_3	τ_3	ε_4	τ_4	ε_5	τ_5	ε_∞	$10^3\sigma^2$
0^b	997.047		78.4							8.32	5.87	0.3	3.48	48.5
$0.00997^{c,d}$	1000.68	0.380	80.2											
0.01993^d	1003.89	0.428	81.5	329	80.7	186	77.3	14.3	75.8	8.26			5.90	5.74
0.03981^d	1010.26	0.513	84.2	332	82.4	179	76.4	16.6	74.6	8.23			5.93	8.83
0.05964^d	1016.58	0.589	86.7	335	83.6	176	75.7	16.6	72.9	8.20			6.08	43.8
0.07943^d	1022.85	0.670	89.1	328	84.1	172	74.9	17.0	71.5	8.17			6.13	12.2
0.09916	1029.09	0.737	91.2	326	84.4	169	74.2	19.7	71.4	8.24	6.45	0.4^e	3.15	50.3
0.1188^d	1035.26	0.804	93.6	355	85.8	171	73.5	17.9	68.9	8.12			6.36	18.0
0.1385	1041.50	0.868	95.8	370	86.5	171	72.9	17.5	66.9	7.99	6.03	0.4^e	5.88	50.9
0.1581^d	1047.60	0.921	97.9	377	86.7	170	72.2	19.1	66.8	8.08			6.33	27.2
0.1776	1053.64	0.986	99.8	380	86.9	170	71.7	19.4	65.8	8.05	6.45	0.4^e	4.06	86.7
0.1971	1059.75	1.04	102	402	87.6	172	71.0	19.9	64.8	8.05	6.47	0.4^e	4.69	42.2
0.3885	1118.22	1.41	124	571	91.3	193	66.0	22.5	55.9	7.91	6.96	0.4^e	3.78	72.2
0.5741	1173.90	1.56	144	659	87.2	198	61.4	24.0	48.9	7.97	7.58	0.4^e	2.14	69.6
0.7534	1226.64	1.56	159	737	80.3	193	57.0	23.7	41.9	7.72	7.23	0.4^e	6.73	58.4
0.9205^f	1274.81													

[a] Units: c in M, ρ in kg m^{-3}, κ in S m^{-1}, τ_j in ps. [b] Neat H_2O.[58] [c] Fit did not converge. [d] VNA data only. [e] Fixed value. [f] No DRS data measured.
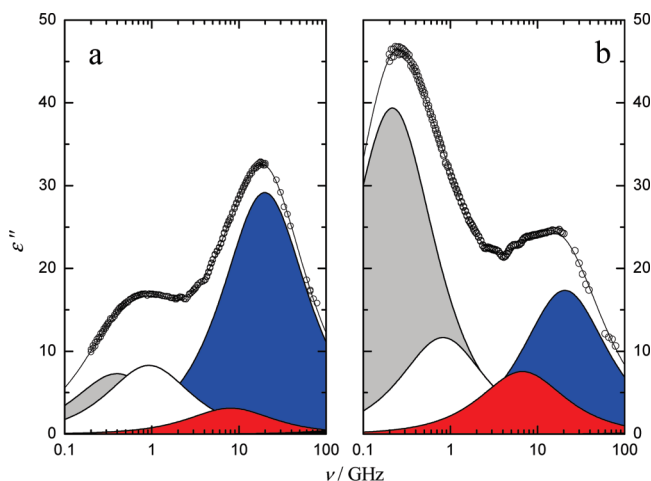

Figure 2. Fits (solid line) of dielectric loss spectra (a, 0.2 M; b, 0.8 M) of $Sc_2(SO_4)_3$(aq) by a superposition of five Debye terms. Contributions from the individual processes are also shown ($j = 1$ (gray), 2 (white), 3 (red), 4 (blue), 5 (black)). Note that contribution 5 is small and mostly outside the upper frequency limit of the present spectra; it is thus barely visible.
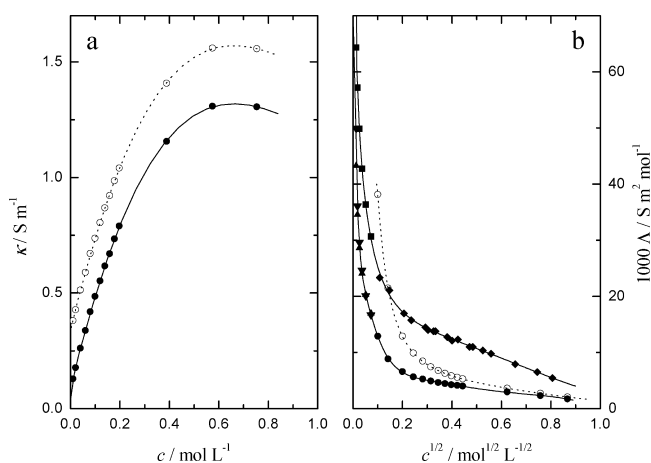

Figure 3. Conductivity, κ (a), and molar conductivity, Λ (b), of scandium sulfate (●, this study; ▲, ref ; ▼, ref 31) and aluminum sulfate (■, ref 74; ◆, ref 39) solutions at 25 °C. Open symbols represent the raw values, not corrected for the added H_2SO_4 contribution.

limited to $\nu < 20$ GHz), it was included for physical and mathematical (fitting) consistency.

Table 2. Half Axes, a,b,c Dipole Moments, μ, and Polarizabilities, α, of Proposed Associated Species and Water[a]

species	a	$b = c$	μ	α
2SIP	590	230	106.3	8.99
SIP	447.5	230	72.3	7.54
CIP	305	230	35.8	6.10
cis-[Sc(SO_4)_2]^-	382.9	383	33.0	11.57
$trans$-[Sc(SO_4)_2]^-	535	230	0	11.57
mer-[Sc(SO_4)_3]^{3-}	514.0	514.0	16.6	17.03
fac-[Sc(SO_4)_3]^{3-}	395.7	395.7	28.8	17.03
H_2O	142.5	142.5	1.834	1.444

[a] Units: a, b, c in pm; μ in D (1 D = 3.336×10^{-30} C m); α in $4\pi\varepsilon_0 \times 10^{-30}$ m^{-3}.
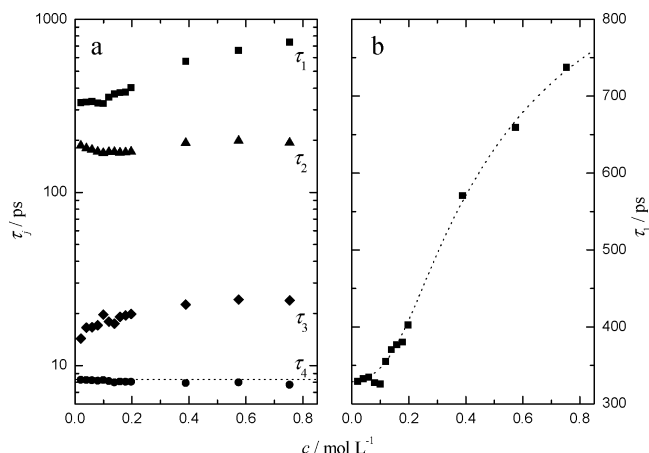
Figure 4. Relaxation times (a, τ_1 to τ_4; b, τ_1 only) derived from complex dielectric spectra of $Sc_2(SO_4)_3$(aq). The dotted line (a, τ_4) indicates the relaxation time of pure water.[58]

The virtual constancy of the dominant process relaxation time τ_4 is typical for aqueous electrolyte solutions and indicates that even up to quite high solute concentrations there is sufficient bulk water present in solution to display a relatively undisturbed H-bond network. As will be shown in section 4.3, quantitative information on ion hydration can be obtained from the solvent contribution to the spectra.

4.2. Solute Response. The much lower molar conductivities of $Sc_2(SO_4)_3$(aq) cf. $Al_2(SO_4)_3$(aq) indicate stronger overall complex formation in the former (Figure 3b). As noted in section 3, a total of three solute-related processes were required to account for the observed spectral features
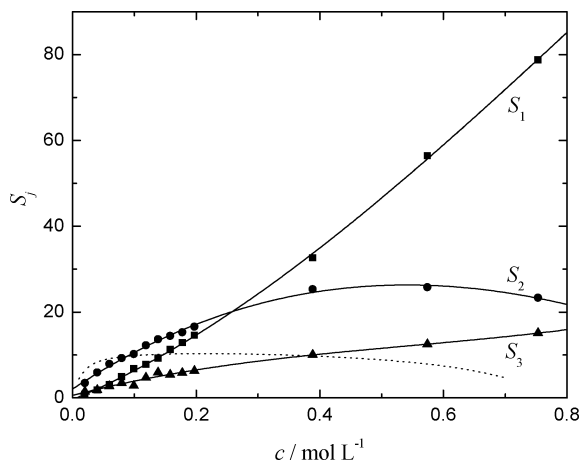
Figure 5. Relaxation amplitudes, S_j, for the solute-related species calculated from fits of the present spectra for $Sc_2(SO_4)_3(aq)$ ($\blacksquare$, S_1; $\bullet$, S_2; $\blacktriangle$, S_3). The dotted line represents S_1 for $Al_2(SO_4)_3(aq)$.[39]

at lower frequencies (Figures 1 and 2) as a function of solute concentration for $Sc_2(SO_4)_3(aq)$. In aqueous solutions of other higher-valent metal sulfates,[59] including $Al_2(SO_4)_3(aq)$,[39] the three lower frequency solute-related processes have been attributed to the presence of the various types of 1:1 ion pairs shown in scheme 1. Because of their relative sizes (larger species rotate more slowly), these IPs invariably appear in the DR spectrum in the order $\nu_{2SIP} < \nu_{SIP} < \nu_{CIP}$.

However, there is a marked difference between the present DR spectra for $Sc_2(SO_4)_3(aq)$ and those of $Al_2(SO_4)_3(aq)$ with regard to the lowest frequency process (S_1, τ_1). In Al_2-$(SO_4)_3(aq)$,[39] and in a number of other metal sulfate solutions,[44,46,59,64] the amplitude (intensity) of the lowest frequency process passes through a maximum as a function of c (Figure 5, dotted line). This is consistent with this process arising from the presence of 2SIPs and the existence of the stepwise equilibria in scheme 1. In contrast, for $Sc_2(SO_4)_3(aq)$, the amplitude (S_1) of the process centered at ~350 MHz shows a dramatic increase with increasing c over the entire concentration range studied (Figure 5), ultimately even exceeding that of the solvent (Figure 2). Furthermore, this process produces an extraordinary increase in the relative permittivity (dielectric constant) of the solutions, which rises to more than double that of neat water. These observations cannot be explained in terms of 2SIPs alone and will be further considered below.

The other two solute-related processes (S_2, τ_2 and S_3, τ_3) largely follow the pattern observed for other high-valent metal sulfate solutions.[39,44,46,59,64] Thus, the second process (amplitude S_2) shows a maximum at $c \approx 0.5$ M, while the contribution of S_3 increases gradually over the whole concentration range studied (Figure 5). Furthermore, the relaxation times τ_2 and τ_3 are very similar to the values recently reported for $Al_2(SO_4)_3(aq)$.[39] On the basis of all these observations, it is reasonable to assign these two processes

to the presence of SIP and CIP species of 1:1 stoichiometry (scheme 1) respectively.

Returning now to the lowest frequency process (S_1, τ_1), both the relaxation time (Figure 4) and especially the amplitude (Figure 5) show a dependence on solute concentration that differs starkly from those of other metal sulfate solutions,[59] including $Al_2(SO_4)_3(aq)$.[39] Given the general validity of the Eigen mechanism, scheme 1, for the association of highly charged ions in aqueous solutions, it is probable that 2SIPs are present at low c. Evidence for this comes from the small plateau, possibly even with a slight maximum, in τ_1 at $c \lesssim 0.1$ M (Figure 4b). However, the dramatic increase of S_1 at higher c (Figure 5) precludes process 1 from being solely ascribed to the presence of 2SIPs.

Superficially similar increases in S_1 (and τ_1) have been observed for some,[44,59] but not all,[46] $MSO_4(aq)$ solutions. In these cases, S_1 also passed through a maximum at low c (as expected for 2SIPs, scheme 1) but then increased again at higher c. This second increase in S_1 was assigned to the formation of "triple ions" $[M_2SO_4]^{2+}(aq)$ and was confirmed, at least for $[Mg_2SO_4]^{2+}(aq)$, by Raman spectroscopy.[44,59] Similar but less pronounced effects were also observed for τ_1. However, the change in S_1 was considerably smaller than that observed in the present spectra. Furthermore, a cationic triple ion for $Sc_2(SO_4)_3(aq)$ is unlikely on charge grounds since the association:

$$[ScSO_4]^+(aq) + Sc^{3+}(aq) \rightleftharpoons [Sc_2SO_4]^{4+}(aq) \qquad (5)$$
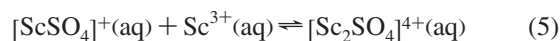
should be negligible, and it is notable that no such species was detected in $Al_2(SO_4)_3(aq)$.[39] Note too that, while the analogous anionic "triple ion" $[Sc(SO_4)_2]^-(aq)$ may well form, as does $[Al(SO_4)_2]^-(aq)$,[39] steric considerations suggest that it would probably have a (pseudo) trans geometry. With this symmetry, such a species would have a near-zero dipole moment and thus would not be detected by DRS (similar conclusions have been reached for other metal sulfate solutions).[39,59] It follows that the anomalous changes in S_1 and τ_1 must be due to the presence of one or more species other than 2SIPs and "triple ions".

To help determine the nature of such species, it is instructive to consider what is known about Sc^{3+}/SO_4^{2-} species in the solid state and from other techniques in solution. Various mixed solid sulfates of the type A[Sc-$(SO_4)_2$] and $A_3[Sc(SO_4)_3]$ (A = Na, K, Rb, Cs, NH_4) have been structurally characterized[33,65,66] and it is possibly significant that the structural unit $[Sc(SO_4)_3]^{3-}$ has been found to persist in hydrated salts such as $Na_3[Sc(SO_4)_3] \cdot 5H_2O$[66] and even $Sc_2(SO_4)_3 \cdot 5H_2O$.[67] On the other hand, as already noted in the Introduction, little is known about the nature of the species present in aqueous Sc^{3+}/SO_4^{2-} solutions. The low molar conductivity (Figure 3) of $Sc_2(SO_4)_3(aq)$ has, in combination with ion migration data, been attributed to the formation of $[Sc(SO_4)_3]^{3-}(aq)$.[30−33] Some ion exchange
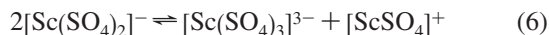
(64) Akilan, C.; Rohman, N.; Hefter, G.; Buchner, R. *ChemPhysChem* **2006**, 7, 2319.

(65) Komissarova, L. N.; Bashkov, B. I.; Shatskii, V. M. *Russ. J. Inorg. Chem.* **1970**, *15*, 773.

(66) Sizova, R. G.; Voronkov, A. A.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1974**, *1974*, 1073.

(67) Ilyukhin, A. B.; Petrosyants, S. P. *Zh. Neorg. Khim.* **2004**, *49*, 1338.

studies[25,26] have suggested both [Sc(SO$_4$)$_2$]$^-$(aq) and [Sc-(SO$_4$)$_3$]$^{3-}$(aq) exist, while other studies report only [ScSO$_4$$^+$]-(aq) and [Sc(SO$_4$)$_2$]$^-$(aq). Ivanov-Emin et al.[33] claim their conductivity measurements indicate that the latter disproportionates in solution

$$2[\text{Sc(SO}_4)_2]^- \rightleftharpoons [\text{Sc(SO}_4)_3]^{3-} + [\text{ScSO}_4]^+ \qquad (6)$$

Since *trans*-[Sc(SO$_4$)$_2$(OH$_2$)$_4$]$^-$(aq) will not be detected by DRS (see above), it seems reasonable to assume that, apart from *cis*-[Sc(SO$_4$)$_2$(OH$_2$)$_4$]$^-$(aq), the only other species contributing to process 1 is [Sc(SO$_4$)$_3$]$^{3-}$(aq). No information could be found on the structure of this species in solution but, assuming monodentate sulfate and an octahedrally coordinated [Sc(SO$_4$)$_3$(OH$_2$)$_3$]$^{3-}$ species, both *mer* and *fac* isomers are possible. The overall sizes of these two species are similar (Table 1) and thus they cannot easily be distinguished on the basis of their dielectric relaxation times. However, the relatively small dipole moment of *mer*-[Sc(SO$_4$)$_3$(OH$_2$)$_3$]$^{3-}$ requires physically impossible SO$_4$$^{2-}$ concentrations (greater than the total present) to account for the observed DR spectra, so it can ruled out as a major constituent.

From the foregoing discussion, the most likely species contributing to process 1 are therefore *fac*-[Sc(SO$_4$)$_3$(OH$_2$)$_3$]$^{3-}$ and/or *cis*-[Sc(SO$_4$)$_2$(OH$_2$)$_4$]$^-$, hereafter abbreviated as f3C and c2C, respectively. It is emphasized that using the present DRS data alone, it is not possible to unequivocally rule out the existence of small amounts of other species such as polynuclear complexes, particularly in the more concentrated solutions. Raman spectroscopy, for example, indicates[15,68] that the symmetry of SO$_4$$^{2-}$ in ∼1 M Sc$_2$(SO$_4$)$_3$(aq) may be lower than the C_{3v} expected for monodentate coordination, although no detailed assignment was given. To simplify the quantitative analysis of the present data, the small contribution of 2SIPs at low c will be ignored (see also below) and it will be assumed that only one species (c2C or f3C) contributes significantly to process 1.

Relaxation amplitudes (S_j) can be related to species concentrations (c_j) in solution via the Cavell equation:[69]

$$S_j = \frac{\varepsilon}{\varepsilon + A_j(1-\varepsilon)} \frac{N_A}{3k_B T \varepsilon_0} \frac{g_j \mu_j^2}{(1-f_j \alpha_j)^2} c_j \qquad (7)$$

where $\varepsilon = \varepsilon'(\nu \rightarrow 0)$ is the static solution permittivity, N_A and k_B are respectively the Avogadro and Boltzmann constants, g_j is the Kirkwood orientational correlation coefficient, and μ_j and α_j are the dipole moment and polarizability of the relaxing species. The latter two quantities were derived for each complex from the ionic values tabulated by Marcus.[35] Dipole moments for charged particles were calculated using the center of mass as the reference point and it was assumed that there was no orientational correlation of the dipolar complexes ($g_j = 1$). The geometric factors f_j and A_j for the relaxing species were calculated as described
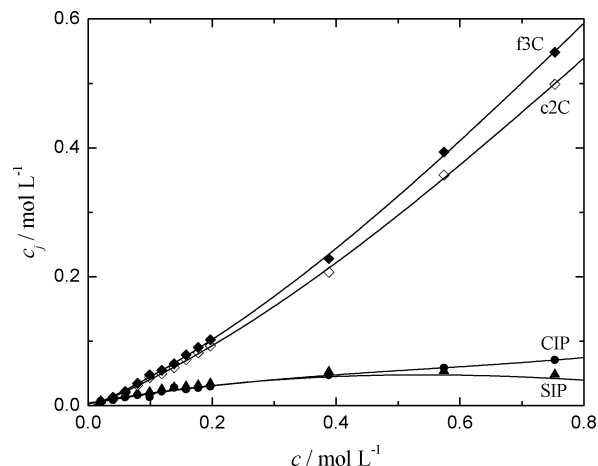
(68) Strauch, B.; Kommissarova, L. N. *Collect. Czech. Chem. Commun.* **1967**, *32*, 1484.
(69) Barthel, J.; Hetzenauer, H.; Buchner, R. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 1424.

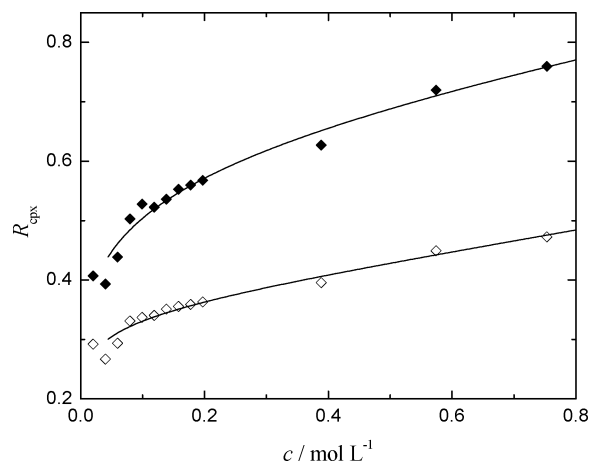**Figure 6.** Concentrations of complexes formed in Sc$_2$(SO$_4$)$_3$(aq) as derived from the present dielectric spectra.

Figure 7. Ratio of bound (inner-sphere complexed) sulfate to total sulfate, R_{cpx}, in Sc$_2$(SO$_4$)$_3$(aq) assuming process 1 is due to *fac*-[Sc(SO$_4$)$_3$]$^{3-}$ (♦) or *cis*-[Sc(SO$_4$)$_2$]$^-$ (◊).

elsewhere[69] assuming the species were ellipsoids (for 1:1 associates) or spheres (for 1:2 and 1:3 complexes). The concentrations of the most likely species as discussed above: [ScSO$_4$]$^+$(aq) (both SIP and CIP forms) and the inner sphere complexes c2C and f3C, were obtained via eq 7 and are shown in Figure 6. As expected from Figure 2, the higher order complexes c2C and/or f3C, responsible for process 1, dominate the speciation at higher solute concentrations.

Because of the similarity of their molecular parameters (Table 2), it is difficult to decide which of c2C and f3C is the major species producing process 1 using the DRS data alone. Fortunately, complexes of different stoichiometry affect the concentration of free sulfate differently. This effect can be expressed conveniently as the ratio of complex bound to total sulfate, R_{cpx}, which is plotted in Figure 7 as a function of the solute concentration. This ratio can also be probed by Raman spectroscopy, providing the complexes are inner sphere.[40] The present DRS data suggest that both c2C and f3C are inner-sphere species (solvent-separated species would be larger and hence have longer relaxation times) so it is valid to compare the Raman and DRS data. Rudolph and Pye[15] have reported, by Raman spectroscopy, 80% complexation of sulfate for a 1.0 M solution of Sc$_2$(SO$_4$)$_3$(aq). This is in excellent agreement with

the (extrapolated) DRS value if f3C is assumed to be responsible for process 1 but very much higher than that predicted if only c2C were present (Figure 7).

Thus, comparison of the DRS and Raman data suggests that the very large amplitude of process 1 at higher c is mostly due to fac-$[Sc(SO_4)_3(OH_2)_3]^{3-}$(aq). Some contribution from c2C may also occur but to prove this would require further investigation using techniques that are more species-selective than DRS. As already noted, and by analogy with $Al_2(SO_4)_3$(aq),[39] a minor contribution to process 1 from 2SIPs almost certainly also occurs at low c. However, this contribution must be small because S_1 is rather low at $c <$ 0.15 M. The small value of S_1 at low c makes separation of the naturally broad DR modes particularly difficult, as has been noted for related systems.[46,64] Accordingly, it was not possible to evaluate quantitatively the extent of formation of 2SIPs in $Sc_2(SO_4)_3$(aq).

4.3. Ion Hydration. Further information on the nature of the species formed can be inferred from the effective hydration numbers derived from the quantitative analysis of the solvent process (S_4). Details of the underlying theory have been discussed fully elsewhere.[39,63] In short, the solvent amplitude S_S is obtained from S_4 and the high-frequency limit of dielectric relaxation ε_∞, with $S_S(c) = S_4(c) - \varepsilon_\infty(c)$.[39] Note that for this calculation a constant value of $\varepsilon_\infty(0) = 3.48$[58] which is based on extensive high-frequency measurements of pure water was used for $\varepsilon_\infty(c)$ rather than the fit values shown in Table 1. This is because the current spectra were limited to $\nu \leq 89$ GHz which does not allow a sufficiently accurate determination of $\varepsilon_\infty(c)$[39] The equilibrium amplitude S_S^{eq} is obtained by correcting S_S for kinetic depolarization (due to the movement of ions in the field) assuming slip hydrodynamic boundary conditions.[59] The hydration of the solute can then be quantified from the difference of the analytical water concentration of the sample (c_S) and the apparent concentration of free water, c_S^{ap}.[59]

$$c_S^{ap}(c) = \frac{S_S^{eq}(c)}{S_S(0)} \frac{2\varepsilon(c)+1}{\varepsilon(c)} \frac{\varepsilon(0)}{2\varepsilon(0)+1} c_S(0) \qquad (8)$$

The average numbers of water molecules present in the hydration shells of the ions are referred to as "irrotationally bound" and can be expressed in terms of an effective hydration number, Z_{ib}.

$$Z_{ib} = [c_S - c_S^{ap}(c)]/c \qquad (9)$$

It should be noted that Z_{ib} is not necessarily identical to the sum of the (primary) coordination numbers of the ions present since it is a measure of all the water molecules that are effectively immobilized on the DRS time scale.[38,59]

The values of Z_{ib} for the free sulfate ion as a function of concentration have been established by DRS measurements on Na_2SO_4(aq).[38] These data can be used to determine the hydration of the other ions present in $Sc_2(SO_4)_3$(aq) by assuming that the ionic values are additive

$$Z_{ib}(Sc_2(SO_4)_3) = 2Z_{ib}(Sc^{3+}) + 3Z_{ib}(SO_4^{2-}) \qquad (10)$$

Up to moderate concentrations ($c \lesssim 0.2$ M), $Z_{ib}(Sc^{3+})$ is quite large (Figure 8), as would be expected for a highly

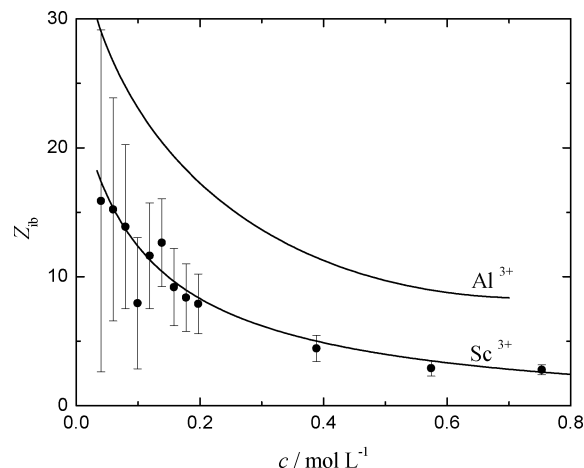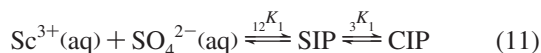**Figure 8.** Apparent solvation numbers of Sc^{3+} (present work) and Al^{3+} (ref.[39]) in $M_2(SO_4)_3$(aq) as a function of c. Calculated from eq 10 using literature values[38] for $Z_{ib}(SO_4^{2-})$.

charged cation, but it is significantly less than $Z_{ib}(Al^{3+})$.[39] At higher c, $Z_{ib}(Sc^{3+})$ decreases considerably. Studies on other highly charged ions in aqueous solutions[39,44] have shown that, in addition to their primary hydration shell, such ions often have a significant second[44,46,59] (or possibly even more extended)[39] solvation sheath. At low concentrations ($c \lesssim 0.15$ M, $I \lesssim 2.5$ M) this appears to be true for Sc^{3+}(aq). While some decrease in Z_{ib} with increasing c is observed for most cations in aqueous solution, the decline for $Z_{ib}(Sc^{3+})$ is large in relative terms, from $\sim$18 at infinite dilution to $\sim$3 at high c (Figure 8). Both these observations are consistent with (but do not prove) the formation of a dominant charge-delocalized (and thus relatively weakly hydrated outside its primary coordination shell) $[Sc(SO_4)_3(OH_2)_3]^{3-}$ species. Of course it must follow from mass- and charge-balance considerations that in solutions where $Sc(SO_4)_3^{3-}$ predominates there must be appropriate concentrations of $ScSO_4^+$ and Sc^{3+} also present. Note that the predominance of $Sc(SO_4)_3^{3-}$ is qualitatively consistent with the notion[33] that $Sc(SO_4)_2^-$ is unstable. Such effects are not unknown in inorganic chemistry, e.g., "AgCN" is in fact $Ag^+[Ag(CN)_2^-]$ and the species $AgCN^0$(aq) does not appear to exist.
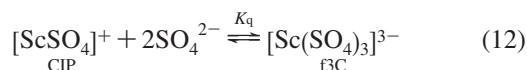
4.4. Formation Constants. As discussed in section 4.2, apart from a small contribution at $c \lesssim 0.1$ M attributable to 2SIPs, only three solute species (1:1 SIPs, 1:1 CIPs, and f3C) are required to account for the observed DR spectra for $Sc_2(SO_4)_3$(aq). To derive the corresponding formation constants, it will be assumed that only the latter three species exist. It follows therefore that the values of all the formation constants presented below should be considered as indicative only. Given the assumptions made in deriving them (section 4.2) and the modest accuracy of current DRS measurements, the true errors may be higher.

As the concentration of 2SIPs is low compared with all other species at most of the solute concentrations studied, an equilibrium constant $_{12}K_1$ ($=_1K_1 \times _2K_1$) will be used to describe the first observable association step. Thus scheme 1 is now truncated to

$$\text{Sc}^{3+}(\text{aq}) + \text{SO}_4{}^{2-}(\text{aq}) \underset{}{\overset{{}_{12}K_1}{\rightleftharpoons}} \text{SIP} \overset{{}_{3}K_1}{\rightleftharpoons} \text{CIP} \qquad (11)$$

The overall association constant K_A for the formation of the 1:1 species (as would for example be determined by thermodynamic or transport methods) is then given by $K_A = {}_{12}K_1 + {}_{12}K_1 \times {}_{3}K_1$.

To quantify the formation of f3C in thermodynamic terms, it will be assumed for convenience that it is formed via the following equilibrium
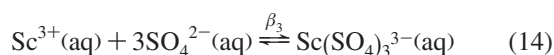
$$\underset{\text{CIP}}{[\text{ScSO}_4]^+} + 2\text{SO}_4{}^{2-} \overset{K_q}{\rightleftharpoons} \underset{\text{f3C}}{[\text{Sc}(\text{SO}_4)_3]^{3-}} \qquad (12)$$

Application of eq 7 to the spectra, assuming only these complexes are present, produces the K values summarized in Table 3 and shown in Figure 9 as functions of c. Clearly, K_q follows the trend of K_A but is about 2 orders of magnitude larger, reflecting the dominance of the higher order complex (f3C) at higher c. Within its estimated error, the stepwise formation constant for the 1:1 CIP ($_3K_1$, scheme 11) is almost independent of c (or I) as would be expected for an equilibrium that involves only loss of a solvent molecule.

For convenience, the overall equilibrium constant for the 1:1 complex was extrapolated to infinite dilution using an extended Guggenheim-type equation:[70]

$$\log K_A = \log K_A^\circ - \frac{2A_{DH}|z_+z_-|\sqrt{I}}{1+\sqrt{I}} + B_K I + C_K I^{3/2} \qquad (13)$$

where K_A° is the standard state (infinite dilution) value of the overall formation constant, A_{DH} is the Debye–Hückel constant for activity coefficients,[71] and B_K and C_K are adjustable parameters. Stoichiometric values of $I = 15c$ were used throughout (i.e., the ionic strength was not corrected for ion association). This is sufficient for both interpolation and extrapolation purposes, since the error in using I_{stoich} rather than I_{corr} is readily absorbed into the empirical parameters B_K and C_K, while having little effect on $\log K_A^\circ$. From the data given in Table 3, a value of $\log K_A^\circ(\text{ScSO}_4{}^+) = 3.52 \pm 0.04$ was obtained, with $B_K = 0.258 \pm 0.034$ and $C_K = -0.060 \pm 0.010$. This result is in reasonable agreement with the value of $\log K_A^\circ = 4.04$ obtained by Izatt et al.[22] using calorimetry. Other reported values of K_A[25-27] are not directly comparable because of the differences in the ionic medium but are broadly compatible with the present value. Application of eq 13 to the K_q data in Table 3 gave $\log K_q^\circ = 5.23 \pm 0.08$, with $B_K = 0.251 \pm 0.066$ and $C_K = -0.050 \pm 0.019$. This in turn gives an estimate of $\log(\beta_3^\circ = K_q^\circ K_A^\circ) = 8.9 \pm 0.1$ for the equilibrium

$$\text{Sc}^{3+}(\text{aq}) + 3\text{SO}_4{}^{2-}(\text{aq}) \overset{\beta_3}{\rightleftharpoons} \text{Sc}(\text{SO}_4)_3{}^{3-}(\text{aq}) \qquad (14)$$

It is emphasized that these numbers are included only as an indication: they need to be considered with caution. Direct

(70) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1970.
(71) Archer, D. G.; Wang, P. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371.

Table 3. Concentrations, c, Stoichiometric Ionic Strength, I, and Equilibrium Constants, K, for $\text{Sc}_2(\text{SO}_4)_3(\text{aq})$ at 25 °C[a]

c	I	$_{12}K_1$	$_{3}K_1$	K_A	K_q
0.0199	0.2989	12.7	0.971	25.0	1042
0.0398	0.5971	4.50	0.705	7.67	406
0.0596	0.8946	2.89	0.784	5.16	240
0.0794	1.1914	2.19	0.845	4.04	215
0.0992	1.4874	1.54	0.631	2.51	251
0.1188	1.7826	1.30	0.867	2.43	118
0.1385	2.0772	1.11	0.983	2.21	86.2
0.1580	2.3707	0.912	0.843	1.68	93.7
0.1776	2.6636	0.766	0.860	1.42	80.3
0.1970	2.9557	0.685	0.854	1.27	70.8
0.3885	5.8273	0.307	0.897	0.583	33.1
0.5741	8.6108	0.195	1.09	0.408	36.6
0.7533	11.299	0.117	1.46	0.288	31.7

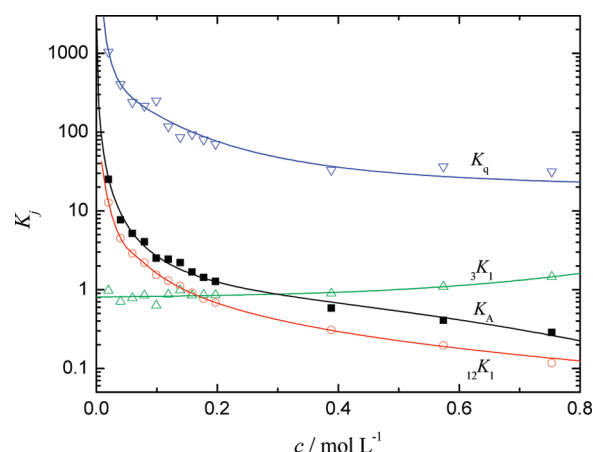[a] Units: c, I in M; $_{12}K_1$, K_A in M^{-1}; K_q in M^{-2}.

Figure 9. Equilibrium constants for the formation of complexes in $\text{Sc}_2(\text{SO}_4)_3(\text{aq})$ at 25 °C as determined by the present DRS study: 1:1 SIPs ($_{12}K_1$, $\bigcirc$); 1:1 CIPs ($_3K_1$, $\triangle$); [ScSO$_4$]$^+$(aq) (K_A, $\blacksquare$); and *fac*-[Sc(SO$_4$)$_3$]$^{3-}$(aq) (K_q, $\triangledown$). See text for definitions.

comparisons of the other constants listed in Table 3 with literature data are also not possible because they do not refer to the same equilibrium reactions. For these reasons, no standard values for $_{12}K_1$ or $_3K_1$ were derived.

Regardless of the probable uncertainties, the present result of $\log K_A^\circ(\text{ScSO}_4{}^+) = 3.52$ is only slightly lower than the corresponding value of $\log K_A^\circ(\text{AlSO}_4{}^+) = 3.84$[72] or 3.72.[39] A much larger difference would be expected from Coulombic considerations. The plot of Izatt et al. (Figure 1 in ref 22) suggests that it is the [ScSO$_4$]$^+$(aq) complex that is stronger than expected. Even more remarkable is the strength of the formation of [Sc(SO$_4$)$_3$]$^{3-}$(aq). In the Al^{3+}/SO$_4{}^{2-}$ system, for example, the formation of [Al(SO$_4$)$_2$]$^-$(aq) is relatively weak[39] and [Al(SO$_4$)$_3$]$^{3-}$(aq) has not been reported to date even at high [SO$_4{}^{2-}$]/[Al^{3+}] ratios.[72]

As noted in the Introduction, the strength of the complexes formed by Sc^{3+}(aq) with both fluoride[20] and hydroxide[21] lie far above the rather good trend lines established using simple electrostatic correlations for the stability constants of these ligands with other metal ions, including Al^{3+}(aq), Y^{3+}(aq), and La^{3+}(aq). Why Sc^{3+}(aq) should display such different behavior from its congeners Y^{3+}(aq) and La^{3+}(aq) is not immediately obvious. Given that ion hydration and complex

(72) Xiao, C.; Wesolowski, D. J.; Palmer, D. A. *Environ. Sci. Technol.* **2002**, *36*, 166.

formation are to some extent competitive processes, this might be related to differences in hydration of these ions. However, while the structure of Sc^{3+}(aq) is undoubtedly complicated[18] its hydration energy is not abnormal when compared with those of other ions.[73] The unusual behavior of Sc^{3+} in solution clearly warrants more detailed investigation, especially using techniques, such as NMR and Raman spectroscopies, that are more species-selective.

5. Concluding Remarks

The present DRS investigation has provided important insights into the nature of the complexes formed in aqueous solutions of $Sc_2(SO_4)_3$. Structures of the three major species present have been proposed and their formation constants quantified, although minor amounts of other species may also exist. Unlike Al^{3+}(aq) with which it has often been compared, Sc^{3+}(aq) has a pronounced tendency to form stable higher-order-inner sphere complexes with sulfate. This emphasizes that there are limits to the often-invoked[8,9] similarities between the aqueous solution chemistry of these two ions.

(73) Phillips, C. S. G.; Williams, R. J. P. *Inorganic Chemistry*; Oxford University Press: London, 1965; Vol. *1*, p 162.
(74) Walden, P. *Z. Phys. Chem.* **1887**, *1*, 529.