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Geochimica et Cosmochimica Acta 71 (2007) 5287–5300

Geochimica et Cosmochimica Acta

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Ion association and hydration in 3:2 electrolyte solutions by dielectric spectroscopy: Aluminum sulfate

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Received 13 March 2007; accepted in revised form 1 August 2007; available online 21 September 2007

Abstract

Broadband dielectric measurements utilizing state-of-the-art coaxial reflectometry and traveling-wave interferometry have been made on aqueous solutions of the 3:2 electrolyte aluminum sulfate at 25 °C over the frequency range $0.2 \leqslant \nu\,(\mathrm{GHz}) \leqslant 89$ and at total solute concentrations $0.012 \leqslant c\,(\mathrm{M}) \leqslant 0.65$. Detailed analysis of the solute contribution to the dielectric spectra revealed the simultaneous presence of double solvent-separated (2SIP), solvent-shared (SIP) and contact (CIP) ion pairs. Concentrations of the various ion-pair types and the equilibrium constants for their formation were determined using calculated dipole moments and other relevant quantities. The 2SIPs and SIPs were found to persist down to low concentrations in this notionally strong electrolyte. Good agreement was found with earlier Raman and NMR studies for CIP concentrations and with thermodynamic determinations of the overall ion association constant. In contrast to divalent metal sulfate solutions, both SIPs and, to a lesser extent, 2SIPs remain present at quite high $Al_2(SO_4)_3$(aq) concentrations. The persistence of SIPs and 2SIPs was consistent with the effective hydration numbers obtained from an analysis of the cooperative H-bond relaxation mode of bulk water in the solutions. This analysis indicated that the hydration of Al^{3+} ions is extremely strong, with significant effects on the dielectric relaxation timescale even beyond the second hydration shell, at least in dilute solutions.

1. INTRODUCTION

Since aluminum is one of the most common elements in the lithosphere the aqueous chemistry of its salts is of considerable importance in environmental science, geochemistry and water treatment. One of the most important of these salts is aluminum sulfate, significant concentrations of which can be found in acid mine drainage, some natural thermal waters (Zotov, 1971) and, as a result of the weathering of alumino-silicates in acidic soils, in many streams (Hartikainen and Yli-Halla, 1986; Åström and Björklund, 1995). Furthermore, hygroscopic aerosol particles in the atmosphere, which can adversely affect air quality, may contain metal sulfates at near-saturation concentrations (Zhang and Chan, 2000).

While there is extensive knowledge about the hydrolytic behavior of Al^{3+}(aq), and its ability to form complexes with a wide variety of ligands, relatively little is known about even the most simple of its salts. In particular, the properties of solutions of 3:2 electrolytes such as aluminum sulfate have in general been poorly investigated compared with other electrolyte types (Robinson and Stokes, 1970; Barthel et al., 1998). This is due mostly to practical considerations such as the tendency of these salts to undergo hydrolysis, which renders study of solutions of the pure electrolyte difficult, or sometimes even impossible. However, knowledge of the behavior of 3:2 (and other highly charged) electrolytes is important as they provide a stern assessment of the theories and models of electrolyte solutions that have mostly been applied to lower-charged salts. For example,

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doi:10.1016/j.gca.2007.08.026

the theoretical Debye–Hückel slope for the activity or osmotic coefficients of a 3:2 electrolyte is *six* times that of a 1:1 electrolyte under identical conditions; the ionic strength of such a salt is *fifteen* times that of a 1:1 electrolyte at the same concentration.

A more profound difference between the behavior of 3:2 and 1:1 electrolytes in aqueous solutions is that the former are strongly affected, perhaps dominated, by their tendency towards ion association. This is true even in dilute solutions of salts that might notionally be considered 'strong' electrolytes (Marcus and Hefter, 2006). The origin of this association is the large coulombic attraction of the ions, which is only partially attenuated even in strongly solvating and/or high dielectric constant solvents like water. Any serious account of the behavior of 3:2 electrolytes in aqueous solution therefore requires a detailed understanding of the nature of their ion association.

The study of association in aqueous solutions of 3:2 electrolytes, M_2L_3(aq), which in thermodynamic terms can be represented (ignoring the possibility of 'polynuclear' complexes):

$$M^{3+}(aq) + zL^{2-}(aq) \rightleftharpoons ML_z^{(3-2z)}(aq) \qquad \text{(I)}$$

is more complicated than for symmetrical electrolytes. In addition to the practical problems already alluded to, there are two general difficulties. First, the strong attraction between the ions often results in the formation of 'higher order' associates ($z > 1$) and, second, the 1–1 ion pairs ($z = 1$) that are formed are charged rather than neutral.

Because both of the ions of a typical 3:2 electrolyte are very strongly solvated (e.g., the 'absolute' Gibbs energies of hydration for Al^{3+} and $SO_4{}^{2-}$ are −4531 and −1090 kJ/mol, respectively, cf. −375 and −347 kJ/mol for Na^+ and Cl^-, respectively) (Marcus, 1985) it is probable that they associate via the well-known Eigen mechanism (Eigen and Tamm, 1962):

$$M^{3+} + L^{2-} \overset{K_1}{\rightleftharpoons} \underset{\text{2SIP}}{[M\ S_2\ L]^+} \overset{K_2}{\rightleftharpoons} \underset{\text{SIP}}{[M\ S\ L]^+} \overset{K_3}{\rightleftharpoons} \underset{\text{CIP}}{[M\ L]^+} \qquad \text{(II)}$$

where all species are taken to be hydrated and S represents specific oriented water molecules that separate, and are bound to, the cationic and anionic centers (Fig. 1) . In Scheme (II) the (unknown) changes in solvent concentration that occur as a result of substitution and charge neutralization are incorporated into the solvent medium and thus throughout this paper the equilibrium constants K_i, were treated as concentration quotients, with

$$K_1 = \frac{c_{2\text{SIP}}}{c_+c_-}; \quad K_2 = \frac{c_{\text{SIP}}}{c_{2\text{SIP}}}; \quad K_3 = \frac{c_{\text{CIP}}}{c_{\text{SIP}}}$$

where c_i is the concentration of the species i. Note that the present K_i symbols, which are consistent with our previous usage (Buchner et al., 2004; Akilan et al., 2006a,b), should not be confused with those commonly used to represent the equilibrium constants for the stepwise addition of ligands to a metal ion.

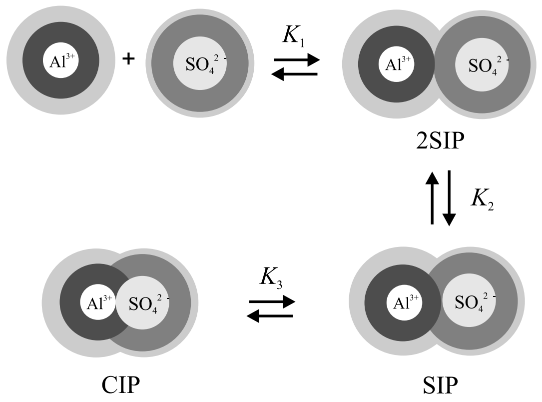

Fig. 1. Stepwise formation (Scheme (II)) of 1:1 ion pairs in $Al_2(SO_4)_3$(aq). The first hydration shells of the ions are represented by dark gray areas. The outermost light gray areas indicate the presence of additional hydration shells (ignoring changes due to charge neutralization).

According to Scheme (II) the solvated free ions, M^{3+} and L^{2-}, associate by first forming a double solvent-separated ion pair (2SIP) or, in the language of inorganic chemistry an outer–outer sphere complex, $[MS_2L]^+$, with their primary solvation shells essentially intact and the intervening bound solvent molecules (S) oriented, consistent with their net dipole vectors, with respect to the cation and anion. The 2SIP subsequently loses the intervening solvent molecules to form sequentially a solvent-shared ion pair (SIP) or outer sphere complex $[MSL]^+$, and finally a contact ion pair (CIP) or inner sphere complex, $[ML]^+$. These steps are accompanied by considerable desolvation due to the loosening of the hydration shells around the ion pairs as a result of charge neutralization. Note that chelated sulfate complexes can be ruled out on the basis of Raman investigations (Rudolph and Schönherr, 1991a), which showed that the C_{3v} symmetry of the unidentate sulfate ligand is preserved in $Al_2(SO_4)_3$(aq) solutions even at very high concentrations.

Unfortunately, there are very few methods available that can distinguish the individual steps in the overall ion pairing process, Scheme (II) (Marcus and Hefter, 2006). It is particularly noteworthy that the normally powerful spectroscopic techniques, such as NMR, IR, Raman and UV–vis, are of limited use for studying such equilibria because they generally detect only CIPs (Hefter, 2006). On the other hand, thermodynamic methods such as potentiometry detect only the overall association, Scheme (I) (Hefter, 2006).

The method most widely employed to date to study the stepwise formation of ion pairs is variable-frequency ultrasonic absorption, UA (Atkinson and Petrucci, 1966; Bonsen et al., 1978; Kaatze et al., 2000). Such measurements have provided great insights into the kinetics of formation and dissociation of ion pairs, revealing reaction times ranging from diffusion-controlled (nanoseconds) to many tens of seconds (Kaatze et al., 2000). The only viable alternative method to UA at the present time is broadband dielectric relaxation spectroscopy (DRS). This technique measures the complex permittivity, $\hat{\varepsilon}(\nu)$, of a solution as a function of the frequency, ν, of an applied electric field (Buchner and Barthel, 2001; Buchner, 2004). DRS has two advantages over UA: it detects species rather than equilibria and, because the dielectric response is proportional to the square of the dipole moment of the relaxing species, DRS has a *unique* sensitivity to the various ion-pair types in the order: 2SIP > SIP > CIP.

As a result of the ongoing improvements in microwave technology over the last few decades with regard to speed and accuracy, improved calibration procedures, and data analysis methods, DRS has become a practical tool for investigating ion association in electrolyte solutions (Buchner and Barthel, 2001; Buchner, 2004). For example, in recent years DRS has been used to establish the simultaneous presence of all three ion-pair types as well as triple ions in aqueous solutions of several 2:2 electrolytes (Buchner et al., 2004; Chen et al., 2005; Akilan et al., 2006a;Akilan et al., 2006b). DRS has also been used to evaluate the kinetics of ion pair formation/dissociation (Buchner et al., 2003; Tromans et al., 2004), to deduce structural information about solvent-separated IPs (Buchner and Hefter, 2002), and to determine the thermodynamic parameters for the individual steps in Scheme (II) (Akilan et al., 2006a;Akilan et al., 2006b).

This paper presents the first detailed investigation of a 3:2 electrolyte using modern broadband DRS. The only previous DRS study of such systems appears to be that of Kaatze and Giese (1987) who investigated three 3:2 metal sulfate systems. However, their measurements were performed at only three (or fewer) concentrations over a limited frequency range ($0.01 \leqslant \nu$ (GHz) $\leqslant 60$, with most measurements at $\nu \leqslant 8$ GHz) and they were unable to disentangle the individual ion-pair contributions with the data accuracy then achievable.

Aluminum sulfate is a classical, nominally ‘strong’, electrolyte in aqueous solutions. It was selected for the present study on the basis of its geochemical and environmental importance, as outlined above, and because it is widely used in the paper industry, for the fixing of dyes, clarification of water and so on (Kroschwitz, 1991). Measurements on $Al_2(SO_4)_3(aq)$ can also be directly compared with previous measurements on 1:2 and 2:2 metal-sulfate systems (Buchner et al., 1999a, 2004; Chen et al., 2005; Akilan et al., 2006a;Akilan et al., 2006b).

Ion association in aluminum sulfate solutions has been studied by potentiometry using various electrodes (Sharma and Prasad, 1970; Matsushima et al., 1988; Ridley et al., 1999; Xiao et al., 2002), conductivity (Nishide and Tsuchiya, 1965), solubility (Ridley et al., 1999), calorimetry (Lo et al., 1982), ultrasonic absorption (Bonsen et al., 1978; Kaatze et al., 1999), stopped-flow (Knoche and López-Quintela, 1983), and pressure/temperature jump (Miceli and Stuehr, 1968; Kalidas et al., 1971) methods. Spectroscopic techniques such as NMR (Akitt et al., 1969, 1972, 1985; Jin and Ichikawa, 1988; Akitt and Howarth, 1989), Raman (Rudolph and Schönherr, 1989, 1991a,b; Rudolph and Mason, 2001) and UV–vis (Kryzhanovskii et al., 1971; McIntyre et al., 1982) have also been employed. However, as discussed in detail elsewhere (Rudolph et al., 2003; Hefter, 2006), such techniques usually detect only CIPs and their interpretation is often problematic. In particular, values of K_A obtained from such measurements may be lower (even by many orders of magnitude) than those determined by thermodynamic methods (Hefter, 2006). Furthermore, the constants obtained are not always thermodynamically well-defined, because they may contain unknown contributions from the species not detected (Rudolph et al., 2003; Hefter, 2006).

Results of the thermodynamic studies of the $Al^{3+}/SO_4{}^{2-}$ system have been reviewed by Ridley et al. (1999). The values listed by them for the standard association constant, K_A^0, of the equilibrium:

$$Al^{3+}(aq) + SO_4^{2-}(aq) \overset{K_A}{\rightleftharpoons} AlSO_4{}^+(aq) \tag{III}$$

vary over the range $1.9 \leqslant \log K_A^0 \leqslant 3.9$ Even if the outliers (Sharma and Prasad, 1970; Jha et al., 1989) are rejected, the average of the remaining values ($\log K_A^0 = 3.4 \pm 0.3$) still has an unsatisfactorily-large uncertainty. The most recent determination: $\log K_A^0 = 3.84 \pm 0.12$, obtained using sulfate-electrode potentiometry (Xiao et al., 2002), is larger than most previous estimates although still broadly consistent with them within the stated error limits. Surprisingly, except for the investigation of Xiao et al. (2002) almost no data are available for K_A values at high ionic strengths, even though these are in general more geochemically and technologically useful.

Reasons for the wide variation in the reported log K_A^0 values are not hard to find. First, there are the inevitable uncertainties attached to the study of highly charged ions that are related to their activity coefficients and their extrapolation to infinite dilution (Powell et al., 2005). Second, there are specific difficulties in quantifying ion association in the $Al^{3+}/SO_4{}^{2-}$ system (Ridley et al., 1999; Xiao et al., 2002). These include the ready hydrolysis of $Al^{3+}(aq)$, which for simplicity can be represented as:

$$xAl^{3+}(aq) + yH_2O \rightleftharpoons Al_x(OH)_y^{(3x-y)+}(aq) + yH^+(aq) \tag{IV}$$

and which requires the presence of significant amounts of acid to suppress it (Baes and Mesmer, 1976). However, at low pH values the sulfate ion becomes protonated:

$$H^+(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4{}^-(aq) \tag{V}$$

which then also needs to be taken into account, along with the possibility of $Al^{3+}/HSO_4{}^-$ interactions.

Last, there are problems in applying many of the standard techniques used for studying ion association. For example, the strength of the hydrolysis reactions, Equilibrium (IV), the high conductivity of $H^+(aq)$ and the charges on the ion pairs make application of the powerful conductometric method (Justice, 1983) problematic. Potentiometric characterization is also difficult because of the absence of convenient and/or reliable electrodes responsive to Al^{3+} or $SO_4{}^{2-}$ (Xiao et al., 2002). Fortunately, direct complexation of Al^{3+} by $HSO_4{}^-$ ions does not appear to be significant within the pH region relevant for this study (Rudolph and Schönherr, 1991a) so the competition equilibrium:

$$Al^{3+}(aq) + xHSO_4^-(aq) \rightleftharpoons Al(SO_4)_x^{(3-2x)+}(aq) + xH^+(aq) \tag{VI}$$

which can be followed with reliable H^+-responsive electrodes can, in principle, be used to quantify Equilibrium (III), providing the constant for (V) is known. However, at 25 °C the relative values of the constants for equilibria

(V) and (VI) and the uncertainty in the HSO_4^- dissociation constant (Dickson et al., 1990; Luts et al., 1994) lowers the accuracy of this approach, at least at low temperatures (Ridley et al., 1999). Some of these difficulties have been circumvented by the use of concentration cells employing sulfate-responsive electrodes (Xiao et al., 2002), although problems arising from diffusion (liquid junction) potentials and activity coefficient corrections may still be important. Clearly, much remains to be learnt about the Al^{3+}/SO_4^{2-} system, even though it is perhaps the best-studied of any 3:2 electrolyte.

The great power of DRS for quantifying ion pairing processes makes it an attractive tool for the investigation of this system. The only previous DRS study of $Al_2(SO_4)_3$(aq) is that of Kaatze and Giese (1987) but as already noted above only limited information was obtained. This paper therefore presents a detailed investigation of aqueous solutions of aluminum sulfate at 25 °C using modern broadband dielectric relaxation spectroscopy over a wide a range of solute concentrations and frequencies.

2. EXPERIMENTAL

Stock solutions were prepared from hydrated $Al_2(SO_4)_3$ of the highest available purity (Sigma–Aldrich/Riedel, aluminum sulfate octadecahydrate, batch assay 100.7%) with small amounts of sulfuric acid added to minimize hydrolysis reactions. Solutions so prepared had pH values in the region: $2.3 \leqslant \text{pH} \leqslant 3.3$, decreasing with increasing $Al_2(SO_4)_3$ concentration, and were stable towards precipitation. The Al^{3+} concentrations in the stock solutions were determined (to 0.2%) by complexometric titration against standard EDTA solution (BDH, UK, Concentrated Volumetric Standard) using xylenol orange as an indicator (Vogel, 1961). More dilute solutions were prepared volumetrically from stock solutions using calibrated A-grade glassware and high purity water (Millipore Milli-Q systems). All concentrations are given in mol L^{-1}, M. Densities required for interconversion of concentrations were measured with a vibrating tube densimeter (Anton Paar, Austria, Model mPDS4000) and are estimated to be accurate to better than ±0.02%.

Dielectric spectra consisting of 101 points measured at equally spaced increments of $\log \nu$ over the frequency range $\nu_{\min} \leqslant \nu\,(\text{GHz}) \leqslant 20$ were measured at Murdoch University using a Hewlett–Packard model 85070M Dielectric Probe System based on a HP 8720D vector network analyzer (VNA) as described elsewhere (Buchner et al., 1999b). Temperature was controlled by a Hetofrig (Denmark) circulator-thermostat to 25 ± 0.02 °C, with an accuracy of better than 0.05 °C (NIST-traceable). The minimum frequency of investigation, $\nu_{\min}$, was governed by the conductivity contribution to the loss spectrum (see below) and varied from about 0.2 to 0.5 GHz. All VNA spectra were recorded using at least two independent calibrations (with air, water and mercury as the standards). Higher frequency data for selected solutions were recorded at Regensburg using two waveguide interferometers (IFMs): A-band ($27 \leqslant \nu\,(\text{GHz}) \leqslant 39$) and E-band ($60 \leqslant \nu\,(\text{GHz}) \leqslant 89$) at approximately 10 selected frequencies as described in detail previously (Barthel et al., 1991). Temperature control and accuracy were similar to those at Murdoch. The overall precision of the combined data is of the order of 1–2% of the static permittivity. As has been found for many other systems (Buchner et al., 1999a; Akilan et al., 2006b), the VNA reflectometric and IFM transmission data could be combined seamlessly, although the VNA data become rather noisy at higher concentrations. Typical spectra for $Al_2(SO_4)_3$(aq) are shown in Fig. 2. Occasional checks for pH effects were made by lowering the solution pH to ~1.5 by addition of small amounts sulfuric acid. This increased the total sulfate concentration by less than 1.5% so that shifts of the association equilibria by the common ion effect can be neglected. No detectable differences in the dielectric spectra were observed and it is therefore reasonable to conclude that the small change in pH amongst the sample solutions ($2.3 \leqslant \text{pH} \leqslant 3.3$, decreasing with increasing solute concentration) is unlikely to significantly influence the present results.

3. DATA ANALYSIS

By combining the VNA and IFM results, dielectric permittivity spectra, $\varepsilon'(\nu)$, and total loss spectra, $\eta''(\nu) = \varepsilon''(\nu) + (\kappa/2\pi\nu\varepsilon_0)$, of the samples were obtained as a function of frequency, where $\varepsilon''(\nu)$ is the dielectric loss, ε_0 is the permittivity of free space and κ is the solution conductivity. For reasons discussed previously (Akilan et al., 2006b), κ was treated as an adjustable parameter in the data-fitting procedure. However, the values of κ so obtained were found to be in good agreement (Fig. 3) with the rather limited literature data obtained from conventional low frequency conductivity measurements.[2]

Analysis of complex dielectric spectra, $\hat{\varepsilon}(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, such as those shown in Fig. 2, is usually carried out by fitting sums of appropriate bandshape functions, $F_j(\nu)$, Eq. (1), of amplitude $S_j = \varepsilon_j - \varepsilon_{j+1}$, to a set of complex permittivities measured at discrete frequencies (Buchner et al., 1999a; Chen et al., 2005).

$$\hat{\varepsilon}(\nu) = \sum_{j=1}^{n} S_j F_j(\nu) + \varepsilon_\infty \tag{1}$$

Note that in this formulation ε_1 corresponds to the static dielectric constant ε, while ε_∞ is the so-called "infinite frequency" permittivity, of the solution. The latter was also treated as a fitting parameter because the maximum frequency of this investigation (89 GHz) does not cover the full relaxation region of water (Fukasawa et al., 2005).

A central question in analyzing DR spectra is the number of processes detected (n) and the number of parameters required to describe each process. The simplest approach is to use a set of n Debye functions, $F^{D}(\nu)$ Eq. (2), each characterized by a single relaxation time τ_j.

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[2] Conductivities at 25 °C have also been reported by Ivanov et al. (1987) that disagree with the present selected values (McIntyre et al., 1982) and with other data at 50 °C (Vasil'eva et al., 1976). However, the concentrations reported by Ivanov et al. (1987) are internally inconsistent and the solutions appear to have contained excess sulfuric acid.

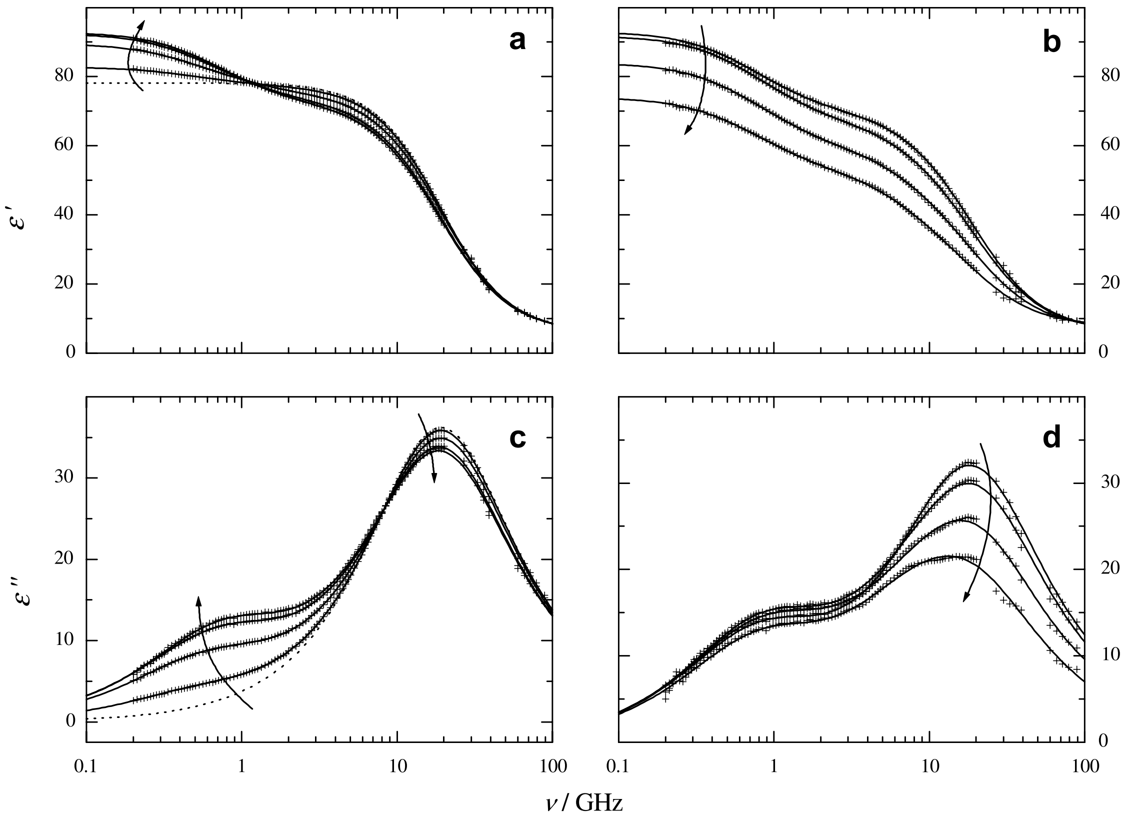

Fig. 2. Dielectric permittivity, ε' (a and b), and loss, ε'' (c and d), spectra of $Al_2(SO_4)_3$(aq) at 25 °C. Arrows indicate increasing concentrations ((a, c) 0.0115, 0.0425, 0.0855, 0.1054 M; (b, d) 0.1601, 0.2343, 0.4302, 0.6506 M). The dotted line represents pure water (Fukasawa et al., 2005).

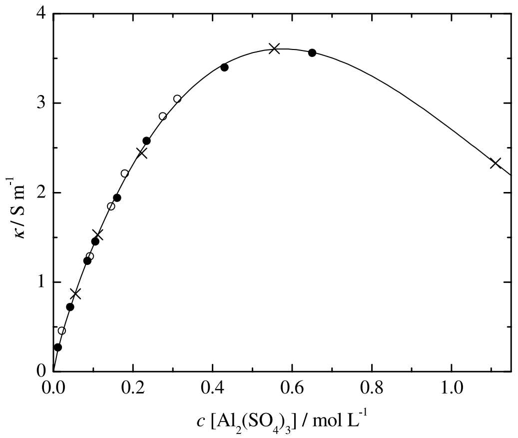

Fig. 3. Conductivity, κ, of $Al_2(SO_4)_3$(aq) at 25 °C derived from fitting the present DRS data (filled circles: VNA + IFM; circles: VNA only) and conventional low frequency values (McIntyre et al., 1982) (crosses). The line is a Casteel–Amis fit (Barthel et al., 1998) to all the data.

$$F_j^{\mathrm{D}}(\nu) = (1 + \mathrm{i}2\pi\nu\tau_j)^{-1} \tag{2}$$

As discussed previously (Buchner et al., 2004; Fukasawa et al., 2005), the bulk water response is best described by the sum of two Debye relaxations, corresponding to the dominant cooperative mode at ~8.3 ps and a faster process ($\tau \approx 0.3$ ps) of small amplitude that is thought to be due to the re-insertion of 'free' water molecules into the H-bond network and memory effects associated with dielectric friction (Fukasawa et al., 2005). During the present fitting procedure, the relaxation time of the fast water process was fixed at 0.4 ps, as no data were available at frequencies above 89 GHz, which would be required for precise definition of this process in the present solutions. The value chosen differs slightly from that for pure water, where data up to THz frequencies were available (Schrödle, 2005). It yields smaller values for the reduced error function χ_r^2 and smoother data for ε_∞ without noticeably affecting the other parameters of the fit.

The general approach adopted for analyzing the DR spectra of electrolyte solutions has been discussed in detail previously (Buchner et al., 2004) and so only a few salient features will be noted here. Because dielectric relaxations are particularly broad and the relaxation times are not well separated, fitting the spectra must be done with great care. As for most other types of spectroscopic analysis, species can be reliably identified by the growth and decline of spectral features with changing concentration (Figs 2 and 4). In addition, it must be understood that both the in-phase, $\varepsilon'(\nu)$, and out-of-phase, $\varepsilon''(\nu)$, components are fitted simultaneously and that the fitting parameters obtained must be physically realistic and behave smoothly with respect to concentration (Buchner et al., 2004).

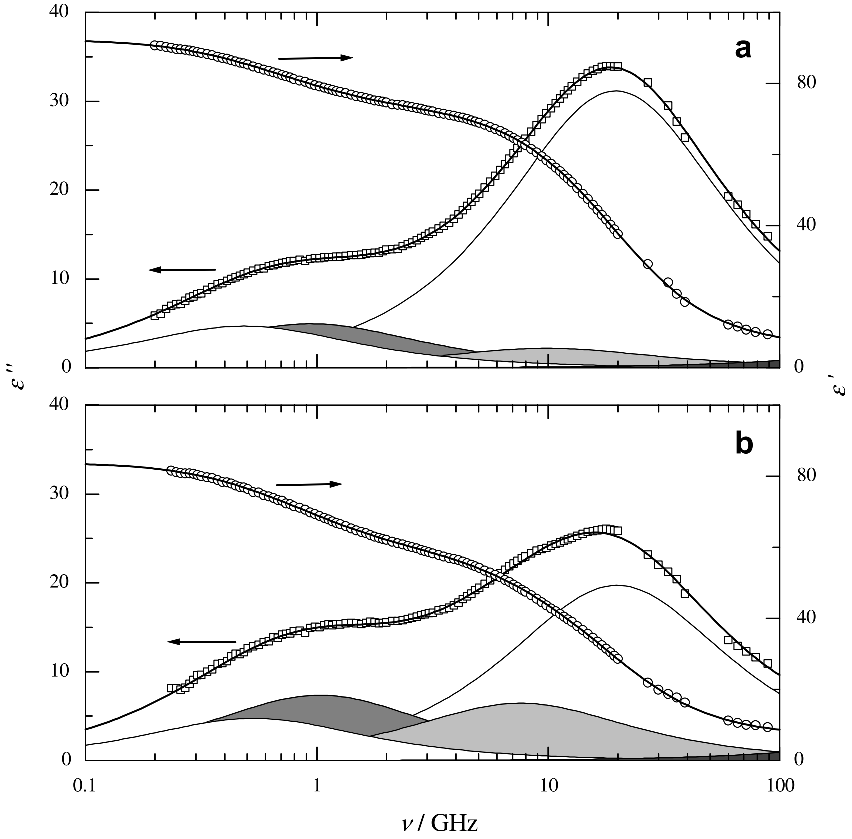

Fig. 4. Dielectric permittivity, ε', and loss, ε'', spectra of $Al_2(SO_4)_3$(aq) at 25 °C: 0.0855 M (a) and 0.4317 M (b), showing the contributions from the five Debye processes to ε'' and the resulting fit (solid line).

A numerically satisfactory description of the present solution spectra required a *minimum* of two low-frequency processes in addition to the two higher frequency bulk water processes discussed above. However, for this $n = 4$ model, a strong concentration dependence of the two solute-related relaxation times τ_1 and τ_2 was observed, with a rapid decrease in both at ~0.1 M. Assuming the origin of the lower-frequency relaxation processes ($j = 1$ and 2) to be a tumbling mode of individual dipolar aggregates (ion pairs), these effects cannot be explained easily and are atypical for electrolyte solutions (Buchner et al., 1999a, 2004; Chen et al., 2005). Using only two Debye terms for the solute contributions also led to an increase of the bulk-water relaxation time at higher electrolyte concentrations, whereas previous studies (Buchner et al., 1999a, 2004; Chen et al., 2005) have exhibited a more-or-less pronounced decrease.

In consequence, a sum of *five* Debye contributions was ultimately selected as the most appropriate description of the present dielectric spectra of $Al_2(SO_4)_3$(aq) solutions. Such a model is also consistent with the number of equilibria established for $Al_2(SO_4)_3$(aq) by pressure-jump and ultrasonic absorption experiments (Kalidas et al., 1971; Bonsen et al., 1978). With one exception, the resulting reduced error function χ_r^2, which is normalized with respect to the number of adjustable parameters (Schrödle et al., 2004), was significantly lower for the $n = 5$ fits than for those with $n = 4$. The exception was the lowest concentration (0.0115 M), where the solute contributions were small and it was not possible to separate the $j = 3$ solute process from the overlapping and much greater amplitude bulk water ($j = 4$) relaxation. Thus a fit with $n = 4$ had to be used for this concentration. Typical fits are shown in Fig. 4 and the derived values of τ_j and ε_j are summarized in Table 1. The relaxation times τ_1 to τ_4, as well as the solute-related amplitudes S_1 to S_3, are shown in Fig. 5.

4. RESULTS AND DISCUSSION

4.1. Amplitudes of the solute-related processes

From the results of the present spectra, and consistent with the evidence provided by pressure-jump (Miceli and Stuehr, 1968; Kalidas et al., 1971) and UA (Bonsen et al., 1978; Kaatze et al., 1999) measurements, it can be concluded that there are three solute-related species present in the solutions that give rise to the three observed lower-frequency Debye terms. Identification of these species is more difficult than for the relatively straightforward symmetrical (2:2 and 1:1) electrolytes investigated previously (Buchner et al., 2004; Chen et al., 2005; Akilan et al., 2006a,b) because a number of possibilities exist.

The nature of the species present in aqueous solutions of $Al_2(SO_4)_3$ has been controversial. Akitt et al. (1969)

Table 1
Concentrations, (c) densities (ρ), conductivities (κ), limiting permittivities (ε_j), relaxation times (τ_j), and reduced variance of the fits (χ^2_r) for the DR spectra of $Al_2(SO_4)_3(aq)$ 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_∞	$10^3\chi^2_r$
0	0.9970	0.000							78.32	8.32	5.87	0.3	3.48	48.5
0.0115	1.0011	0.269	82.73	352	78.34	179	77.32		77.32	8.30	6.21	0.4	3.53	17.7
0.0425	1.0117	0.720	89.48	357	81.05	174	75.40	17.5	72.95	8.09	6.18	0.4	4.10	23.0
0.0855	1.0263	1.237	92.39	326	83.02	170	73.12	16.2	68.76	8.13	6.44	0.4	3.01	22.2
0.1054	1.0330	1.452	92.79	288	82.21	163	72.32	16.4	66.32	8.05	6.47	0.4	2.61	32.4
0.1601	1.0518	1.941	92.89	291	83.09	161	69.76	16.8	63.06	8.08	6.67	0.4	2.64	39.1
0.2343	1.0754	2.577	91.70	270	81.32	157	67.08	20.4	57.05	7.81	6.65	0.4	3.33	37.2
0.4302	1.1369	3.398	83.84	298	74.35	154	59.63	21.0	46.74	8.02	7.31	0.4	3.48	50.6
0.6506	1.2030	3.560	73.91	346	67.64	172	52.84	22.1	36.83	8.28	7.87	0.4	6.44	84.8

[a] Units: c in mol L^{-1}; ρ in g cm^{-3}; κ in S m^{-1}, τ_j in ps.

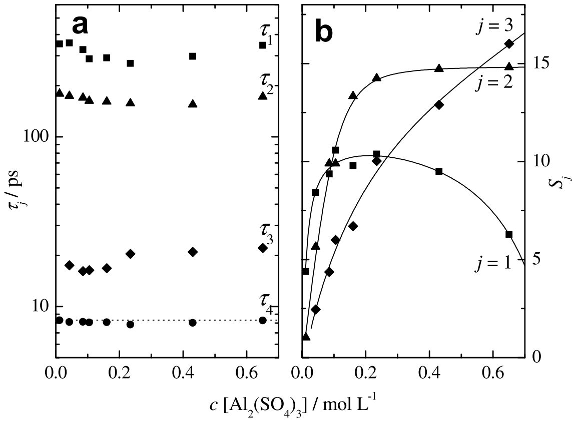

Fig. 5. (a): Relaxation times, τ_j for $j = 1$ to 4 (dotted line: $\tau_4(c = 0) = 8.3$ ps); (b) amplitudes, S_j, of the solute contributions ($j = 1$–3) to the complex dielectric spectra of $Al_2(SO_4)_3(aq)$ at 25 °C.

postulated Al^{3+}/HSO_4^- complexes on the basis of their initial ^{27}Al NMR measurements. However, later investigations by the same authors (Akitt et al., 1972, 1985) and others (Rudolph and Schönherr, 1991a) led to the now generally-accepted picture that, at least for CIPs (the only associated species detected by ^{27}Al NMR) and consistent with the C_{3v} symmetry of the bound anion (Rudolph and Schönherr, 1991a), only monodentate SO_4^{2-} is directly bound to Al^{3+}. The number of monodentate sulfate ions in the complex has been discussed (Ridley et al., 1999; Xiao et al., 2002). Unfortunately, measurements of the Al^{3+}/SO_4^{2-} ratios in ionic associates are difficult using only ^{27}Al NMR or Raman spectroscopies if the measurements are confined (which is usually the case) to whole-salt solutions. However, the effect of exchanging H_2O with D_2O on the ^{27}Al NMR spectra suggested (Akitt and Howarth, 1989) that the 1–1 associate is the predominant species in $Al_2(SO_4)_3(aq)$, and this was corroborated by Raman spectroscopy (Rudolph and Schönherr, 1991a). No higher order complexes ($z > 1$ in Equilibrium (I)) could be found within the accuracy of these two methods, at least at the whole salt stoichiometry ($SO_4^{2-}/Al^{3+} = 1.5$) employed (Rudolph and Schönherr, 1991a). On the other hand, such complexes are almost certainly present in solutions with higher SO_4^{2-}/Al^{3+} ratios, as shown by various thermodynamic measurements (Ridley et al., 1999). More recently, Xiao et al. (2002) have reported the overall stability constant of a second complex, $Al(SO_4)_2^-(aq)$ (corresponding to $z = 2$ in Equilibrium (I) but referred to here, for consistency with our previous work, as a triple ion) to be log $K^0_T = 5.58 \pm 0.09$ from their potentiometric measurements in sodium triflate (NaOTf) media. Note however, that this finding is not necessarily immediately applicable to the present study, which employed whole-salt solutions. More importantly, coulombic and steric repulsions almost certainly dictate that $Al(SO_4)_2^-(aq)$ would possess *trans* geometry. This means that it would have an overall dipole moment of zero and thus would not be detectable by DRS.[3] In line with previous experience (Buchner et al., 2004; Chen et al., 2005; Akilan et al., 2006a,b) it is therefore reasonable to assign the τ_1 relaxation process to 2SIP, τ_2 to SIP and τ_3 to CIP. This assignment can then be tested to see if the analysis of the corresponding amplitudes yields meaningful results consistent with information from other methods.

Quantitative evaluation of the contributions of individual species to the total dielectric spectrum can be made via the modified Cavell equation, which connects the dispersion amplitude, S_j, of the relaxation process j, to the concentration c_j of the species responsible for that process:

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

where k_B and N_A are the Boltzmann and Avogadro constants, respectively, and T is the thermodynamic (Kelvin) temperature (Barthel et al., 1992). The polarizability, α_j, and dipole moment, μ_j, are characteristic for the relaxing species, while the reaction field factor, f_j, and shape factor A_j are functions of its geometry (Barthel et al., 1992). In our calculations IPs were assumed to be ellipsoids with half-axes $x_j > y_j = z_j$. The empirical Kirkwood factor g_j allows for same-species (j –j) dipole–dipole orientational correlations. For the relatively low ion pair concentrations

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[3] Significant formation of the alternative triple ion, the cationic species $[Al_2SO_4]^{4+}$, whose analog was detected in $MSO_4(aq)$ solutions (Buchner et al., 2004; Chen et al., 2005) and which would have a net dipole, is unlikely on charge and relative concentration grounds.

present here a value of $g_j \approx 1$ (corresponding to zero correlation) can be reasonably assumed.

Of the parameters in Eq. (3), the dipole moment μ_j is probably the most critical. In contrast to bivalent metal sulfate solutions, which essentially form only neutral 1–1 associates, the 1–1 species formed in $Al_2(SO_4)_3$(aq) solutions are charged and therefore their dipole moments depend on the coordinate system used. Ideally the center of hydrodynamic stress should be taken to be the pivot of ion-pair rotation (Barthel et al., 1992). In the case of $AlSO_4^+$(aq) species, however, this calculation is flawed by the presence of strongly bound water molecules, arising from the high charge density of the Al^{3+} ion, which may significantly alter the shape of the rotating entity. Accordingly, the center of mass was used as the reference point for estimating the dipole moments of the probable ion-pair species. The values so obtained were corrected for the induced dipole moment caused by polarization of the ions in the field of the counterions and, for 2SIPs and SIPs, the effect of the dipoles of the intervening water molecules (Barthel et al., 1992). Half axes $x_j = r_+ + r_- + qr(H_2O)$, with $q = 0$, 1, 2 corresponding to CIPs, SIPs and 2SIPs, respectively; and $y_j = z_j = r_-$ were assumed. Polarizabilities of the dipolar species (Table 2) were likewise estimated to be the sum of the ion and water polarizabilities: $\alpha_j = \alpha_+ + \alpha_- + q\alpha(H_2O)$. The required radii and polarizabilities were taken from the literature (Hasted, 1972; Marcus, 1997).

Fig. 6 and Table 3 summarize the concentrations of the associated species calculated with Eq. (3) from the data of Table 1 and the parameters in Table 2 (note that the species concentrations c_j (Fig. 6) and the amplitudes S_j (Fig. 5b) are linked via μ_j^2 when comparing these figures). As would be expected, the concentration of 2SIPs is higher than the other species only in quite dilute solutions, $c < 0.03$ M. At higher solute concentrations, SIPs and CIPs are the dominant species. From the sequential nature of the equilibria (Scheme (II)), the concentrations of 2SIPs and SIPs should pass through a maximum. While such a maximum is present for c_{2SIP} it is much less pronounced than those observed for bivalent metal sulfate solutions (Buchner et al., 2004; Chen et al., 2005). Furthermore, the values of c_{SIP} show only a broad plateau over the concentration range studied. Although artefacts arising from correlations in the data cannot be totally ruled out, these differences are consistent with the Al^{3+} ion maintaining a strong hydration shell even upon association with the sulfate ion (see Section 4.2 below).

As would be expected from Scheme (II), c_{CIP} shows a steady increase with c (Fig. 6). More importantly there is good agreement, within the probably rather large uncertainties for all of the techniques, with results from Raman spectroscopy (Rudolph and Schönherr, 1991a) and two independent ^{27}Al NMR studies (Akitt et al., 1985; Rudolph and Schönherr, 1991a), except at $c \approx 0.1$ M. At such low solute concentrations, it is possible that c_{CIP} derived from the present DRS data might be somewhat overestimated, as the separation of the small CIP signal from the proximate and much larger contribution of the bulk water relaxation process is inherently difficult. However, the error cannot be large as the derived step-wise association constant K_3 behaves reasonably (see below and Fig. 7a). At higher solute concentrations, not only is S_{CIP}, and thus c_{CIP}, larger but so too is τ_3 (Fig. 5a), making the CIP contribution easier to separate from the total dielectric spectrum (since the position of the overlapping bulk water process, reflected in the value of τ_4, remains constant). By the same token, evaluation of the ^{27}Al NMR spectra at low c is also difficult, due to departures of the signals from Lorentzian shape and the rather high noise level of ^{27}Al NMR spectroscopy (Akitt et al., 1985). Similar considerations (Buchner et al., 2004) apply to the (rather few) quantitative results reported from Raman investigations (Rudolph and Schönherr, 1991a). Unfortunately, no other studies report concentrations of the solvent-separated species at higher ionic strengths. In particular, the few ultrasonic adsorption studies (Bonsen et al., 1978; Kaatze et al., 1999) are marred by conflicting band assignments and they focus more on kinetic aspects.

The ability of DRS to detect all ion-pair types in $Al_2(SO_4)_3$ solutions allows calculation of the stepwise and overall association constants, K_i and K_A. From Schemes I–III and the total ion pair concentration, $c_{IP} = c_{2SIP} + c_{SIP} + c_{CIP}$, it follows that

Table 2
Half axes, dipole moments and polarizabilities of the ion pair species and water[a]

Species (j)	x_j	$y_j = z_j$	μ_j	α_j
2SIP (1)	568	230	106.4	7.88
SIP (2)	425.5	230	71.8	6.44
CIP (3)	283	230	35.1	4.99
H_2O	142.5	142.5	1.834	1.444

[a] Units: x_j, y_j, z_j in pm; μ_j in D ($1 D = 3.336 \times 10^{-30}$ C m); α_j in $4\pi\varepsilon_0 10^{-30}$ m^{-3}.

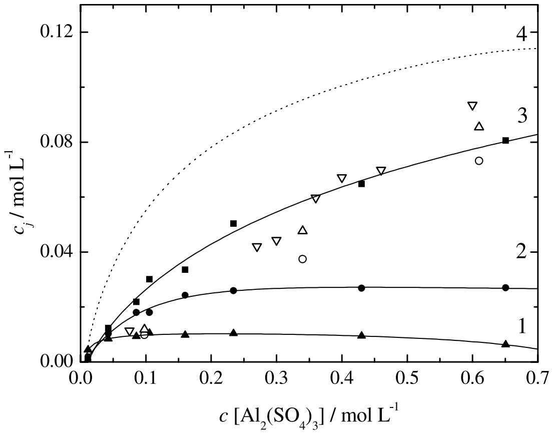

Fig. 6. Concentrations of 2SIPs (curve 1, filled triangles), SIPs (curve 2, filled circles) and CIPs (curve 3, filled squares) in $Al_2(SO_4)_3$(aq) at 25 °C, obtained from the present DRS data using Eq. (3) and the parameters from Table 2. Also included are CIP concentrations obtained from measurements using ^{27}Al NMR (upwards triangles, Rudolph and Schönherr, 1991a; downwards triangles, Akitt et al., 1985) and Raman (circles; Rudolph and Schönherr, 1991a) spectroscopy. Curve 4 represents the total ion pair concentration (c_{IP}).

Table 3
Concentrations (c), ionic strength (I) and equilibrium constants, K_i and K_A for $Al_2(SO_4)_3$(aq) at 25 °C[a] (ignoring possible triple ion formation)

c	I	c_{CIP}	c_{SIP}	c_{2SIP}	K_1	K_2	K_3	K_A
0.0115	0.173	0	0.00186	0.00437	10.5	—	—	—
0.0425	0.637	0.01231	0.01027	0.00839	1.84	1.22	0.835	5.97
0.0855	1.283	0.02188	0.01801	0.00933	0.403	1.93	0.823	1.82
0.1054	1.581	0.03008	0.01801	0.01053	0.289	1.71	0.599	1.08
0.1601	2.402	0.03358	0.02426	0.00975	0.0987	2.49	0.722	0.522
0.2343	3.515	0.05030	0.02593	0.01033	0.0456	2.51	0.515	0.219
0.4302	6.453	0.06474	0.02680	0.00946	0.0107	2.83	0.414	0.0534
0.6506	9.759	0.08060	0.02699	0.00625	0.0029	4.32	0.335	0.0196

[a] Units: c, I in mol L^{-1}; K_1, K_A in L mol^{-1}.

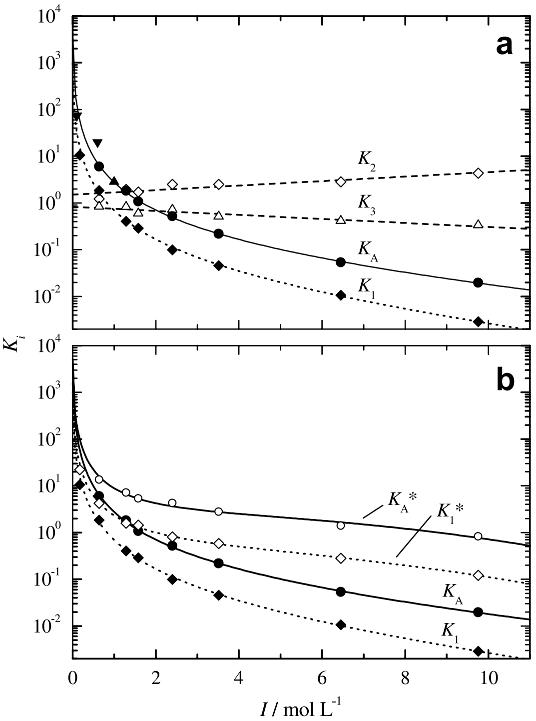

Fig. 7. (a) Stepwise formation constants K_1, K_2, and K_3 for the various ion-pair species (Scheme (II)) and for the overall association constant, K_A (Scheme (I)). Curves for K_A and K_1 were obtained from Guggenheim-type fits, Eq. (5), of the data; those for K_2 and K_3 are empirical straight-line fits. Filled triangles downward (Behr and Wendt, 1962) and upward (Lo et al., 1982) denote potentiometric and calorimetric determinations of K_A, respectively. (b) Comparison of formation constants obtained with (open symbols) or without (full symbols) correction of the DRS data for TI ($Al(SO_4)_2{}^-$) formation.

$$K_A = \frac{c_{IP}}{c_+ c_-} = K_1 + K_1K_2 + K_1K_2K_3 \qquad (4)$$

Fig. 7 and Table 3 summarize the various association constants as a function of the total (stoichiometric) ionic strength, $I = 1/2\sum c_k z_k^2$ (with concentrations, c_k, and charges, z_k, of the ions). Ion association was not taken into account for the calculation of I. As would be expected from electrolyte theory, K_1 (and hence also K_A, Eq. (4)) shows a pronounced decrease with increasing I, although interestingly neither shows the expected increase at high I. On the other hand both K_2 and K_3, which involve only the loss of water molecules (Scheme (II) and Fig. 1), are essentially independent of I. For direct comparison with values obtained from thermodynamic methods such as potentiometry and calorimetry, which measure only K_A, the present DRS values were extrapolated to infinite dilution using, an extended Guggenheim-type equation (Robinson and Stokes, 1970):

$$\log K_A = \log K_A^0 - \frac{2A_{DH}|z_+z_-|\sqrt{I}}{1+\sqrt{I}} + B_K I + C_K I^{3/2}, \qquad (5)$$

where A_{DH} is the Debye–Hückel constant for activity coefficients ($A_{DH} = 0.51005$; Archer and Wang, 1990) and B_K and C_K are empirical parameters.[4] Unlike the 1:2 and 2:2 electrolytes studied previously (Buchner et al., 2004; Chen et al., 2005; Akilan et al., 2006a,b), the present results did not require a term in $I^{3/2}$ (*i.e.*, $C_K = 0$) to satisfactorily describe the $K_A(I)$ data. This might be because of the smaller concentration range covered, or possibly the use of stoichiometric rather than actual I values, or perhaps the dubious validity of the ionic strength concept for such highly charged ions. It may be noteworthy that a similar result was obtained by Xiao et al. (2002).

The standard state (infinite dilution) value of the overall association constant so obtained, $\log K_A^0 = 3.56 \pm 0.02$ (Table 4), lies within the wide range of literature results (ignoring outliers as discussed above): $\log K_A^0 = 3.2$ (Behr and Wendt, 1962), 3.3 (Kalidas et al., 1971), 3.35 (Matsushima et al., 1988), 3.73 (Nishide and Tsuchiya, 1965), 3.84 (Xiao et al., 2002). A mean value of $K_3 = 0.2 \pm 0.05$ was reported from pressure-jump relaxation experiments in dilute solutions (Kalidas et al., 1971), which is somewhat smaller than the present DRS result ($K_3^0 = 0.6 \pm 0.2$ at $I = 0$) but still agrees within the stated error limits. Unfortunately, no step-wise association constants for the ion pairs in $Al_2(SO_4)_3$(aq) could be obtained from the UA studies (Bonsen et al., 1978; Kaatze et al., 1999).

The error of ±0.02 cited for the present value of $\log K_A^0$ is derived from the fit of Eq. (5) to the $K_A(I)$ values calcu-

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[4] The Guggenheim-type equation is chosen purely as a convenient way of fitting the data; no special validity is claimed for it. Other authors (Ridley et al., 1999; Xiao et al., 2002) have used related but different expressions. This will slightly affect the extrapolated K^0 values but any such differences are likely to be much smaller than the (unknown) systematic errors.

Table 4
Equilibrium constants and fit parameters describing their dependence on I at 25 °C in $Al_2(SO_4)_3$(aq) solutions[a]

	$\log K_i^0$	B_K	C_K
K_1[b]	2.99 ± 0.02	-0.092 ± 0.005	0
K_A[b]	3.56 ± 0.02	-0.066 ± 0.003	0
K_1^*[b]	3.19 ± 0.03	0.315 ± 0.025	-0.084 ± 0.008
K_A*[b]	3.72 ± 0.07	0.381 ± 0.062	-0.096 ± 0.019
K_2[c]	0.180 ± 0.047	0.048 ± 0.010	—
K_3[c]	-0.081 ± 0.032	-0.043 ± 0.007	—

[a] Asterisk (*) indicates TI formation has been taken into account; see Appendix A. Note that K_2 and K_3 are unaffected by TI formation.

[b] Eq. (5).

[c] $\log K_i = \log K_i^0 + B_K I (i = 2 \text{ or } 3)$

lated from the experimental ion-pair dispersion amplitudes via Eqs. (3) and (4). This error is almost certainly smaller than the overall uncertainties in the DRS data because it does not take into account, for example, possible systematic errors in the ion-pair dipole moments, which are difficult to assess. Even so, our value for $\log K_A^0$ is significantly smaller than the most recent potentiometric value of $\log K_A^0 = 3.84 \pm 0.12$ reported by Xiao et al. (2002). Potentiometric measurements of equilibrium constants are usually considered to be more reliable than spectroscopic ones (Rossotti, 1978) and this is particularly true for DR measurements given the current state of the art. On the other hand, the K_A^0 value of Xiao et al. (2002) was derived by extrapolation of only three measurements (at I (mol kg^{-1}) = 0.3, 0.5 and 1.0). As recognized by Xiao et al. (2002), extrapolation of such data to infinite dilution depends strongly on the activity coefficient model adopted. In addition, the correction for liquid junction (diffusion) potentials is always problematic (Hefter, 1982) and, again as noted by Xiao et al. (2002), their result is higher than those reported by most other researchers.

Nevertheless, it is possible that the present value may be low, because the formation of the triple ion $Al(SO_4)_2^-$(aq), for which Xiao et al. (2002) report $\log K_{TI}^0 = 5.58 \pm 0.09$, cannot be detected by DRS (see above). Even though the formation constant for the triple ion (TI) drops considerably with increasing I (Xiao et al., 2002), significant concentrations of $Al(SO_4)_2^-$(aq) may still be present in $Al_2(SO_4)_3$(aq). Any Al^{3+} and SO_4^{2-} present as the TI would be counted as free ions in the DRS calculations, thereby producing an underestimate of $K_A(I)$ and hence of K_A^0. Although the formation of the TI was studied by Xiao et al. (2002) only at $I \leqslant 1$ mol kg^{-1} in NaOTf, an approximate correction of the present results for its presence was attempted (Appendix A). The results of these calculations are summarized in Table 5 and Fig. 7b and reveal a small but significant increase of the $K_A(I)$ values, which gives a corrected value of $\log K_A^{0^*} = 3.72 \pm 0.07$ (Table 4; note that K_2 and K_3 are not affected by TI formation). This value is still slightly lower than the potentiometric result of Xiao et al. (2002) but agrees within the stated error limits, which provides circumstantial evidence for the existence of the symmetric triple ion $Al(SO_4)_2^-$(aq) in moderately concentrated $Al_2(SO_4)_3$(aq).

It is interesting to note that even after allowance is made for the presence of undetected $Al(SO_4)_2^-$(aq), the present $K_A(I)$ values obtained in the 'self-medium' of $Al_2(SO_4)_3$(aq) are somewhat lower than those obtained in notionally non-interacting NaOTf media (Xiao et al., 2002). While systematic errors (especially in the estimation of μ_j) cannot be ruled out, similar differences have been observed for other systems studied by DRS (Buchner et al., 1999a; Buchner et al., 2004; Chen et al., 2005; Akilan et al., 2006a,b) and have been attributed to "medium" (activity coefficient) effects. Small differences might also arise from the different activity coefficient models employed in the present work and by others (Ridley et al., 1999; Xiao et al., 2002).

4.2. Solvent contribution

The decrease of the total solvent amplitude $S_s(c) = S_4(c) + S_5(c) = \varepsilon_4(c) - \varepsilon_\infty(0)$[5] with increasing $Al_2(SO_4)_3$ concentration is mostly caused by the 'loss' of water dipoles from the solution due to their strong interactions with the ions. This in turn leads to a significant cancellation of dipole moments in the roughly centro-symmetric hydration shells, so-called *irrotational bonding* (Buchner, 2004). As described in detail previously (Buchner et al., 2004), apparent solvent concentrations in the solutions, $c_s^{ap}(c)$, can be calculated via

$$c_s^{ap}(c) = \frac{S_s^{eq}(c)}{S_s(0)} \cdot \frac{2\varepsilon(c) + 1}{\varepsilon(c)} \cdot \frac{\varepsilon(0)}{2\varepsilon(0) + 1} c_s(0) \tag{6}$$

In Eq. (6), $S_s^{eq}(c)$ is the equilibrium amplitude of the bulk-water dispersion obtained by correcting $S_s(c)$ for kinetic depolarization assuming *slip* hydrodynamic boundary conditions, as explained elsewhere (Buchner et al., 2004). Eq. (6) is obtained by normalizing Eq. (3) to the expression for pure water, assuming $A_s = 1/3$. Note that $c_s^{ap}(c)$ not only reflects irrotational bonding but also possible changes in the correlation factor $g_s(c)$ due to the breakdown of the water structure at high electrolyte concentrations (Buchner et al., 2002) as the influence of these two effects on $S_s^{eq}(c)$ cannot be distinguished.

Combination of $c_s^{ap}(c)$ with the (known) analytical water concentration of the solution, c_s, enables calculation of the number of irrotationally-bound water molecules, Z_{ib}, as

$$Z_{ib} = \left[c_s - c_s^{ap}(c)\right]/c \tag{7}$$

The quantity Z_{ib} can be thought of as an effective hydration number: it is in essence the number of solvent molecules that are immobilized on the DR timescale by the presence of the solute. As such, Z_{ib} not only reflects the occupation of the hydration shells by H_2O molecules—as does the coordination number (CN)—but also the strength of ion-solvent interactions. A plot of Z_{ib} as a function of solute concentration, c, is given in Fig. 8 (curve 3). The values are large and depend strongly on c, with $Z_{ib} \approx 90$ at low

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[5] $\varepsilon_\infty(0) = 3.48$, derived from a combination of GHz and THz data (Schrödle, 2005), is more accurate than the $\varepsilon_\infty(c)$ derived from the present DR spectra restricted to $\nu \leqslant 89$ GHz (Buchner et al., 2004).

Table 5
Concentrations, c, c_+^*, c_-^*, c_{TI}, ionic strengths, I, I_m, and equilibrium constants, K_i^*, for $Al_2(SO_4)_3(aq)$ at 25 °C, obtained after correction of the DRS data for triple ion $(Al(SO_4)_2{}^-)$ formation[a]

c	I	I_m	Q_2[b]	c_+^*	c_-^*	c_{TI}	K_1^*	K_A^*
0.0115	0.173	0.1735	1602	0.0113	0.0174	0.00550	22.2	—
0.0425	0.637	0.6390	167.0	0.0346	0.0577	0.0194	4.20	13.6
0.0855	1.283	1.286	105.6[c]	0.0641	0.0920	0.0577	1.58	7.14
0.1054	1.581	1.586	105.6[c]	0.0735	0.100	0.0786	1.43	5.33
0.1601	2.402	2.409	105.6[c]	0.104	0.116	0.148	0.808	4.27
0.2343	3.515	3.531	105.6[c]	0.138	0.129	0.244	0.581	2.79
0.4302	6.453	6.520	105.6[c]	0.236	0.143	0.523	0.279	1.40
0.6506	9.759	9.954	105.6[c]	0.343	0.150	0.844	0.122	0.823

[a] Units: c, I, c_+^* (free Al^{3+}), c_-^* (free $SO_4{}^{2-}$), c_{TI} (triple ion) in mol L^{-1}; I_m in mol kg^{-1}. Asterisk (*) indicates TI formation has been taken into account; see Appendix A.

[b] Overall association constant for TI formation (Xiao et al., 2002).

[c] Assuming $I_m = 1$.

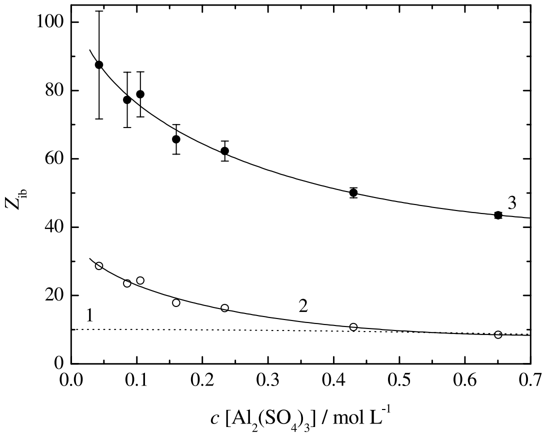

Fig. 8. Effective hydration numbers, Z_{ib}, obtained by assuming kinetic depolarization with "slip" boundary conditions at 25 °C: $Al_2(SO_4)_3(aq)$ (curve 3), $SO_4{}^{2-}$ (curve 1, Buchner et al., 1999a) and Al^{3+} (curve 2) assuming ionic additivity.

concentrations decreasing towards ~40 at higher concentrations.

Single ion Z_{ib} values can be estimated by assuming that Z_{ib}(ion) values are independent of each other and add up to Z_{ib}(salt) at all concentrations: $Z_{ib}(Al_2(SO_4)_3) = 2Z_{ib}(Al^{3+}) + 3Z_{ib}(SO_4{}^{2-})$. The basis for assigning ionic values is the observation that $Z_{ib}(Cl^-) \approx 0$ at all concentrations (Buchner et al., 2002). Using data for NaCl(aq) (Buchner et al., 1999b) and $Na_2SO_4(aq)$ (Buchner et al., 1999a), a value of $Z_{ib}(SO_4{}^{2-}) \approx 10$ can be deduced over the present concentration range (Fig. 8, curve 1), thereby yielding $Z_{ib}(Al^{3+})$ (Fig. 8, curve 2), which decreases from ~30 at $c \to 0$ to ~8.5 for $c > 0.5$ M. This formal splitting into ionic contributions is strictly true only at infinite dilution because the hydration of the ion pairs—and thus their Z_{ib} values—differs from that of the free ions due to the partial charge neutralization. However, a more detailed analysis of the Z_{ib} numbers is not appropriate at this stage as the results cannot be independently cross-checked.

The value of $Z_{ib}^0(Al^{3+}) \approx 30$ at $c \to 0$ is much larger than those of other cations also determined by DRS at 25 °C: ($Z_{ib}^0(Na^+) \approx 4.5$ (Buchner et al., 1999b), $Z_{ib}^0(Mg^{2+}) \approx 14$ (Buchner et al., 2004; Akilan et al., 2006a), $Z_{ib}^0(Ni^{2+}, Co^{2+}) \approx 17$ (Chen et al., 2005), $Z_{ib}^0(Cu^{2+}) \approx 19$ (Akilan et al., 2006b). This is consistent with the much higher surface-charge density of Al^{3+} and its correspondingly large Gibbs energy of hydration (Marcus, 1985). X-ray diffraction data (Bol and Welzen, 1977; Caminiti et al., 1979; Caminiti and Radnai, 1980) suggest a hydration number of 18 for a fully hydrated $Al^{3+}(aq)$ complex ion, corresponding to a CN of six H_2O molecules in the primary hydration shell and a well-developed second hydration sphere containing 12 water molecules. This is consistent with the need to use a (6 + 12) hydration model for *ab initio* calculation of the Raman spectra of unassociated $Al^{3+}(aq)$ to accurately account for the observed band positions (Rudolph et al., 2000). Computer simulations are unanimous that Al^{3+} has a CN of 6 with an octahedral primary hydration shell (Martinez et al., 1999; Lauenstein et al., 2000; Hofer et al., 2005). These simulations also agree on the existence of a second hydration shell, albeit with differing numbers of bound water molecules: ~14 (Martinez et al., 1999), ~19 (Lauenstein et al., 2000) and 12.2 (Hofer et al., 2005). The most elaborate investigation (Hofer et al., 2005) even suggests a third shell encompassing on average ~37 water molecules for infinitely dilute $Al^{3+}(aq)$. The dynamics of these molecules are naturally less affected than those in the second and (especially) first shells but they still exhibit a preferential orientation imposed by the cation. The present DRS result of $Z_{ib}^0(Al^{3+}) \approx 30$ is broadly compatible with the scenario of 6 tightly, 12 moderately, and at least some weakly-bound (and thus partially immobilized) water molecules, as proposed by Hofer et al. (2005).

In more concentrated solutions, where there is stronger competition among the ions for water molecules, the value of $Z_{ib}(Al^{3+}) \approx 8.5$ still indicates the presence of at least a partial second hydration shell. These observations are consistent with the unusual persistence of 2SIPs and (especially) SIPs at high solute concentrations (Fig. 6).

Given the evidence for the existence of at least a partial 3rd hydration shell around $Al^{3+}(aq)$ in dilute solutions, it is reasonable to ask whether there is any evidence for a triple-solvent separated ion pair of the type proposed erroneously (Rudolph et al., 2003; Chen et al., 2005) by Rull et al. (1994) for $MgSO_4(aq)$. Such a species would have an extremely large dipole moment and should therefore be readily detectable in the DR spectrum at low frequencies. No such species is discernible in the present spectra even in the most dilute solutions. Furthermore, given that the present value of K_A^0 is in broad agreement with the values obtained from thermodynamic measurements, it is difficult to accept that a significant amount of ion association has been missed in the present study. All the features observed in the current DR spectra of $Al_2(SO_4)_3(aq)$ can be explained in terms of the presence of hydrated 2SIPs, SIPs and CIPs along with even more strongly hydrated free ions, although DRS-undetectable triple ions $Al(SO_4)_2^-(aq)$ are almost certainly present.

4.3. Implications of the present work

The positive and quantitative identification of all three ion-pair types (2SIPs, SIPs and CIPs) in the present study, where previous attempts both by DRS (Kaatze and Giese, 1987) and UA (Bonsen et al., 1978; Kaatze et al., 1999) were only partially successful, represents a significant advance in understanding the nature of aluminum sulfate solutions. In particular, it directly explains why the formation constants for $AlSO_4^+(aq)$ obtained by ^{27}Al NMR and Raman spectroscopy (Akitt et al., 1985; Rudolph and Schönherr, 1991a,b), although in excellent agreement with each other, are almost four orders of magnitude smaller than the values obtained from thermodynamic measurements (Ridley et al., 1999). Note that the inability of ^{27}Al NMR and Raman spectroscopy to detect the presence of 2SIPs and SIPs (Hefter, 2006), which produces the low apparent formation constant, does not invalidate the comparison of CIP concentrations in Fig. 6 because each technique (DRS, NMR and Raman) directly detects the concentration of CIPs.

The persistence of 2SIPs and especially SIPs even at high concentrations of aluminum sulfate also helps to explain why the fitting of activity/osmotic data for this salt using models such as that of Pitzer (Reardon, 1988) that ignore existence of such species, requires so many empirical parameters.

Although restricted to one salt at one temperature, the present results, in combination with our earlier studies (Akilan et al., 2006a,b and references therein), suggest that ion pairing is a major or even the dominant feature of all aqueous solutions of electrolytes containing highly charged ions in spite of the strong hydration of such ions. Progress in electrolyte theory would seem to require explicit recognition of the species that are present in even nominally strong electrolyte solutions.

The present data also provide direct evidence, via the values of Z_{ib} (Fig. 8), to support the notion of a second and possibly even a third hydration shell for $Al^{3+}(aq)$ as has been invoked in Raman spectroscopy (Rudolph et al., 2000) and computational studies (Hofer et al., 2005 and references therein) respectively.

5. CONCLUSIONS

The present investigation shows the power of modern broadband DRS as a tool for studying ion pairing and ion hydration in highly charged electrolyte solutions. The existence of all three types of 1–1 ion pairs (2SIPs, SIPs and CIPs) has been established in aqueous solutions of $Al_2(SO_4)_3$ at 25 °C. Where direct comparisons are possible (e.g., for CIP concentrations) the present results are in good agreement with literature measurements using UA, pressure-jump, ^{27}Al NMR and Raman. The overall standard association constant (K_A^0) for $AlSO_4^+(aq)$ lies within the range of values reported from the reliable thermodynamic studies and is in good agreement with the most recent potentiometric study of Xiao et al. (2002) after correction for DRS-undetectable $Al(SO_4)_2^-(aq)$. Analysis of the dielectric response of the solvent has indicated that the hydration of Al^{3+} is extremely strong with significant effects even beyond the second hydration shell.

ACKNOWLEDGMENTS

The authors thank Prof. W. Kunz for the provision of laboratory facilities at Regensburg, the Deutsche Forschungsgemeinschaft for a Mercator Visiting Professorship to G.H. and Murdoch University for partial support for W.W.R. The authors appreciate the valuable comments and suggestions of Associate Editor Dr. D. J. Wesolowski during the preparation of this manuscript.

APPENDIX A. CORRECTION OF THE FREE Al^{3+} AND SO_4^{2-} CONCENTRATIONS FOR THE FORMATION OF $Al(SO_4)_2^-$

From the DRS data and the (analytical) aluminum sulfate concentration, c, the total concentration of aluminum (c_A^t) and sulfate (c_S^t) ions that are not associated in 1:1 stoichiometry (CIP, SIP, or 2SIP), can be calculated for each sample:

$$c_A^t = 2c - c_{CIP} - c_{SIP} - c_{2SIP}$$
$$c_S^t = 3c - c_{CIP} - c_{SIP} - c_{2SIP}$$

Using the known mass of water per 1 L solution, $m_W = \rho - cM$, where ρ is the density of the solution and M the molar mass of $Al_2(SO_4)_3$, the molalities, m_A^t and m_S^t, can be calculated from c_A^t and c_S^t: $m = c/m_W$.

The formation of $Al(SO_4)_2^-$ can be described by the equilibrium

$$A + 2S \rightleftharpoons TI$$

with an equilibrium quotient, expressed in molalities, of

$$Q_2 = \frac{m_{TI}}{m_A m_S^2}.$$

Q_2 was taken from Xiao et al. (2002), who reported a correlation valid up to $I_m = 1\ \mathrm{mol\,kg^{-1}}$ in NaOTf media. At higher I_m (i.e., for most of the samples of the current study), the value of Q_2 at $I_m = 1$ was used because the calculation is anyway only approximate due to the media differences.

From the mass balance of the equilibrium:

$$m_A^t = m_A + m_{TI}$$
$$m_S^t = m_S + 2m_{TI}$$

Thus, $Q_2 = \frac{m^t_A - m_A}{m_A\left(m^t_S - 2m^t_A + 2m_A\right)^2}$, which can be solved for m_A. Then, m_{TI} and m_S can be calculated and yield, after conversion back to mol L^{-1} concentrations, the concentrations of free Al^{3+} and ${SO_4}^{2-}$, c^*_+ and c^*_-, corrected for TI formation.

Corrected equilibrium constants K^*_1 and K^*_a (Table 5 and Fig. 7b) can then be calculated according to Eq. (4), with c^*_+ and c^*_- substituted for c_+ and c_-.

REFERENCES

Akilan C., Hefter G., Rohman N. and Buchner R. (2006a) Temperature effects on ion association and hydration in $MgSO_4$ by dielectric spectroscopy. *ChemPhysChem* **7**, 2319–2330.

Akilan C., Hefter G., Rohman N. and Buchner R. (2006b) Ion association and hydration in aqueous solutions of copper(II) sulfate from 5 to 65 °C by dielectric spectroscopy. *J. Phys. Chem. B* **110**, 14961–14970.

Akitt J. W. and Howarth O. W. (1989) Isotope effects in the nuclear magnetic resonance spectra of mixed aqua complexes of Al^{III}. *J. Chem. Soc., Faraday Trans. 1* **85**, 121–125.

Akitt J. W., Greenwood N. N. and Lester G. D. (1969) Aluminium-27 nuclear magnetic resonance studies of acidic solutions of aluminium salts. *J. Chem. Soc. A* **1969**, 803–807.

Akitt J. W., Greenwood N. N. and Khandelwal B. L. (1972) Aluminium-27 nuclear magnetic resonance studies of sulphato-complexes of the hexa-aquo aluminium ion. *J. Chem. Soc., Dalton Trans.* **1972**, 1226–1229.

Akitt J. W., Farnsworth J. A. and Letellier P. (1985) Nuclear magnetic resonance and molar-volume studies of the complex formed between aluminium(III) and the sulphate anion. *J. Chem. Soc., Faraday Trans. 1* **81**, 193–205.

Archer D. G. and Wang P. (1990) The dielectric constant of water and Debye–Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **19**, 371–411.

Åström M. and Björklund A. (1995) Impact of acid sulfate soils on stream water geochemistry in western Finland. *J. Geochem. Explor.* **55**, 163–170.

Atkinson G. and Petrucci S. (1966) Ion association of magnesium sulfate in water at 25 °C. *J. Phys. Chem.* **70**, 3122–3128.

Baes C. F. and Mesmer R. E. (1976) *The Hydrolysis of Cations*. Wiley, New York.

Barthel J., Bachhuber K., Buchner R., Hetzenauer H. and Kleebauer M. (1991) A computer-controlled system of transmission lines for the determination of the complex permittivity of lossy liquids between 8.5 and 90 GHz. *Ber. Bunsen-Ges. Phys. Chem.* **95**, 853–859.

Barthel J., Hetzenauer H. and Buchner R. (1992) Dielectric relaxation of aqueous electrolyte solutions. II. Ion-pair relaxation of 1:2, 2:1, and 2:2 electrolytes. *Ber. Bunsen-Ges. Phys. Chem.* **96**, 1424–1432.

Barthel J., Krienke H. and Kunz W. (1998) *The Physical Chemistry of Electrolyte Solutions—Modern Aspects*. Steinkopff-Springer, Darmstadt, Berlin.

Behr B. and Wendt H. (1962) Fast ion reactions in solution. I. Formation of the aluminium sulfato complex. *Z. Elektrochem.* **66**, 223–228.

Bol W. and Welzen T. (1977) The interpretation of X-ray diffraction by aqueous solutions of aluminum(III) nitrate and chromium(III) nitrate. *Chem. Phys. Lett.* **49**, 189–192.

Bonsen A., Knoche W., Berger W., Giese K. and Petrucci S. (1978) Ultrasonic relaxation studies in aqueous solutions of aluminum sulfate and scandium sulfate. *Ber. Bunsen-Ges. Phys. Chem.* **82**, 678–683.

Buchner R. (2004). In *Novel Approaches to the Structure and Dynamics of Liquids NATO Science Series II*, 133 (eds. J. Samios and V. A. Durov). Kluwer, Dordrecht.

Buchner R. and Barthel J. (2001) Dielectric relaxation in solutions. *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.* **97**, 349–382.

Buchner R. and Hefter G. (2002) Dielectric spectroscopy of cesium fluoride in methanol. *J. Solution Chem.* **31**, 521–535.

Buchner R., Capewell S. G., Hefter G. and May P. M. (1999a) Ion-pair and solvent relaxation processes in aqueous Na_2SO_4 solutions. *J. Phys. Chem. B* **103**, 1185–1192.

Buchner R., Hefter G. T. and May P. M. (1999b) Dielectric relaxation of aqueous NaCl solutions. *J. Phys. Chem. A* **103**, 1–9.

Buchner R., Hölzl C., Stauber J. and Barthel J. (2002) Dielectric spectroscopy of ion-pairing and hydration in aqueous tetra-*n*-alkylammonium halide solutions. *Phys. Chem. Chem. Phys.* **4**, 2169–2179.

Buchner R., Samani F., May P. M., Sturm P. and Hefter G. (2003) Hydration and ion pairing in aqueous sodium oxalate solutions. *ChemPhysChem* **4**, 373–378.

Buchner R., Chen T. and Hefter G. (2004) Complexity in "simple" electrolyte solutions: ion pairing in $MgSO_4$(aq). *J. Phys. Chem. B* **108**, 2365–2375.

Caminiti R. and Radnai T. (1980) X-Ray diffraction study of a concentrated $Al(NO_3)_3$ solution. *Z. Naturforsch., A: Phys. Sci.* **35a**, 1368–1372.

Caminiti R., Licheri G., Piccaluga G., Pinna G. and Radnai T. (1979) Order phenomena in aqueous $AlCl_3$ solutions. *J. Chem. Phys.* **71**, 2473–2476.

Chen T., Hefter G. and Buchner R. (2005) Ion association and hydration in aqueous solutions of nickel(II) and cobalt(II) sulfate. *J. Solution Chem.* **34**, 1045–1066.

Dickson A. G., Wesolowski D. J., Palmer D. A. and Mesmer R. E. (1990) Dissociation constant of bisulfate ion in aqueous sodium chloride solutions to 250 °C. *J. Phys. Chem.* **94**, 7978–7985.

Eigen M. and Tamm K. (1962) Sound absorption in electrolytes as a consequence of chemical relaxation. I. Relaxation theory of stepwise dissociation. *Z. Elektrochem.* **66**, 107–121.

Fukasawa T., Sato T., Watanabe J., Hama Y., Kunz W. and Buchner R. (2005) Relation between dielectric and low-frequency Raman spectra of hydrogen-bond liquids. *Phys. Rev. Lett.* **95**, 197802.

Hartikainen H. and Yli-Halla M. (1986) Oxidation-induced leaching of sulphate and cations from acid sulphate soils. *Water, Air, Soil Pollut.* **27**, 1–13.

Hasted J. B. (1972) *Water a Comprehensive Treatise*. (ed. F. Franks) Plenum, New York, vol. 1.

Hefter G. T. (1982) Calculation of liquid junction potentials for equilibrium studies. *Anal. Chem.* **54**, 2518–2524.

Hefter G. T. (2006) When spectroscopy fails: the measurement of ion pairing. *Pure Appl. Chem.* **78**, 1571–1586.

Hofer T. S., Randolf B. R. and Rode B. M. (2005) Influence of polarization and many body quantum effects on the solvation shell of Al(III) in dilute aqueous solution-extended ab initio QM/MM MD simulations. *Phys. Chem. Chem. Phys.* **7**, 1382–1387.

Ivanov A. A., Kirilenko I. A., Selin A. N. and Zaitseva L. A. (1987) Properties of concentrated aqueous solutions of aluminium sulphate. *Zh. Neorg. Khim.* **32**, 1052–1056.

Jha S. K., Jha S. N., Mahaseth A. and Agrawal S. C. (1989) A recalculation of the first dissociation constant of aluminium sulfate ion $(Al(SO_4)_2{}^-)$ and the corresponding thermodynamic functions. *J. Ind. Chem. Soc.* **66**, 196–197.

Jin T. and Ichikawa K. (1988) An aluminium-27 nuclear magnetic resonance study of ligand exchange. *J. Chem. Soc., Faraday Trans. 1* **84**, 3015–3025.

Justice J. C. (1983). In *Comprehensive Treatise of Electrochemistry*, 5 (eds. B. O. Conway, J. O. Bockris and E. Yeager). Plenum, New York, Chap. 2.

Kaatze U. and Giese K. (1987) Dielectric spectroscopy on some aqueous solutions of 3:2 valent electrolytes. A combined frequency and time domain study. *J. Mol. Liq.* **36**, 15–35.

Kaatze U., Telgmann T. and Miecznik P. (1999) Solvatomer dynamics of aluminium sulfate in dimethyl sulfoxide/water mixtures. *Chem. Phys. Lett.* **310**, 121–129.

Kaatze U., Hushcha T. O. and Eggers F. (2000) Ultrasonic broadband spectrometry of liquids: a research tool in pure and applied chemistry and chemical physics. *J. Solution Chem.* **29**, 299–368.

Kalidas C., Knoche W. and Papadopoulos D. (1971) On the mechanism of ligand substitution in weak complexes III. *Ber. Bunsen-Ges. Phys. Chem.* **75**, 106–110.

Knoche W. and López-Quintela M. A. (1983) Stability constants of Al(III) complexes in aqueous solutions obtained from kinetic measurements. *Thermochim. Acta* **62**, 295–306.

Kroschwitz, J. I. (ed.) (1991) *Kirk-Othmer Encyclopedia of Chemical Technology*, fourth ed., Vol. 2, pp. 330–338. Wiley-Interscience, New York.

Kryzhanovskii M. M., Volokhov Y. A., Pavlov L. N., Eremin N. I. and Mironov V. E. (1971) Aluminum sulfate complexes. *Zh. Prikl. Khim. (Leningrad)* **44**, 476–479.

Lauenstein A., Hermansson K., Lindgren J., Probst M. and Bopp P. A. (2000) Molecular dynamics simulation of an aqueous aluminium(III) chloride solution with three-body interactions. *Int. J. Quant. Chem.* **110**, 892–906.

Lo C.-C., Meites L. and Matjević E. (1982) A microcalorimetric investigation of the thermodynamics of formation of the $HSO_4{}^-$, $AlSO_4{}^+$, and $Al(SO_4{}^{2-})$ ions in aqueous solutions at temperatures between 25 and 70 °C. *Anal. Chim. Acta* **139**, 197–205.

Luts P., Vanhees J., Yperman J., Mullens J. and Van Poucke L. C. (1994) The determination of the second dissociation constant of sulfuric acid. *J. Solution Chem.* **23**, 75–80.

Marcus Y. (1985) *Ion Solvation*. Wiley-Interscience, Chichester, UK.

Marcus Y. (1997) *Ion Properties*. Dekker, New York.

Marcus Y. and Hefter G. T. (2006) Ion pairing. *Chem. Rev.* **106**, 4585–4621.

Martinez J. M., Pappalardo R. R. and Sanchez M. E. (1999) First-principles ion–water interaction potentials for highly charged monatomic cations. Computer simulations of Al^{3+}, Mg^{2+}, and Be^{2+} in water. *J. Am. Chem. Soc.* **121**, 3175–3184.

Matsushima Y., Matsunaga A., Sakai K. and Okuwaki A. (1988) Potentiometric studies on sulfato complex of aluminium(III) in aqueous solution at elevated temperatures. *Bull. Chem. Soc. Jpn.* **61**, 4259–4263.

McIntyre J. F., Foley R. T. and Brown B. F. (1982) Ultraviolet spectra of aluminium salt solutions. *Inorg. Chem.* **21**, 1167–1172.

Miceli J. and Stuehr J. (1968) Ligand penetration rates into metal ion coordination spheres. Aluminum(III), gallium(III), and indium(III) sulfates. *J. Am. Chem. Soc.* **90**, 6967–6972.

Nishide T. and Tsuchiya R. (1965) The formation of $Al^{3+} - SO_4{}^{2-}$ ion-pair in an aqueous solution of potassium aluminum alum. *Bull. Chem. Soc. Jpn.* **38**, 1398–1400.

Powell K. J., Brown P. L., Byrne R. H., Gajda T., Hefter G. T., Sjöberg S. and Wanner H. (2005) Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: The Hg^{2+}–Cl^-, OH^-, $CO_3{}^{2-}$, $SO_4{}^{2-}$ and $PO_4{}^{3-}$ aqueous systems. *Pure Appl. Chem.* **77**, 739–800.

Reardon E. J. (1988) Ion interaction parameters for aluminum sulfate and application to the prediction of metal sulfate solubility in binary salt systems. *J. Phys. Chem.* **92**, 6426–6431.

Ridley M. K., Wesolowski D. J., Palmer D. A. and Kettler R. M. (1999) Association quotients of aluminum sulphate complexes in NaCl media from 50 to 125 °C: results of a potentiometric and solubility study. *Geochim. Cosmochim. Acta* **63**, 459–472.

Robinson R. A. and Stokes R. H. (1970) *Electrolyte Solutions*, second ed. Butterworth, London.

Rossotti H. (1978) *The Study of Ionic Equilibria*. Longman, London.

Rudolph W. W. and Mason R. (2001) Study of aqueous $Al_2(SO_4)_3$ solution under hydrothermal conditions: sulfate ion pairing, hydrolysis, and formation of hydronium alunite. *J. Solution Chem.* **30**, 527–548.

Rudolph W. and Schönherr S. (1989) Raman- und Infrarotspektroskopische Untersuchungen an konzentrierten Aluminium salzlösungen. I. Zur schwingsspektroskopischen Charakterisierung des Hexaquoaluminium(III)-komplexions. *Z. Phys. Chem. (Leipzig)* **270**, 1121–1134.

Rudolph W. and Schönherr S. (1991a) Raman- und Infrarotspektroskopische Untersuchungen an konzentrierten Aluminiumsalzlösungen. II. Zur Sulfatkomplexbildung in Aluminiumsulfat-Lösungen und-Hydratschmelzen. *Z. Phys. Chem. NF* **172**, 31–48.

Rudolph W. and Schönherr S. (1991b) Raman- und Infrarotspektroskopische Untersuchungen an konzentrierten Aluminiumsalzlösungen. III. Valenz- und Deformationsschwingungsbereich des Wassers im Hexaaquo-Al(III)-Komplexion. *Z. Phys. Chem. NF* **173**, 167–177.

Rudolph W. W., Mason R. and Pye C. C. (2000) Aluminium(III) hydration in aqueous solutions. A Raman spectroscopic investigation and an *ab initio* molecular orbital study of aluminium(III) water clusters. *Phys. Chem. Chem. Phys.* **2**, 5030–5040.

Rudolph W. W., Irmer G. and Hefter G. T. (2003) Raman spectroscopic investigation of speciation in $MgSO_4$(aq). *Phys. Chem. Chem. Phys.* **5**, 5253–5261.

Rull F., Balarew C., Alvarez J. L., Sobron F. and Rodriguez A. (1994) Raman spectroscopic study of ion association in aqueous magnesium sulfate solutions. *J. Raman Spectrosc.* **25**, 933–941.

Schrödle S. (2005) Effects of non-ionic surfactants and related compounds on the cooperative and molecular dynamics of their aqueous solutions. Ph.D. thesis, Regensburg University.

Schrödle S., Buchner R. and Kunz W. (2004) Effect of the chain length on the inter- and intramolecular dynamics of liquid oligo(ethylene glycol)s. *J. Phys. Chem. B* **108**, 6281–6287.

Sharma L. and Prasad B. (1970) Ionic equilibria in tri-bivalent salts and corresponding heats of dissociation: I. Aluminium sulphate. *J. Ind. Chem. Soc.* **47**, 693–698.

Tromans A., May P. M., Hefter G., Sato T. and Buchner R. (2004) Ion pairing and solvent relaxation processes in aqueous solutions of sodium malonate and sodium succinate. *J. Phys. Chem. B* **108**, 13789–13795.

Vasil'eva L. F., Gitis E. B. and Shmorgun V. I. (1976) Electric conductivity of aluminum sulfate aqueous solutions. *Zh. Prikl. Khim. (Leningrad)* **49**, 2539–2541.

Vogel A. I. (1961) *A Text-Book of Quantitative Inorganic Analysis*, third ed. Longman, London.

Xiao C., Wesolowski D. J. and Palmer D. A. (2002) Formation quotients of aluminium sulphate complexes in $NaCF_3SO_3$ media at 10, 25, and 50 °C from potentiometric titrations using a mercury/mercurous sulfate electrode concentration cell. *Environ. Sci. Technol.* **36**, 166–173.

Zhang Y.-H. and Chan C. K. (2000) Study of contact ion pairs of supersaturated magnesium sulfate solutions using Raman scattering on levitated single droplets. *J. Phys. Chem. A* **104**, 9191–9196.

Zotov V. (1971) Dependence of the composition of alunite on the temperature of its formation. *Geochem. Int.* **1971**, 71–75.

Associate editor: David J. Wesolowski