

When spectroscopy fails: The measurement of ion pairing*

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Abstract: Spectroscopic techniques such as UV/vis, NMR, and Raman are powerful tools for the investigation of chemical speciation in solution. However, it is not widely recognized that such techniques do not always provide reliable information about ion association equilibria. Specifically, spectroscopic measurements do not in general produce thermodynamically meaningful association constants for non-contact ion pairs, where the ions are separated by one or more solvent molecules. Such systems can only be properly quantified by techniques such as dielectric or ultrasonic relaxation, which can detect all ion-pair types (or equilibria), or by traditional thermodynamic methods, which detect the overall level of association. Various types of quantitative data are presented for metal ion/sulfate systems in aqueous solution that demonstrate the inadequacy of the major spectroscopic techniques for the investigation of systems that involve solvent-separated ion pairs. The implications for ion association equilibria in general are briefly discussed.

Keywords: ion pairing; spectroscopy; NMR; Raman; dielectric relaxation; UV/vis; ultrasonic relaxation.

INTRODUCTION

There is no doubt that UV/vis (electronic), nuclear magnetic resonance (NMR), and vibrational (especially Raman) spectroscopies are extremely powerful tools for studying chemical speciation in solution. Used separately or in combination, such techniques have been employed successfully to measure the stability (association) constants of hundreds of metal-ligand (including ion-ion) systems [1–3]. Spectroscopic methods often have advantages over other techniques, especially for the study of very complicated equilibria [4]. They have provided valuable information about the binding sites of multidentate ligands [5] and on the kinetics and structures of many species in solution [6,7].

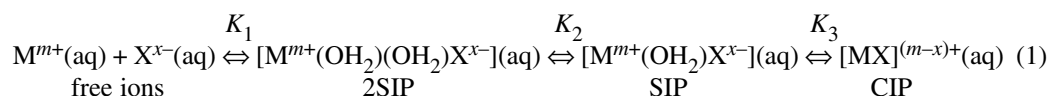
What is less widely recognized is that these popular spectroscopic techniques also have some significant limitations. Specifically, this paper aims to show that extreme care must be exercised in interpreting UV/vis, NMR, or Raman spectroscopic data whenever non-contact (solvent-separated) ion pairs are present in significant amounts in solution.

ION ASSOCIATION IN SOLUTION

Ions of opposite charge are generally considered to associate (form complexes) in aqueous solution via the well-known Eigen mechanism [8–10]. This mechanism (eq. 1) posits that ions combine initially

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with their solvation sheaths essentially intact, forming a double-solvent-separated ion pair (2SIP) or, in coordination chemistry terminology, an outer–outer-sphere complex. The two solvent molecules between the ions may then be ejected to form successively a solvent-shared ion pair (SIP) or outer-sphere (bridged) complex, and ultimately a contact ion pair (CIP) or inner-sphere complex in which the cation and anion are in direct physical contact.



Note that this mechanism is well established for highly charged ions in aqueous solutions, but each step is not always significant (observable) for every system. Although few techniques are able to distinguish between these three types of species, this mechanism has been widely accepted in the interpretation of solution equilibria and kinetics [10].

THERMODYNAMICS OF ION ASSOCIATION IN SOLUTION

Traditional thermodynamic methods such as potentiometry, cryoscopy, etc., detect only the overall association represented (assuming 1:1 stoichiometry) by the equilibrium



for which the corresponding equilibrium (association) constant, K_A , may be written, ignoring activity coefficients:

$$K_A = \frac{[MX^{(m-x)+}(\text{aq})]}{[M^{m+}(\text{aq})][X^{x-}(\text{aq})]} \quad (3)$$

where here and subsequently the square brackets denote equilibrium concentrations. Of course, complexes with other stoichiometries may also form, but these need not concern us here. The important point to note is that thermodynamic measurements do not differentiate between dissolved species having the same stoichiometry but differing levels of hydration, i.e., between 2SIPs, SIPs, and CIPs [11–13]. The same is true for conductometric measurements where no distinction is thought to exist between the various (hydrated) ion-pair types of the same stoichiometry, especially for symmetrical electrolytes where the ion pairs are neutral [14]. For this reason, and for convenience, conductivity will be referred to throughout this article as a “thermodynamic” technique even though it is, of course, a transport property.

The stepwise equilibrium constants K_i corresponding to eq. 1 can be written (again ignoring activity coefficients and dropping the “aq” symbol for convenience):

$$K_1 = \frac{[2\text{SIP}]}{[M^{m+}][X^{x-}]}; \quad K_2 = \frac{[\text{SIP}]}{[2\text{SIP}]}; \quad K_3 = \frac{[\text{CIP}]}{[\text{SIP}]} \quad (4)$$

from which it can be readily shown that

$$K_A = K_1 + K_1K_2 + K_1K_2K_3 \quad (5)$$

Note that K_A is calculable from K_1 , but that the reverse is not the case. For many applications, and in particular for chemical speciation modeling, only the value of K_A is required. On the other hand, for other purposes such as kinetic studies and molecular modeling, knowledge of K_i (i.e., the relative amounts of 2SIPs, SIPs and CIPs) may be essential.

MEASUREMENT OF EQUILIBRIUM CONSTANTS

Very few techniques have a general capability for detecting all of the ion-pair types and/or their associated equilibria. The most broadly applicable are undoubtedly the relaxation methods. Of these, dielectric relaxation spectroscopy (DRS) is probably the most useful [13,15,16]. DRS measures the complex electric permittivity of a sample in response to an applied electromagnetic field in the microwave region ($0.01 \leq \nu/\text{GHz} \leq 100$), as a function of the frequency of that field, ν . The use of DRS for quantifying ion-pairing equilibria is discussed at length elsewhere [13,15,16].

A key feature of DRS is that it detects species possessing a permanent dipole moment, μ . DRS is therefore able to discriminate between ion-pairs (which are dipoles) and free ions (for which μ is generally zero). More importantly, the amplitude (magnitude) of the DRS response is proportional to μ^2 and thus, since μ is given by the size of the charges multiplied by their separation, DRS possesses a unique sensitivity towards the various ion-pair types in the order: 2SIP > SIP > CIP. These characteristics make DRS particularly apt for the study of ion-pairing processes. In favorable cases, it is also possible to determine the kinetics of ion pair formation and dissociation [17] and even structural information [18]. On the downside, DR spectra in aqueous solutions at moderate frequencies are dominated by the solvent-water response, which must be carefully subtracted to reveal the (usually much smaller) ion-pair contributions. At sufficiently low frequencies, the dielectric response is eventually swamped by the electrical conductivity of the free ions. Coupled with the technical complexity of the instrumentation, these factors have tended to restrict the application of DRS to specialist laboratories [15,16].

The other important relaxation technique is that of ultrasonic absorption, which was used by Eigen and Tamm [8,9] originally to establish the existence of eq. 1. Ultrasonic relaxation (USR) involves measuring the absorbance by a sample of sound waves at ultrasonic frequencies. USR actually detects equilibria (the perturbation of which by the ultrasonic wave causes their partial absorption) rather than species [19]. It is then necessary to make (reasonable) assumptions to deduce information about the species involved. Despite its complexity, USR is a powerful and accurate method for determining both the equilibrium constants for ion-pairing (K_1 values) and the kinetics of their interconversion [19].

ION ASSOCIATION IN METAL-SULFATE SYSTEMS

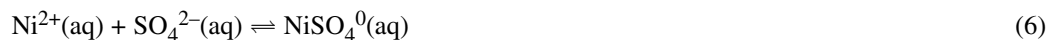
Divalent and trivalent metal sulfates are classic systems in the study of solution equilibria [20–22]. Most importantly in the present context, for such salts both the cation and the anion are strongly hydrated [23] and thus will have a propensity to form non-CIPs. Such systems have been investigated extensively by a variety of techniques [1,3,20–22]. They exhibit a moderate level of association and thus, unlike many ion-paired systems, are relatively easy to quantify; nor do they in general suffer complications from limited solubility. Higher-valent metal sulfate solutions are also of practical importance because of their occurrence in natural waters [24] and many hydrometallurgical process solutions [25], and their use as synthetic reagents [26].

For these reasons, and for convenience, the present paper will focus on the quantification of ion association in higher-valent metal sulfate systems. However, it is emphasized that the findings have implications far beyond this limited range of systems.

CASE STUDY 1: THE $\text{Ni}^{2+}/\text{SO}_4^{2-}$ SYSTEM

Thermodynamic methods

The association between nickel(II) and sulfate ions in aqueous solution can be represented by the equilibrium



This system has been studied extensively [1,3,27] although, as is encountered frequently for higher-valent metal ion-sulfate systems, the uncertainty in the measured constant is much larger than might be expected for such an apparently simple equilibrium. The reasons for this are only partly related to the presence of non-CIPs, which is the present focus. Other factors include the dearth of suitable probes for the interacting species [21], the large Debye–Hückel term associated with highly charged ions [20] and the inadequacy of current models for activity coefficients [28]. The last two make problematic the rigorous extrapolation or correction to infinite dilution of data obtained at finite ionic strengths.

For the $\text{Ni}^{2+}/\text{SO}_4^{2-}$ system, the five available high-quality conductivity studies [27] are in reasonable agreement, giving $\log K_A^0 = 2.28 \pm 0.12$. Other studies [1,3] using hydrogen electrode potentiometry, chromatography, and cryoscopy (the last at $\sim 0^\circ\text{C}$, but note that $\Delta_r H^0 \approx 0$ for equilibrium 6) give similar results.

Relaxation methods

Good-quality studies by both DRS [29] and USR [30,31] exist for the $\text{Ni}^{2+}/\text{SO}_4^{2-}$ system. DRS detects all three ion pair types: 2SIPs, SIPs, and CIPs, as shown in the dielectric loss spectrum, Fig. 1, which also includes the individual contributions from the various ion-pair types and the solvent [29]. Despite the broadness of the dielectric loss spectra, the reliable identification of individual species is achieved as for any spectroscopic method: by the rise and fall of intensity (amplitude in DRS) at specific frequencies in the spectrum as a function of species concentrations. This is seen more easily in Fig. 2, which presents what is in essence a series of “difference” spectra from which the solvent contribution has been removed [29]. The solute contributions so obtained clearly show behavior consistent with three distinct processes/species.

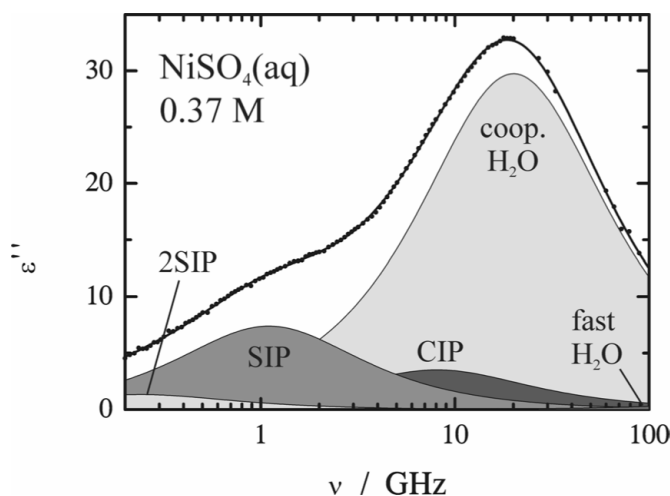


Fig. 1 Dielectric loss (ϵ'') spectrum for 0.37 M $\text{NiSO}_4(\text{aq})$ at 25°C , showing the contributions due to the solvent and the various types of ion pairs [29].

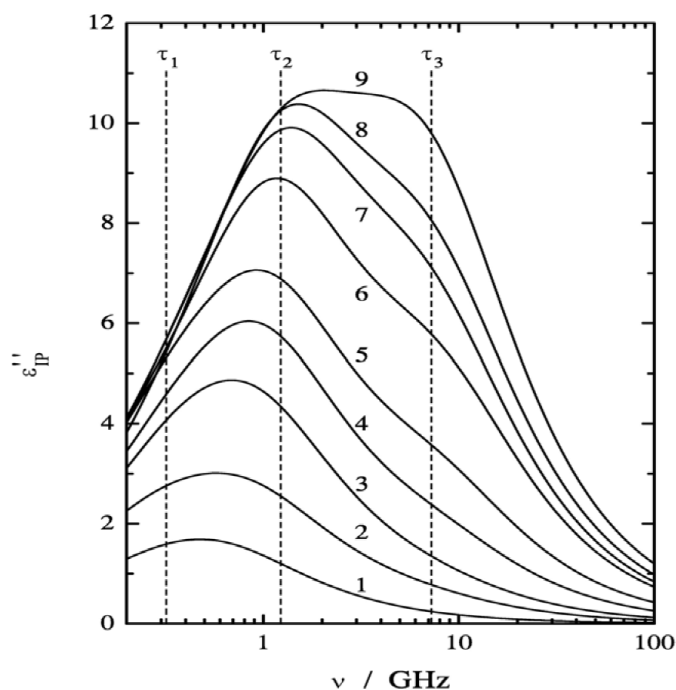


Fig. 2 Solute contribution (ϵ''_{IP}) to the dielectric loss spectra of $\text{NiSO}_4(\text{aq})$ at 25 °C as a function of concentration (curves 1 to 9): $c/M = 0.025, 0.05, 0.10, 0.15, 0.20, 0.37, 0.65, 0.80, 1.40$ [29]. The dotted lines indicate the positions of the loss maxima for (L to R): 2SIPs, SIPs, and CIPs.

A number of USR studies of $\text{NiSO}_4(\text{aq})$ solutions have been published [30,31]. Although there are some differences, the overall picture is remarkably similar to the DRS: three equilibria are detected with K_i values that are almost identical with the DRS results (Fig. 3). Equally important, the magnitude of K_A calculated from the DRS/USR K_i values via eq. 5 is in good agreement with the thermodynamic results discussed above.

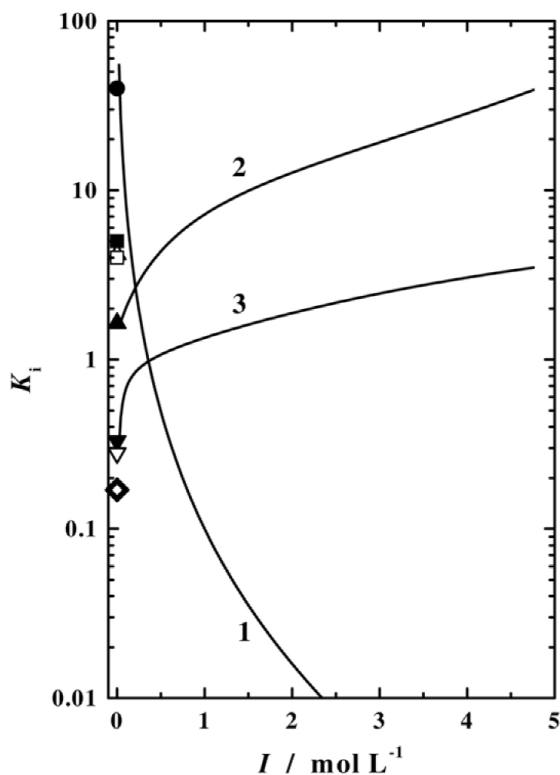


Fig. 3 Stepwise stability constants K_i derived from DRS measurements [29] for the formation of NiSO_4^0 (aq) ion pairs (see eq. 4) as a function of ionic strength I : 1, K_1 (2SIP); 2, K_2 (SIP); 3, K_3 (CIP). Symbols represent K_i values derived from USR data [30,31].

Spectroscopic methods

Neither NMR nor Raman spectroscopy are easily applicable to the $\text{Ni}^{2+}/\text{SO}_4^{2-}$ system, as the solutions are paramagnetic and absorb at most wavelengths in the UV/vis region (corresponding to the common laser Raman sources). The latter implies that electronic (UV/vis) spectroscopy should be a useful tool for investigating $\text{Ni}^{2+}/\text{SO}_4^{2-}$ association.

Figure 4 shows the electronic spectrum of a solution of Ni^{2+} with and without SO_4^{2-} . Despite valiant attempts by some authors [32] to obtain complexation information from them, these spectra are to all intents and purposes identical. That is, UV/vis spectroscopy suggests that $K_A \approx 0$. This result is more than two orders of magnitude below what is determined by the traditional thermodynamic methods *and* both of the relaxation techniques (DRS and USR). Superficially, one might conclude that UV/vis spectrometry was simply “inappropriate” for the investigation of $\text{Ni}^{2+}/\text{SO}_4^{2-}$ association. The reason is of course that the electronic absorption bands in the UV/vis range correspond to *d-d* transitions of Ni^{2+} [33]. Presumably, there is insufficient change in the chromophore when $\text{Ni}(\text{OH}_2)_6^{2+}$ forms a 2SIP or SIP (where SO_4^{2-} is not coordinated directly to the Ni^{2+}) or even a CIP (where a Ni–OSO₃ bond substitutes for a Ni–OH₂ bond) to produce measurable changes in the UV/vis spectrum. Regardless of the cause, the value of $K_A \approx 0$ implied by UV/vis spectroscopy is clearly “wrong”.

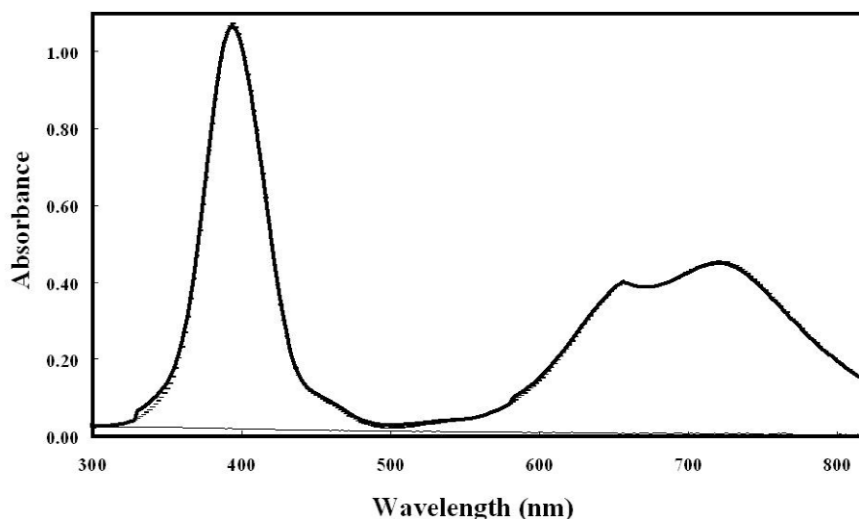


Fig. 4 UV/vis spectra at 25 °C of: 0.2 M Na_2SO_4 (bottom curve), 0.2 M $\text{Ni}(\text{ClO}_4)_2$ (dotted curve, barely visible) and 0.2 M $\text{Na}_2\text{SO}_4 + 0.2 \text{ M Ni}(\text{ClO}_4)_2$ (top curve).

CASE STUDY 2: THE $\text{Cu}^{2+}/\text{SO}_4^{2-}$ SYSTEM

Thermodynamic methods

The association between Cu^{2+} and SO_4^{2-} has only one significant stoichiometry:



There have been six high-quality conductometric studies of $\text{CuSO}_4(\text{aq})$ solutions since 1938 [34]. The values obtained range from 2.27 to 2.43 with an average $\log K_A^0 = 2.35 \pm 0.05$. Numerous other thermodynamic techniques have also been employed and give values ranging from 2.19 to 2.40 with an average of $\log K_A^0 = 2.2 \pm 0.1$ [1,3,34]. Interestingly, with the exception of one investigation employing the hydrogen electrode (which is not optimal for studying the $\text{Cu}^{2+}/\text{SO}_4^{2-}$ system) no high-quality potentiometric measurements have been published [34].

Relaxation methods

Both dielectric [35] and USR [31,36] measurements have been made on aqueous solutions of CuSO_4 . As for $\text{NiSO}_4(\text{aq})$, both techniques detect three ion-pair types/equilibria and give K_1 values that are in good agreement with each other. Equally important, they combine via eq. 5 to give values of $\log K_A^0$ that fall within the range of values obtained by thermodynamic methods.

Spectroscopic methods

The paramagnetic nature of $\text{Cu}^{2+}(\text{aq})$ precludes direct measurement of its association with SO_4^{2-} by conventional NMR spectroscopy but both Raman and UV/vis can be used.

Despite $\text{CuSO}_4(\text{aq})$ being colored, there is a sufficient “window” in the UV/vis spectrum (see below) to allow Raman spectra to be recorded using a suitable laser source. Early Raman studies, mostly employing the strong $\nu_1(\text{SO}_4^{2-})$ symmetric stretching mode, failed to detect any association in $\text{CuSO}_4(\text{aq})$ [37]. However, it is now known that this was essentially due to the rather large slit-widths then available.

A recent high-quality Raman spectrum of $\text{CuSO}_4(\text{aq})$ [38] shows a definite asymmetry in the $\nu_1(\text{SO}_4^{2-})$ mode (Fig. 5). The observed band can be decomposed into two components: the characteristic “free” SO_4^{2-} mode at $\sim 980 \text{ cm}^{-1}$ and a much less intense mode associated with “complexed” SO_4^{2-} which, for the $\text{Cu}^{2+}/\text{SO}_4^{2-}$ system, occurs at $\sim 988 \text{ cm}^{-1}$. A conventional analysis of these modes (see Case Study 3 below) gives $\log K_A^0 \approx 1$, which is more than an order of magnitude less than the thermodynamic and relaxation values. The origin of this discrepancy is discussed further in Case Study 3.

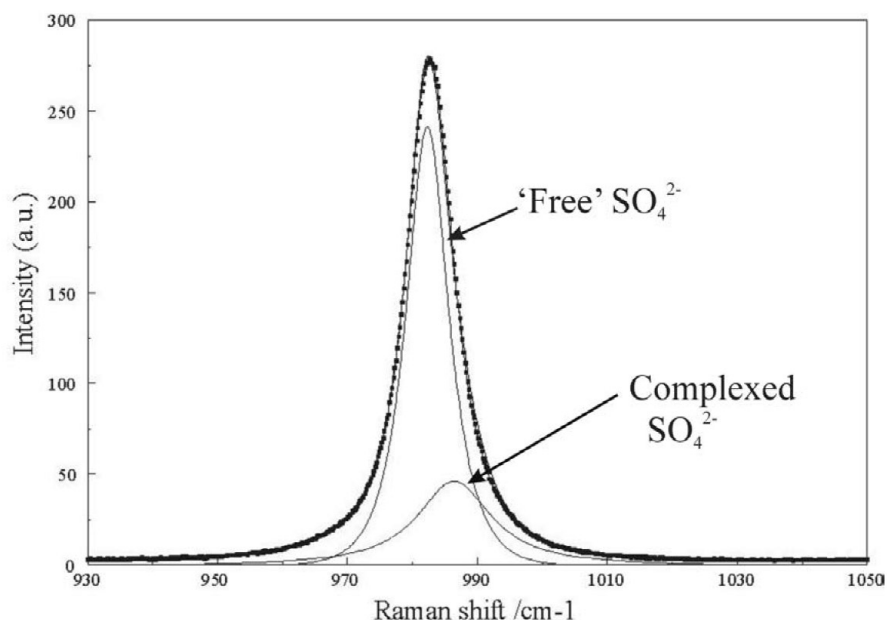


Fig. 5 Raman spectrum of $\sim 0.8 \text{ M CuSO}_4(\text{aq})$ at 25°C , showing the contributions to the $\nu_1(\text{SO}_4^{2-})$ mode from free (at $\sim 980 \text{ cm}^{-1}$) and complexed (at $\sim 988 \text{ cm}^{-1}$) sulfate [38].

In contrast to the problems associated with Raman spectroscopy, the study of the interaction of Cu^{2+} and SO_4^{2-} in aqueous solution by UV/vis spectroscopy has been widely regarded as a paradigm in the measurement of ion association constants. It has been discussed in detail in many classic texts [20–22] and the numerous spectrophotometric results have been critically reviewed under IUPAC auspices [34]. The 10 high-quality studies published to date [34] are in good agreement, with $\log K_A^0 = 2.28 \pm 0.07$ (range 2.15–2.36), which is similar to the values obtained by thermodynamic methods. Thus, it would seem that in spite of the presence of non-CIPs, UV/vis spectroscopy has worked well.

However, these data warrant closer consideration. Typical spectra for the $\text{Cu}^{2+}/\text{SO}_4^{2-}$ system are given in Fig. 6. As for the $\text{Ni}^{2+}/\text{SO}_4^{2-}$ system (see above), no change is observed in the $d-d$ transition, here centered on $\sim 820 \text{ nm}$, when SO_4^{2-} is added to a solution containing Cu^{2+} . However, unlike the $\text{Ni}^{2+}/\text{SO}_4^{2-}$ system, there is a substantial change in the spectrum in the UV region. From its location (at $\sim 260 \text{ nm}$) and absorptivity ($\epsilon \approx 400 \text{ M}^{-1} \text{ cm}^{-1}$) this band would appear to correspond to a ligand-to-metal charge transfer (LMCT), consistent with the relative stability of Cu(I) [33]. Although a LMCT might well detect CIPs and even SIPs, by common consensus (and common sense) it is highly implausible that it would be sensitive to 2SIPs. Accordingly, a potentiometric study using a copper ion-selective electrode was recently undertaken [39]. The results obtained are compared in Fig. 7 with spectrophotometric measurements performed on the same solutions, using modern data processing procedures.

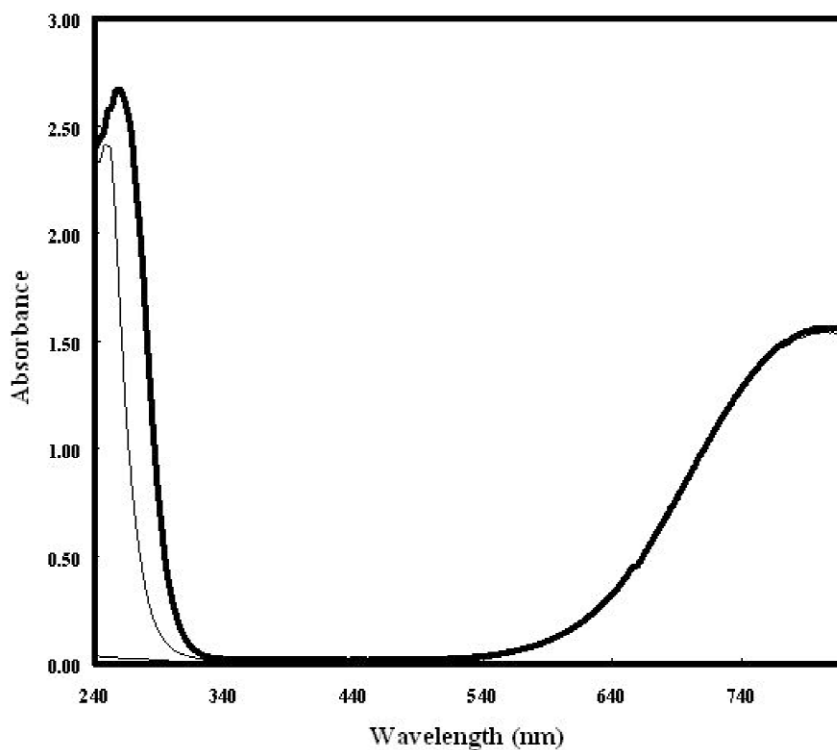


Fig. 6 UV/vis spectrum at 25 °C of (bottom to top): 0.1 M Na_2SO_4 (barely visible), 0.1 M $\text{Cu}(\text{ClO}_4)_2$, and 0.1 M $\text{Na}_2\text{SO}_4 + 0.1 \text{ M Cu}(\text{ClO}_4)_2$ [39].

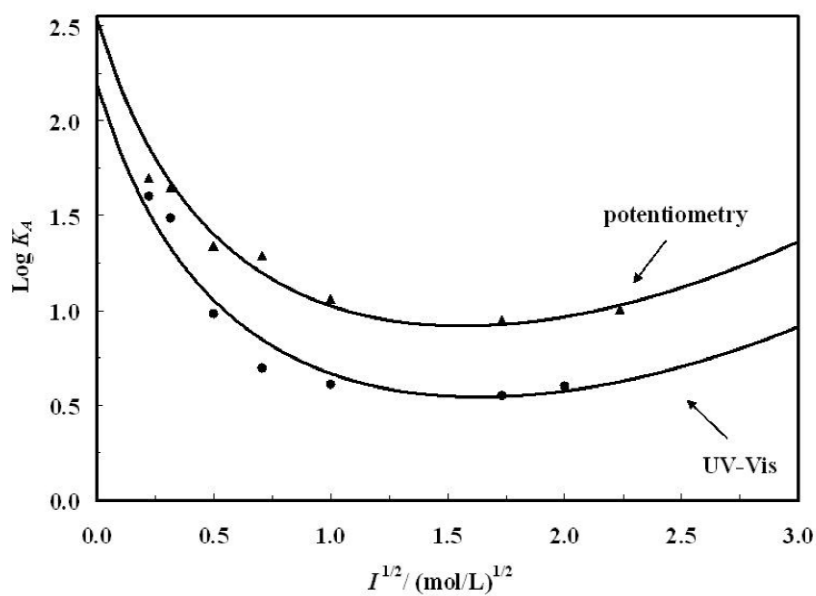


Fig. 7 Comparison of the $\log K_A(\text{CuSO}_4^0(\text{aq}))$ values obtained by potentiometry and UV/vis spectrophotometry as a function of ionic strength at 25 °C [39].

Although the difference is relatively small the spectrophotometric data [39] (which are in excellent agreement with previous UV/vis results [34]) clearly lie below the potentiometric values.

Thus, even when UV/vis spectroscopy appears to work satisfactorily the results may still be somewhat in error since it is likely that not all of the associated species are detected.

CASE STUDY 3: THE $\text{Mg}^{2+}/\text{SO}_4^{2-}$ SYSTEM

Thermodynamic methods

Probably because of its significance as a major component of seawater, the $\text{Mg}^{2+}/\text{SO}_4^{2-}$ system has been investigated extensively by traditional thermodynamic measurements [1,3]. Eight high-quality conductivity studies give an average value of $\log K_A^0 = 2.17 \pm 0.05$ for the overall association:



with values ranging from 2.08 to 2.27 [27]. Detailed investigations by cryoscopy, potentiometry, calorimetry, and solubility measurements present a similar picture with an average value of $\log K_A^0 = 2.3 \pm 0.1$. Surprisingly few measurements have been reported at high ionic strengths, I [1,3].

Relaxation methods

A detailed DRS study of $\text{MgSO}_4(\text{aq})$ has been made recently over a wide range of frequencies and concentrations [13]. All three ion-pair types—2SIP, SIP, and CIP—were detected. Although a number of unusual features were observed in the data, the most important finding in the present context was that the K_i values (eq. 1) gave $\log K_A^0 = 2.3 \pm 0.1$, in excellent agreement with those derived using thermodynamic methods. Equally importantly, the DRS data were in almost quantitative agreement with the earlier USR measurements of Eigen and others [8,9,13], with respect to both K_i and K_A .

Spectroscopic methods

Standard approaches using UV/vis or NMR spectroscopies are not applicable to the $\text{Mg}^{2+}/\text{SO}_4^{2-}$ system due to the absence of a suitable “chromophore”. On the other hand, numerous studies have been made of this system using Raman spectroscopy. Most of these have concentrated on the strong $\nu_1(\text{SO}_4^{2-})$ symmetric stretching mode located at ca. 980 cm^{-1} . Again, no complex formation was observed in the early studies, due to the too-wide slit widths then available [37]. A number of subsequent investigations have clearly established an increasing asymmetry of the $\nu_1(\text{SO}_4^{2-})$ mode with increasing MgSO_4 concentrations. The most plausible explanation [12] of these and related observations is the presence of CIPs. A typical Raman spectrum of $\text{MgSO}_4(\text{aq})$ in the $\nu_1(\text{SO}_4^{2-})$ region is shown in Fig. 8. Note that for non-associated electrolytes such as $(\text{NH}_4)_2\text{SO}_4(\text{aq})$, the $\nu_1(\text{SO}_4^{2-})$ mode remains strictly symmetrical up to high concentrations [12]. Also included in Fig. 8 are the band components, with the free SO_4^{2-} mode centered on $\sim 982 \text{ cm}^{-1}$ and “complexed” SO_4^{2-} at $\sim 993 \text{ cm}^{-1}$. It is readily apparent that only a small level of complex formation is detected by Raman spectroscopy.

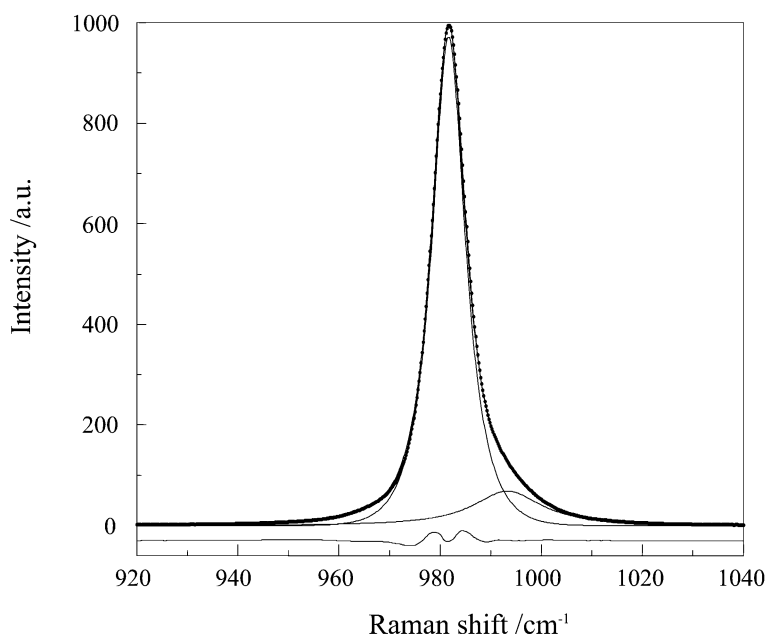


Fig. 8 Raman spectrum of ~0.8 M $\text{MgSO}_4(\text{aq})$ at 25 °C, showing the contributions to the $\nu_1(\text{SO}_4^{2-})$ mode from free (at ~980 cm^{-1}) and complexed (at ~993 cm^{-1}) sulfate [12]. Bottom curve: difference (observed – calculated) spectrum.

The stability constant can be evaluated in the usual way [12] via α , the degree of association:

$$\alpha = I_{993} / (I_{982} + I_{993}) = [\text{complex}] / [\text{Mg}^{2+}]_{\text{T}} \quad (9)$$

giving

$$K_{\text{Raman}} = \alpha / (1 - \alpha)^2 [\text{Mg}^{2+}]_{\text{T}} \quad (10)$$

where the subscript T indicates total or analytical values and I is the corrected Raman scattering intensity at the wavenumber (in cm^{-1}) specified by the subscript.

Following this procedure, a value of $\log K_{\text{A}}^0 \approx 1.3$ is obtained. This result is approximately one order of magnitude lower than the values obtained by thermodynamic and relaxation methods. This is understandable if it is assumed that only CIPs are detected by Raman spectroscopy. It is also reasonable because the perturbation of the $\nu_1(\text{SO}_4^{2-})$ mode in SIPs, and certainly in 2SIPs, would be expected to be little different from “free” $\text{SO}_4^{2-}(\text{aq})$. (In fact, there is evidence that SIPs are detected by Raman spectroscopy in $\text{MgSO}_4(\text{aq})$ solutions. However, the band changes are very slight and difficult to deconvolute, and therefore can only be detected in very high-quality spectra [12]).

Since both Raman and DR spectra detect CIPs directly, the concentrations so obtained should be fully comparable. This is indeed the case as shown in Fig. 9 where the agreement in the fraction of CIPs obtained by the two methods is well within the likely experimental errors. However, it is not widely understood that the equilibrium constant obtained by Raman spectroscopy is **not** comparable with any of the K_i values or with K_{A} [12]. Using the appropriate mass balances, it is readily shown that

$$K_{\text{Raman}} = K_1 K_2 K_3 [\text{Mg}^{2+}]^2 / ([\text{Mg}^{2+}]_{\text{T}} - K_1 K_2 K_3 [\text{Mg}^{2+}]^2) \quad (11)$$

where $[\text{Mg}^{2+}]$ can be obtained by solving the quadratic expression

$$K_{\text{A}} [\text{Mg}^{2+}]^2 + [\text{Mg}^{2+}] - [\text{Mg}^{2+}]_{\text{T}} = 0 \quad (12)$$

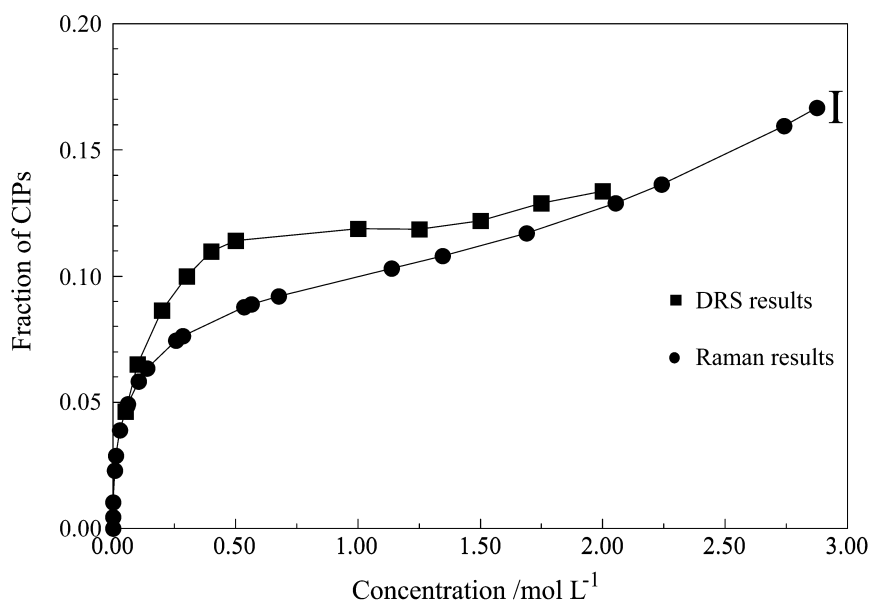
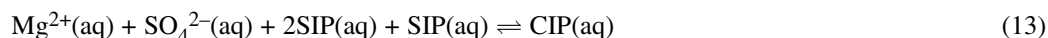


Fig. 9 Comparison of the fraction of CIPs in $\text{MgSO}_4(\text{aq})$ determined directly by DRS and by Raman spectroscopy (see text) as a function of the solute concentration [13].

Thus, $K_{\text{Raman}} \neq K_i$ or K_A and although K_{Raman} can be calculated from a knowledge of K_i the converse is not possible. It is important to recognize that K_{Raman} is not “wrong”, it is simply not useful. This is because it is in essence an “apparent” or conditional constant which refers to the equilibrium



whose value is dependent on the measurement technique (i.e., on the degree to which the technique can distinguish between the free ions, 2SIPs, SIPs, and CIPs). In particular, K_{Raman} cannot be used for normal chemical speciation modeling [12,13].

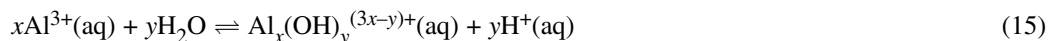
CASE STUDY 4: THE $\text{Al}^{3+}/\text{SO}_4^{2-}$ SYSTEM

Thermodynamic methods

The association of aquated Al^{3+} and SO_4^{2-} ions, which for simplicity may be represented



is particularly difficult to study. Not only is it probable that complexes with other stoichiometries, such as $\text{Al}(\text{SO}_4)_2^-(\text{aq})$, are formed [40], but $\text{Al}^{3+}(\text{aq})$ solutions show a pronounced tendency to hydrolyze, especially at high $[\text{Al}^{3+}]_T$, even at low pH [41]:



Not surprisingly, the availability of reliable data is limited. These data have been reviewed recently by Ridley et al. [40]. In general, the agreement among the limited number of reported studies is modest, but conductometric, potentiometric, and solubility data provide evidence of strong complexation, with an average $\log K_A^0 \approx 3.2 \pm 0.5$ (range 1.9–3.7). The dependence of K_A on I is not well known but is certainly strong [40].

Relaxation methods

Few relaxation studies have been made of $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ solutions, and none has yet been able to fully characterize the equilibria. Unpublished broadband DR spectra over a wide concentration range are consistent with strong complexation probably including all three types of ion pairs [42]. This is readily apparent from the typical DR loss spectra for $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ shown in Fig. 10, which exhibit very strong contributions from ion pairs at $\nu \approx 10$ GHz. Further comment on these spectra is, however, inappropriate until they have been fully analyzed. The DRS findings are broadly supported by two USR investigations [43,44]. The latter data were insufficient for a complete analysis but indicated strong complexation overall and probably the presence of all three equilibria of eq. 1.

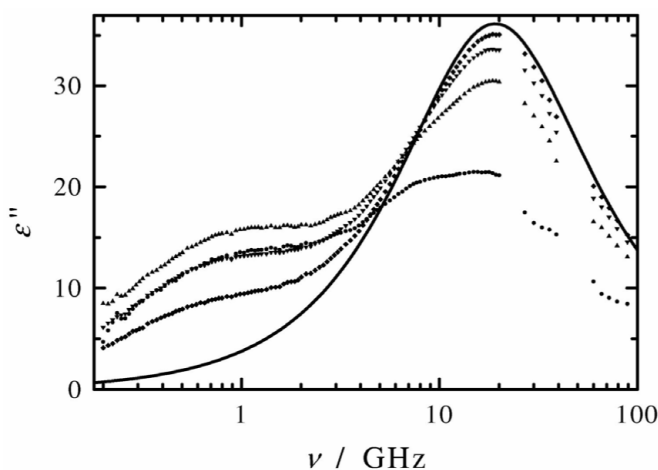


Fig. 10 Dielectric loss (ϵ'') spectra for $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ solutions at 25 °C as a function of solute concentration (top to bottom at $\nu = 10$ GHz): $c/M = 0, 0.04, 0.11, 0.23, 0.65$ [42].

Spectroscopic methods

The $\text{Al}^{3+}/\text{SO}_4^{2-}$ system has been included in the present discussion, notwithstanding the relative paucity of thermodynamic and relaxation data, because there is a useful amount of spectroscopic information available. The latter does not include UV/vis spectra because, despite widespread claims to the contrary, supported by quantum mechanical calculations even, genuinely pure solutions of $\text{Al}^{3+}(\text{aq})$ in the presence of simple anions do not absorb in the UV/vis region (all the reported bands are due to impurities) [45].

The ^{27}Al -NMR spectra of the $\text{Al}^{3+}/\text{SO}_4^{2-}$ system have been investigated on several occasions [46,47]. A typical set of spectra is shown in Fig. 11 [47]. Clearly, only a very small level of complex formation is detected. Standard analysis of the NMR data gives $\log K_A^0 \approx 0.1$, i.e., about four orders of magnitude below the values obtained by thermodynamic methods.

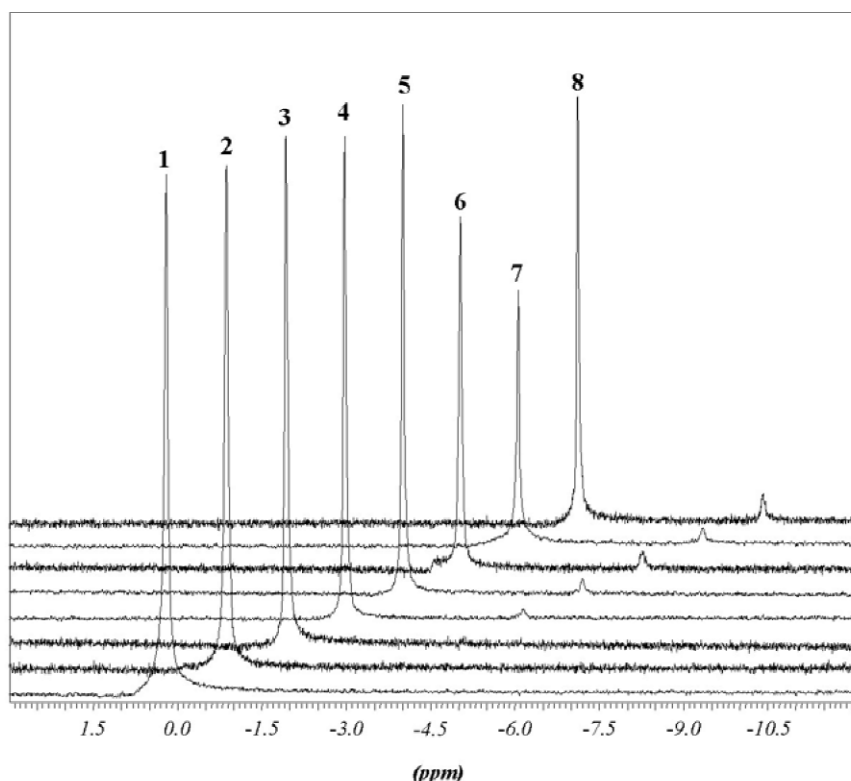


Fig. 11 ^{27}Al -NMR spectra of Al(III)/SO_4^{2-} solutions at $25\text{ }^\circ\text{C}$ and $I = 1\text{ M}(\text{NaClO}_4)$ for $c_{\text{T}}(\text{Al(III)}) = 10\text{ mM}$ and with (curves 1 to 8): $c_{\text{T}}(\text{SO}_4^{2-})/\text{mM} = 0, 5, 10, 30, 50, 100, 200, 400$ [47]. Note the very small growth of the peak, corresponding to the formation of the $\text{AlSO}_4^+(\text{aq})$ CIP, at $\sim 2.5\text{ ppm}$ (vs. that for $\text{Al(OH}_2)_6^{3+}$ at 0 ppm).

A virtually identical result is obtained from Raman spectroscopy. Figure 12 shows a typical spectrum in the $\nu_1(\text{SO}_4^{2-})$ region from a recent high-quality study [48]. The complex (CIP) detected for this system is easily identified as the shoulder at $\sim 1010\text{ cm}^{-1}$ with “Raman-free” SO_4^{2-} as usual at $\sim 980\text{ cm}^{-1}$. Conventional analysis (see previous case study) again gives $\log K_{\text{A}}^{\circ} \approx 0.1$. This is in excellent agreement with the NMR result, as would be expected since the same equilibrium (cf. eq. 14) is detected. The key point here is that, although Raman and NMR spectroscopy agree with each other, the value of K_{A} they produce is low, by many orders of magnitude, when compared with the “true” thermodynamic result [41].

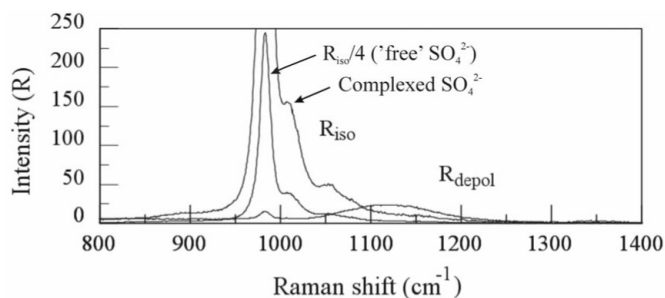


Fig. 12 Isotropic Raman spectrum of $\sim 0.8\text{ M}$ for $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ at $25\text{ }^\circ\text{C}$, showing the contributions to the $\nu_1(\text{SO}_4^{2-})$ mode of free (at $\sim 980\text{ cm}^{-1}$) and complexed (at $\sim 1010\text{ cm}^{-1}$) sulfate [48].

IMPLICATIONS

Although this paper has focused exclusively on higher-valent metal sulfate systems in aqueous solution, the present findings have wide implications. Similar behavior (the formation of significant amounts of non-contact ion-pairs) would be expected whenever highly charged ($|z| > 2$) cations and/or anions are present in aqueous solutions [23]. In nonaqueous or mixed solvents where the relative permittivity (ϵ) is often much less than that of water, ion pairing is likely to be the norm [23]. Whenever significant amounts of non-CIPs (2SIPs and SIPs) are suspected, the traditional spectroscopic methods of UV/vis, NMR, and Raman (IR) should be used with great care. In such situations, the apparent association constants derived from spectroscopy may be seriously in error, even if some species (such as CIPs) are correctly detected.

Typically, conventional spectroscopic K_A values are underestimates of the “true” association constants when undetected (non-contact) IPs are present. The discrepancies may be small (e.g. in the $\text{Cu}^{2+}/\text{SO}_4^{2-}$ system) or large (e.g., $\text{Mg}^{2+}/\text{SO}_4^{2-}$). Such errors may still exist even when there is perfect agreement amongst the different spectroscopic methods (e.g., $\text{Al}^{3+}/\text{SO}_4^{2-}$). Such spectroscopic constants can give a highly misleading view of the chemical speciation in such systems. Because they respond only to a fraction of the complex species present, such constants cannot be used for modeling purposes. Similar considerations will apply to many other systems.

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