Raman and Infrared Spectroscopic Investigation of Speciation in BeSO₄(aq)

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Abstract Measurements have been made of the Raman spectra of aqueous solutions of Be(ClO₄)₂, BeCl₂, (NH₄)₂SO₄ and BeSO₄ to 50 cm⁻¹. In some cases low concentrations (0.000770 mol·kg⁻¹) have been used and two temperatures (23 and 40 °C) were studied. In BeSO₄(aq), the ν₁-SO₄²⁻ mode at 980 cm⁻¹ broadens with increasing concentration and shifts to higher wavenumbers. At the same time, a band at 1014 cm⁻¹ is detectable with this mode being assigned to [BeOSO₃], an inner-sphere complex (ISC). Confirmation of this assignment is provided by the simultaneous appearance of stretching bands for the Be²⁺-OSO₃⁻ bond of the complex at 240 cm⁻¹ and for the BeO₄ skeleton mode of the [(H₂O)₃BeOSO₃] unit at 498 cm⁻¹. The ISC concentration increases with higher temperatures. The similarity of the ν₁-SO₄²⁻ Raman bands for BeSO₄ in H₂O and D₂O is further strong evidence for formation of an ISC. After subtraction of the ISC component at 1014 cm⁻¹, the ν₁-SO₄²⁻ band in BeSO₄(aq) showed systematic differences from that in (NH₄)₂SO₄(aq). This is consistent with a ν₁-SO₄²⁻ mode at 982.7 cm⁻¹ that can be assigned to the occurrence of an outer-sphere complex ion (OSCs). These observations are shown to be in agreement with results derived from previous relaxation measurements. Infrared spectroscopic data show features that are also consistent with a beryllium sulfato complex such as the appearance of a broad and weak ν₁-SO₄²⁻ mode at ~1014 cm⁻¹, normally infrared forbidden, and a broad and asymmetric ν₃-SO₄²⁻ band contour which could be fitted with four band components (including ν₃-SO₄²⁻ (aq)). The formation ofISCs in BeSO₄(aq) is much more pronounced than in the similar MgSO₄(aq) system studied recently.

Keywords Raman spectra · Be(II) tetraaqua ion · Be(ClO₄)₂, BeCl₂, and BeSO₄ solutions · Inner-sphere complexes of beryllium(II)
1 Introduction

The technical importance of beryllium and its compounds in reactor technology, aerospace industry and metallurgy has been well documented [1, 2]. Beryllium compounds have been studied quite extensively in the solid state, with \( \text{BeSO}_4 \cdot 4\text{H}_2\text{O}(\text{cr}) \) [2–9] being, by far, the best characterized solid. Solution chemistry [1], especially aqueous solutions, has been sparsely studied.

When dissolved in water, the \( \text{Be}^{2+} \) ion is strongly hydrated and because of its high charge to ionic radius ratio the bonds between \( \text{Be}^{2+} \) and water are strong. An early study by Fricke and Schützdeller [9] concluded that the \( \text{Be}^{2+} \) ion is the most heavily hydrated of all divalent cations. Later, the existence of the tetra-aquaberyllium(II) ions was experimentally verified through NMR spectroscopy [10–12] and it was also determined that the aqua ion is thermodynamically stable and kinetically quite inert. More recently, a study on vibrational spectra in aqueous solutions of common beryllium salts has established the existence of the \( [\text{Be(OH}_2 \text{)}]_{4}^{2+} \) species in aqueous solutions of perchlorate, chloride, nitrate and sulfate [13]. The \( [\text{Be(OH}_2 \text{)}]_{4}^{2+} \) species also occurs in solid state compounds such as \( \text{BeSO}_4 \cdot 4\text{H}_2\text{O} \) or in \( \text{BeX}_2 \cdot 4\text{H}_2\text{O} \) with \( \text{X} = \text{Cl}^{-}, \text{Br}^{-}, \text{NO}_3^{-}, \) and \( \text{H}_4\text{IO}_6^{-} \) [2, 4–7].

However, \( \text{BeSO}_4 \) solutions show striking features because, besides the well characterized \( [\text{Be(OH}_2 \text{)}]_{4}^{2+} \) species, a beryllium sulfato complex was also verified recently [13]. Therefore, it seemed warranted to study Raman and infrared spectra of aqueous \( \text{BeSO}_4 \) solutions as a function of concentration and temperature in more detail. In order to properly interpret such spectra it is essential to first characterize the spectra of free (unassociated) \( \text{Be}^{2+} \text{(aq)} \) and \( \text{SO}_4^{2-} \text{(aq)} \) ions.

This paper presents a detailed analysis of the spectra of \( \text{BeSO}_4 \text{(aq)} \) over a wide concentration range and also of aqueous solutions of other relevant salts: \( \text{Be(ClO}_4 \text{)}_2, \text{BeCl}_2 \) and \( (\text{NH}_4)_2\text{SO}_4 \). In addition, the relationship between the apparent association constant for \( \text{BeSO}_4 \text{(aq)} \) obtained by Raman spectroscopy and those measured by other techniques is discussed. A comparison of the qualitative and quantitative data on the sulfato complex formation in \( \text{BeSO}_4 \) solutions with the results on \( \text{MgSO}_4 \) solutions obtained by recent Raman and DRS studies [14, 15] are included.

2 Experimental Details and Data Analysis

2.1 Preparation of Solutions

\( \text{Be(ClO}_4 \text{)}_2 \) and \( \text{BeCl}_2 \) solutions were prepared by dissolving \( \text{BeO} \) (Merck; Darmstadt, Germany, p.a. quality) with slightly more than the stoichiometric amount of the appropriate acids. Two \( \text{Be(ClO}_4 \text{)}_2 \) solutions were prepared: Solution A was 3.150 mol\text{-L}^{-1} \( \text{Be(ClO}_4 \text{)}_3 \) with a slight excess of perchloric acid (ca. 0.20 mol\text{-L}^{-1}), Solution B was 1.246 mol\text{-L}^{-1} \( \text{Be(ClO}_4 \text{)}_2 \) with 0.10 mol\text{-L}^{-1} \( \text{HClO}_4 \) excess. Two \( \text{BeCl}_2 \) solutions were prepared: Solution A was 3.350 mol\text{-L}^{-1} \( \text{BeCl}_2 \) with an excess of \( \text{HCl} \) (ca. 0.80 mol\text{-L}^{-1}), Solution B was 1.246 mol\text{-L}^{-1} \( \text{BeCl}_2 \) with 0.5 mol\text{-L}^{-1} \( \text{HCl} \) excess. A 3.050 mol\text{-L}^{-1} \( \text{BeCl}_2 \) stock solution was prepared in \( \text{D}_2\text{O} \) with an excess of \( \sim 0.65 \text{ mol-L}^{-1} \text{DCI} \).

Two \( \text{BeSO}_4 \) stock solutions were prepared by weight from \( \text{BeSO}_4 \cdot 4\text{H}_2\text{O}(\text{cr}) \) purchased from Merck; Darmstadt, Germany (p.a. quality) and ultrapure water produced from Pure-Lab Plus, Ultra-pure Water Purification Systems: (A) a 3.052 mol\text{-L}^{-1} (3.260 mol\text{-kg}^{-1}) solution and (B) a 1.835 mol\text{-L}^{-1} (1.910 mol\text{-kg}^{-1}). The diluted \( \text{BeSO}_4 \) solutions were prepared from stock Solution A and ultrapure water by weight. Five diluted solutions prepared...