Chemical speciation effects on the volumetric properties of aqueous sulfuric acid solutions

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Abstract

Densities of fifteen aqueous solutions of sulfuric acid (H₂SO₄) have been measured by vibrating-tube densimeter at solute molalities (m) from (0.01 to 3.0) mol·kg⁻¹ over the temperature range 293.15 ≤ T/K ≤ 343.15. These data have been used to calculate the corresponding apparent molar volumes \( V_m(H_2SO_4,aq) \), which represent a significant expansion of the volumetric database for this industrially important acid. At 298.15 K the present results agree well with literature data, notably with the century-old values given in the 1926 International Critical Tables. At other temperatures, where comparisons are possible agreement with the present \( V_m \) values is also very satisfactory. Consistent with earlier studies, \( V_m(H_2SO_4,aq) \) was found to exhibit an abnormally-large decrease at low concentrations (\( m \leq 0.1 \) mol·kg⁻¹). This effect is consistent with a change in the chemical speciation of H₂SO₄(aq), from an essentially 1:1 electrolyte (H⁺(aq) + HSO₄⁻(aq)) at higher concentrations to a predominantly 1:2 electrolyte (2H⁺(aq) + SO₄²⁻(aq)) in dilute solutions. The \( V_m \) values were modelled using variants of Young’s rule and the Pitzer formalism. Combination of these results with literature values for the standard volume \( V_0(SO_4^{2-},aq) \) enabled estimation of \( V_0(HSO_4^{\text{-}},aq) \) and the standard volume change, \( ΔV^0 \), for the first protonation of the sulfate ion (H⁺(aq) + SO₄²⁻(aq) → HSO₄⁻(aq)) as functions of temperature. It is shown that \( V_0(HSO_4^{\text{-}},aq) \) is sensitive to the value of the first protonation constant and probably cannot be determined to better than ± 0.3 cm³·mol⁻¹ at present.

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1. Introduction

The global production of sulfuric acid, ca. 260 Mt per year, far exceeds that of all other anthropogenic chemicals. Its main uses are in the manufacture of phosphate-based fertilizers, which consume about 50% of production, and for various chemical and hydrometallurgical processes [1–3]. However, the importance of aqueous solutions of H₂SO₄ goes far beyond their industrial usage. For example, sulfuric acid is the major component in the environmental pollution arising from acid mine drainage from many past and present mine sites [4] and is known to play an important role in upper-atmospheric aerosols [5]. So diverse are the myriad applications of H₂SO₄(aq) that its production has even been suggested as a surrogate measure of national economic development [6].

Given their ubiquitous usage it is to be expected that the properties of aqueous solutions of sulfuric acid are particularly well known. For example, it has been noted [7] that the second deprotonation of sulfuric acid:

\[
\text{HSO}_4^{-}(aq) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}^+(aq) \quad (1)
\]

with equilibrium constant \( K_a \), is the most widely investigated of all solution chemical equilibria apart from the self-ionization of water [8,9]. It is therefore surprising to find that the volumetric properties of H₂SO₄(aq), while exceptionally well-established for some conditions (e.g., at 298.15 K and 0.101 MPa) show major gaps under others (see for example the JESS database of physicochemical properties of electrolyte solutions [10]). Some of these poorly characterised regions are especially relevant for several important industrial applications [2].

Table 1 lists a selection of the high-quality density studies of H₂SO₄(aq) under near-ambient conditions over the concentration range of interest. Of particular note is the comprehensive compilation presented in the International Critical Tables (ICT), published in 1926 [11]. This critical assessment of the then-available experimental data (most of it now more than one hundred years old) not only covers the widest ranges of temperature and concentration (Table 1) but, as will be seen below, proposes densities that are in near-quantitative agreement with the present study.
Noteworthy by their omission from Table 1 are the more recent density compilations of Söhnel and Novotny [12] and of Asayev and Zaytsev [13]. As found for a number of other electrolyte systems, these modern compilations often exhibit significant departures from high-quality experimental data and show many internal inconsistencies [14]. Accordingly they, along with a number of less-reliable measurements, e.g. [15–17], will not be considered further in this paper.

2. Experimental

2.1. Reagents

Details of the reagents used in the present study are given in Table 2. Briefly, two stock solutions of sulfuric acid were prepared. The first was a commercial Concentrated Volumetric Standard (CVS) ampoule with a stated accuracy of ± 0.2%. The second was prepared by diluting analytical grade concentrated sulfuric acid; its concentration was determined by density comparison with the CVS solution. Working solutions were prepared by weight dilutions using high-purity de-ionized water (Labis Technology, Australia). Buoyancy corrections were applied throughout.

2.2. Density determinations

Densities were determined with an Anton-Paar (Graz, Austria) DMA 5000 M vibrating-glass-tube densimeter. The measurement protocol and the calibration of this instrument with water and air have been described in detail elsewhere [25]. Measurements were performed isothermally over the temperature range 293.15 ≤ T/K ≤ 343.15 in 5 K intervals. Temperatures of solutions in the densimeter tube were controlled to ± 0.002 K using the in-built thermostat. The experimental pressure of (0.101 ± 0.001) MPa was obtained from the internal sensor of the densimeter. Reproducibility of the measured densities was generally within ± 10 μg cm⁻³.

3. Results and discussion

3.1. Densities and apparent molar volumes

Experimental density differences, \( \Delta \rho = \rho - \rho_{w,exp} \) (where \( \rho \) and \( \rho_{w,exp} \) are, respectively, the experimental densities of the solution and of pure water at the target conditions) were converted to apparent molar volumes, \( V_w \), using the usual equation

\[
V_w = \frac{M}{\Delta \rho + \rho_w} - \frac{\Delta \rho}{m \rho_w (\Delta \rho + \rho_w)}
\]

where \( M \) is the molar mass of anhydrous (pure) sulfuric acid, 98.072 g mol⁻¹, calculated from the 2013 IUPAC atomic weights [26], and \( m \) is the stoichiometric (total) sulfuric acid molality (mol H₂SO₄/([kg H₂O])⁻¹. Here, the pure water densities \( \rho_w \) were calculated from the IAPWS-95 equation of state [27] and for convenience are included in Table 3.

The values of \( \Delta \rho \) and \( V_w \) obtained for 15 sulfuric acid concentrations spanning the range 0.01 ≤ \( m/\text{mol kg}^{-1} \) ≤ 3 are listed in Table 3. Also given in Table 3 are the standard uncertainties in the density difference \( u(\Delta \rho) \) and the combined standard uncertainties in the apparent molar volumes \( u(V_w) \), estimated in accordance with the GUM guidelines [28].

3.2. Comparisons with literature data

Fig. 1 plots the present and selected literature values of \( V_w \) as a function of the stoichiometric (total) sulfuric acid concentration (as \( m^{1/2} \)) at 298.15 K and 0.101 MPa, where by far the greatest amount of reliable data exists. The agreement among the various studies is excellent with an average spread of just ± 0.3 cm³ mol⁻¹ over the whole concentration range. This is comparable with well characterized electrolyte systems such as NaCl(aq), HCl(aq) and NaBr (aq) [29]. The concordance with the ICT data [11] (with an average difference of ± 0.1 cm³ mol⁻¹) is especially notable. There are too few data at other temperatures to justify plots analogous to Fig. 1 but a more general comparison with the better quality literature data (Table 1) over wide ranges of \( T \) and \( m \) (Fig. 2) shows a high level of agreement. Fig. 2 also shows how the present results have expanded the volumetric database of H₂SO₄(aq) especially in the dilute range (\( m/\text{mol kg}^{-1} \) ≤ 0.1) at T/K > 298.15. Although the uncertainty in \( V_w \) increases rapidly as \( \rho \rightarrow \rho_w \) (cf. Eq. (2)), the observed agreement (Figs. 1 and 2) amongst the independent investigations confirms the unusual decrease in the \( V_w(m^{1/2}) \) values for H₂SO₄(aq) at low solute concentrations (\( m \leq 0.1 \text{ mol kg}^{-1} \)). While this phenomenon has not been widely studied (Table 1) its characteristics, at least at 298.15 K, based mainly on the data of Klotz and Eckert [18], were discussed at length in Robinson and Stokes’ classic monograph [30]. In essence, the dramatic decrease in \( V_w \), at low \( m \) is consistent with a change in the chemical speciation of the sulfuric acid, which alters from being a mainly 1:1 electrolyte (H⁺(aq) + HSO₄⁻(aq)) to become a predominantly 1:2 electrolyte (2H⁺(aq) + SO₄²⁻(aq)) with increasing dilution (cf. Eq. (1)). This effect shifts to lower concentrations at higher temperatures (Fig. 2) as HSO₄ (aq) becomes a weaker acid, ie, as Eq. (1) shifts to the left [31].

3.3. Standard molar volumes

The standard (infinite dilution) molar volume \( V^\wedge(\text{SO}_4^{2-}\text{aq}) \), hereafter \( V_w^\wedge \), can be calculated over the temperature range of interest using the \( V^\wedge \) values of well characterised 1:2 sulfate salts by assuming ionic additivity. On the other hand, the estimation of \( V^\wedge(\text{HSO}_4^{-}\text{aq}) \), hereafter \( V_1^\wedge \), and the standard molar volume change for Eq. (1), from left to right, \( \Delta V^\wedge \), is much less
Table 2
Sample sources and purities.

| chemical name | CASRN   | source | initial mass fraction purity | purification method |
|---------------|---------|--------|-----------------------------|---------------------|
| sulfuric acid | 7664–93-9 | Merck | ≥ 0.98<sup>a</sup> | none |
| sulfuric acid | 7664–93-9 | VWR   | ≥ 0.998<sup>b</sup> | none |

<sup>a</sup> Analytical grade, as supplied, has no significant impurities other than water
<sup>b</sup> Concentrated volumetric standard.

Table 3
Experimental density differences, \( \Delta \rho = \rho - \rho_{\text{exp}} \), and apparent molar volumes, \( V_a \), at molalities \( m \), temperatures \( T \) and pressure \( p = 0.101 \) MPa.<sup>2</sup>

| m/mol kg<sup>-1</sup> | \( \Delta \rho / \text{kg m}^{-3} \) | \( V_a / \text{cm}^3 \text{ mol}^{-1} \) | \( \Delta \rho / \text{kg m}^{-3} \) | \( V_a / \text{cm}^3 \text{ mol}^{-1} \) |
|-----------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|
| \( T = 293.15 \) K, \( \rho_w = 988.207 \) kg m<sup>-3</sup> | \( 0.01028 \) | 0.744(2) | 22.65(26) | 0.757(3) | 24.26(33) |
|                       | \( 0.01028 \) | 0.773(2) | 22.75(31) | 0.755(4) | 24.45(42) |
|                       | \( 0.02000 \) | 1.446(2) | 25.68(19) | 1.413(4) | 27.26(25) |
| 0.04000               | 2.794(2) | 28.08(15) | 2.732(6) | 29.59(20) |
| 0.06000               | 4.111(4) | 29.37(15) | 4.026(3) | 30.74(14) |
|                       | 0.08000* | 6.683(1) | 30.99(13) | 6.563(3) | 32.15(13) |
| 0.1000                | 12.972(1) | 32.74(13) | 12.757(10) | 33.77(14) |
| 0.2000*               | 25.228(2) | 34.10(12) | 24.824(9) | 35.07(12) |
| 0.4000*               | 48.784(2) | 35.36(12) | 48.030(1) | 36.23(12) |
| 0.6000               | 6.683(1) | 30.99(13) | 6.563(3) | 32.15(13) |
| 0.8000*               | 12.972(1) | 32.74(13) | 12.757(10) | 33.77(14) |
| 1.000*                | 25.228(2) | 34.10(12) | 24.824(9) | 35.07(12) |
| 1.2000*               | 48.784(2) | 35.36(12) | 48.030(1) | 36.23(12) |
| 1.4000*               | 6.683(1) | 30.99(13) | 6.563(3) | 32.15(13) |
| 1.6000*               | 12.972(1) | 32.74(13) | 12.757(10) | 33.77(14) |
| 1.8000*               | 25.228(2) | 34.10(12) | 24.824(9) | 35.07(12) |
| 2.000*                | 48.784(2) | 35.36(12) | 48.030(1) | 36.23(12) |

(continued on next page)
| m (mol kg⁻¹) | Δρ (kg m⁻³) | Vᵥ (cm³ mol⁻¹) | Δρ (kg m⁻³) | Vᵥ (cm³ mol⁻¹) |
|--------------|-------------|----------------|-------------|----------------|
| 2.500*       |             |                |             |                |
| 0.01028      | 0.0694(5)   | 30.07(53)      | 0.0686(2)   | 30.78(26)      |
| 0.01028      | 0.7052(2)   | 28.98(26)      | 0.692(2)    | 30.18(27)      |
| 0.01028      | 0.6985(5)   | 29.67(53)      | 0.690(5)    | 30.38(33)      |
| 0.02000      | 1.3094(5)   | 32.17(25)      | 1.2944(2)   | 32.86(25)      |
| 0.03000      | 2.5331(2)   | 34.22(13)      | 2.502(1)    | 35.04(13)      |
| 0.06000      | 3.7331(2)   | 35.40(16)      | 3.698(5)    | 35.93(15)      |
| 0.06000      | 3.7232(2)   | 35.57(13)      | 3.684(1)    | 36.17(13)      |
| 0.07999      | 4.9343(3)   | 35.90(13)      | 4.887(5)    | 36.44(14)      |
| 0.07999      | 4.9421(1)   | 35.80(13)      | 4.896(4)    | 36.30(14)      |
| 1.0000       | 6.1214(1)   | 36.35(13)      | 6.063(1)    | 36.88(12)      |
| 0.2000       | 11.5813(1)  | 37.45(12)      | 11.8813(1)  | 37.90(12)      |
| 0.4000       | 23.4431(1)  | 38.32(12)      | 23.269(3)   | 38.71(12)      |
| 0.5999       | 34.674(5)   | 38.70(11)      | 34.348(1)   | 39.06(11)      |
| 0.8000*      | 45.543(2)   | 39.15(11)      | 45.238(1)   | 39.49(11)      |
| 1.0000*      | 56.4221(1)  | 39.23(11)      | 56.054(3)   | 39.86(11)      |
| 1.5000*      | 82.4452(1)  | 39.66(10)      | 81.922(1)   | 39.97(10)      |
| 2.0000*      | 107.1491(1) | 40.03(10)      | 106.486(1)  | 40.33(10)      |
| 2.5000*      | 130.8322(1) | 40.32(9)       | 130.042(1)  | 40.61(9)       |
| 3.0000*      | 153.3037(1) | 40.62(9)       | 152.404(5)  | 40.89(9)       |

Where ρ is the experimental sample density and ρₑₓₜₚ is the experimental water density at the same T, p. The values ρₑₓₜₚ listed in this Table are calculated using IAPWS-95 equation-of-state [27].

a Where * refer to solutions prepared from a stock solution, itself prepared from concentrated sulfuric acid. Unmarked m refer to solutions prepared from the concentrated volumetric standard.

b Standard uncertainties u(C) = 0.002 K, u(N) = 0.001 MPa and u(ρₑₓₜₚ) = 0.001 kg m⁻³ [27]. Numbers in brackets are standard uncertainties in the density difference u(Δρ) and combined standard uncertainties in the apparent molar volume u(Vᵥ). The values of these uncertainties refer to the corresponding last digits of the relevant values.
that all single-ion volumes discussed here are “conventional” values.

Two general methods have been used to obtain these parameters: indirect estimation from volumetric data (dilatometry or dilatometry) or directly from the pressure dependence of log $K_a$ [32]. Reported values are summarized in Table 4, noting that all single-ion volumes discussed here are “conventional” values, based on the assumption that $V^0(H^+\text{aq}) \equiv 0$ at all temperatures.

The data in Table 4 indicate that the reported $V_1^\circ$ values have a spread of 1.7 cm$^3$ mol$^{-1}$ at 298.15 K. This rather large uncertainty mostly arises from systematic differences in the methods and assumptions used to derive $V_1^\circ$ from the observed $V_\phi$. Four calculation methods are presented here. Method (1) uses the Debye–Hückel (DH) limiting law (LL) for a mixture. Method (2) employs the Pitzer variant of the DHLL for a mixture [33]. Method (3) is based on Young’s rule [34] with the end member $V_\phi$ values calculated from the DHLL. Method (4) also uses Young’s rule but with the end member $V_\phi$ values calculated from the Pitzer variant of the DHLL. The speciation necessary for all of these calculations was modelled using the log $K_a$ values of Dickson et al. (Eq. 6) [31], which are regarded as reliable [7], and the Pitzer variant of the DHLL for activity coefficients [33].

With respect to Methods (1) and (2), the pressure derivative of the LL expression for the excess Gibbs energy of the considered mixture yields the following equation for $V_\phi$(H$_2$SO$_4$aq):

$$V_\phi = (1 - x)V_1 + xV_2 + A_v(1 + 2x)f(I)$$

(3)

where $x$ is the degree of dissociation of HSO$_4^\text{aq}$, $A_v$ is the DH slope for volumes [37] and $f(I)$ represents the chosen ionic strength dependence: $I^{1/2}$ for the DHLL and $\ln(1 + bI^{1/2})/b$ for its Pitzer variant, with $b = 1.2$ (kg·mol$^{-1}$)$^{1/2}$. The ionic strength of the solution is $I = 1 + 2x$ m.

With regards to Methods (3) and (4) Young’s rule for estimating $V_\phi$(H$_2$SO$_4$aq) can be written:

$$V_\phi = (1 - x)V_{\phi,A} + xV_{\phi,B}$$

(4)

where $V_{\phi,A}$ and $V_{\phi,B}$ are the apparent molar volumes of the hypothetical end-members: (A) H$^+$aq + HSO$_4^\text{aq}$ and (B) 2H$^+$aq + SO$_4^{2-}$aq at the same (total) molality $m$. The $V_{\phi,i}$ values are calculated as

$$V_{\phi,i} = V_i + A_v\frac{f(I)}{m}$$

(5)

The ionic strengths of the end-member solutions are $m$ for (A) and 3 $m$ for (B).

The present experimental $V_\phi$ values were used to obtain $V_1^\circ$ at each $T$ using the four different calculation methods outlined above. Because the present treatments assume the absence of higher order interaction terms, only data at $m \leq 0.1$ mol·kg$^{-1}$ were included in the fits. Conventional values of $V_2^\circ$ are given in Table 5 and were estimated by assuming ionic additivity ($M = Li$ or Na: $V_2^\circ = V^0(M_2SO_4\text{aq} - V^0(M^+\text{aq}) - 2V^0(SO_4^{2-}\text{aq}))$ using relevant literature data for Li$_2$SO$_4$ [38] and Na$_2$SO$_4$ [39,40] and conventional values of $V^0(M^+\text{aq})$ based on those of Marcus [41]. All fits were done with the PyMC3 Bayesian statistics package for Python [42]. The combined uncertainties $u(V_\phi)$ (Table 3) were included in the regression.

The four methods of calculation show systematic differences that decrease with increasing temperature (Fig. 3). These differences arise from the slightly different limiting law behaviour of

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**Table 4** Summary of literature values for $V^0$(HSO$_4$aq) and $\Delta V^0$.

| Quantity          | $T$/K | $V_\phi$/cm$^3$ mol$^{-1}$ | Refs.                      |
|-------------------|-------|---------------------------|----------------------------|
| $V^0$(HSO$_4$aq)  | 298.15| 34.52 ± 0.39              | Hovey and Hepler [22]      |
| 298.15            | 35.1  |                           | Klotz and Eckert [18]      |
| 298.15            | 35.68 |                           | Lindstrom and Wirth [20]   |
| 298.15            | 35.2  |                           | Larson et al. [21]         |
| 298.15            | 36.3 ± 0.14 |                      | Larson et al. [21]         |
| 313.15            | 38.22 ± 0.11 |                      | Hovey and Hepler [22]      |
| 328.15            | 39.06 ± 0.13 |                      | Hovey and Hepler [22]      |
| $\Delta V^0$      | 298.15| 20.0 ± 1.0                | Rohwer et al. [35]         |
| 298.15            | 20.2 ± 1.0 |                      | Klotz and Eckert [18]      |
| 298.15            | 21.6 ± 1.0 |                      | Lindstrom and Wirth [20]   |
| 298.15            | 19 ± 1.0 |                           | Bilal and Müller [32]      |
| 323.15            | 21.4 ± 0.6 |                      | Bilal and Müller [32]      |
| 348.15            | 23.3 ± 0.6 |                      | Bilal and Müller [32]      |
| 373.15            | 31.1 ± 0.7 |                      | Bilal and Müller [32]      |

*Assuming $V^0(H^+) = 0$ cm$^3$ mol$^{-1}$ at all $T$. *Value also recommended by Millero [36].

*Recalculated by Hovey and Hepler [22]. *Extrapolated value.
the thermodynamically rigorous formulations (Methods (1) and (2)) and Young’s rule (Methods (3) and (4)), and the difference between the DHLL and its Pitzer variant. Because the Pitzer variants produce lower $V_a$ estimates, they conversely lead to higher $V_{1a}$ values. Likewise, as Young’s rule leads to systematically higher $V_a$ than the thermodynamic approach, the calculated $V_{1a}$ values are systematically lower.

Overall, the $V_{1a}$ values obtained from these various approaches show a spread of ca. 0.4 cm$^3$ mol$^{-1}$ (Fig. 3). There are, however, two additional sources of uncertainty in $V_{1a}$: the values assumed for $V_2^a$ and for the protonation constant, $\log K_a^+$ (Eq. 1). These uncertainties were estimated by finite differences. Varying $V_2^a$ by $\pm$ 0.1 cm$^3$ mol$^{-1}$ resulted in an uncertainty in $V_{1a}$ of $\pm(0.01–0.06)$ cm$^3$ mol$^{-1}$, decreasing in magnitude at higher $T$. Uncertainties stemming from $\log K_a^+$ are significantly larger, with values of $\pm(0.06–0.14)$ cm$^3$ mol$^{-1}$ corresponding to an uncertainty of $\pm 0.01$ in $\log K_a^+$. In principle this uncertainty also decreases as $T$ increases (Fig. 4), but is counteracted to some extent by the increasing uncertainty in $\log K_a^+$ at higher $T$ (Fig. 5).

Recommended values for $V_{1a}$, calculated as the unweighted average of the results from the four calculation methods, are given in Table 5. The uncertainties in $V_{1a}$ are combined values ($\sigma_c$) estimated from the uncertainties in the calculation methods, as discussed above, and assuming $u(V_2^a) = 0.10$ cm$^3$ mol$^{-1}$ and $u(\log K_a^+)$ = 0.01. Both of the latter limits are probably optimistic. The values of $V_{1a}$ and $\sigma_c(V_{1a})$ at 283.15 K were taken from Hovey and Hepler [22] (Table 4).

As would be expected (see above) the values of $V_2^a$ for SO$_3^{2-}$ (Table 5) are similar to those of Marcus [41] but were derived using more recent data [38–40] and so are likely to be more reliable. At 298.15 K the present ‘conventional’ value of $V_1^a$(36.9 ± 0.4) cm$^3$ mol$^{-1}$ (Table 5) agrees almost quantitatively with that of Hovey and Hepler (Table 4), obtained from their combined Pitzer and Young’s rule analysis of their own sulfuric acid data [22]. It also compares well with the other literature values listed in Table 4 [11,18,20–22,36]. At 313.15 and 328.15 K, the only other temperatures where direct comparisons are possible, the present results (Table 5, Figure 5) for $V_{1a}$ again agree within the error limits with those of Hovey and Hepler (Table 4).

With regard to $\Delta V_r$, the standard volume change for the protonation reaction, the present result at 298.15 K (Table 5) is slightly higher than previous estimates (Table 4), although probably within the true uncertainties. At higher temperatures, the agreement between the present results (Table 5) and those of Bilal and Müller [32] (Table 4), obtained from potentiometric measurements of the effects of pressure on $K_a^+$ are within the stated error limits.

3.4. Comparison with other acids

Given the evidence above that indicates that at moderate concentrations H$_2$SO$_4$(aq) behaves essentially as a 1:1 electrolyte, it is interesting to compare its behaviour with common strong monoprotic acids. Fig. 6 plots $V$(HX$_{aq}$) for various mineral acids (extracted from the JESS database [10,38,43,44]) as a function of temperature. Note however that for representational purposes the position of each curve on the $y$-axis is arbitrary, with fixed addends chosen so as to maintain the actual $V$ sequence HTf $>$ HClO$_4$ $>$ H$_2$SO$_4$ $>$ HNO$_3$ $>$ HCl, where HTf is trifluoromethanesulfonic acid. The shapes of the $V$(T) curves for all five acids are broadly similar (Fig. 6) over the present temperature range. It is perhaps noteworthy that the volumetric behaviour of H$_2$SO$_4$(aq) appears to be somewhat more like the very weakly associated HNO$_3$(aq) and HCl(aq), rather than the stronger HClO$_4$(aq) and HTf(aq). This may indicate the presence of traces of H$_2$SO$_4^2$(aq).
Table 5

| T/K  | $V_i^{(\text{SO}_4^{2-})}/$cm$^3$/mol$^{-1}$ | $V_i^{(\text{HSO}_4^-)}$/cm$^3$/mol$^{-1}$ | $\Delta V^c$/cm$^3$/mol$^{-1}$ |
|------|---------------------------------|---------------------------------|---------------------------------|
| 283.15 | -                       | 34.52(39)                     | -                              |
| 293.15 | 13.59                    | 36.17(39)                     | 22.58                          |
| 298.15 | 14.15                    | 36.90(41)                     | 22.75                          |
| 303.15 | 14.52                    | 37.49(49)                     | 22.97                          |
| 308.15 | 14.73                    | 37.93(47)                     | 22.2                           |
| 313.15 | 14.78                    | 38.26(35)                     | 23.48                          |
| 318.15 | 14.72                    | 38.52(32)                     | 23.8                           |
| 323.15 | 14.55                    | 38.70(31)                     | 24.15                          |
| 328.15 | 14.29                    | 38.82(30)                     | 24.53                          |
| 333.15 | 13.94                    | 38.89(28)                     | 24.95                          |
| 338.15 | 13.51                    | 38.88(27)                     | 25.37                          |
| 343.15 | 13.02                    | 38.91(28)                     | 25.89                          |

*Numbers in brackets are the combined standard uncertainties $u_j(V_i)$. All $V_i$(ion) values are based on $V_i(H^+(aq)) = 0$ at all T. Derived from literature data as described in the text. From Hovey and Hepler [22].

4. Conclusions

Densities of aqueous solutions of sulfuric acid determined by vibrating tube densimetry have been used to calculate apparent molar volumes $V_m^{\text{(H}_2\text{SO}_4\text{aq})}$ at temperatures in the range 293.15 $\leq$ T/K $\leq$ 343.15 and concentrations 0.01 molar kg$^{-1}$ to 3.0. Consistent with earlier studies, the present $V_i$ values show an unusually large decrease at low solute concentrations. This is consistent with a change in chemical speciation of the sulfuric acid from a mainly 1:1 electrolyte ($H^+(aq) + HSO_4^-(aq)$) to a predominantly 1:2 electrolyte ($2H^+ + SO_4^{2-}(aq)$). Analysis of these data using combinations of different limiting laws and mixing equations, along with relevant literature data, enabled estimation of the standard state volume of $H_2SO_4(aq)$ and volume change for the first protonation reaction of the sulfate ion ($H^+(aq) + SO_4^{2-}(aq)$) as functions of temperature.

CRediT authorship contribution statement

Tuomas Vielma: Investigation, Writing - original draft, Funding acquisition. Lubomir Hnedkovsky: Methodology, Writing - review & editing. Glenn Hefter: Supervision, Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jct.2021.106408.

References

[1] H. Müller, Sulfuric acid and sulfur trioxide, in: F. Ullmann, W. Gerhartz (Eds.), Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany, 2000.
[2] F.K. Crundwell, M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, Prediction, Prevention, and Remediation, Wiley-Blackwell, Hoboken, USA, 2014.
[3] I.M. Klotz, C.F. Eckert, The apparent molal volumes of aqueous solutions of phosphoric acid (1st, 2nd, and 3rd), bicarbonate ion, and bisulfate ion in water solutions, J. Chem. Eng. Data 49 (4) (2004) 917–922.
[4] B.K. Joshi, N.D. Kandpal, Volumetric and transport properties of aqueous HSO_4 from 10–55 °C and calculation of the second dissociation constant to 350 °C, J. Chem. Soc. Faraday Trans. 86 (1990) 2831–2839.

Fig. 6. Comparison of $V_i^{(\text{HSO}_4,\text{aq})}$ and $V_i^{(\text{H}_2\text{SO}_4\text{aq})}$ for various mineral acids: black dots, present results; blue squares, HT (trifluoromethanesulfonic acid) [38,43,44] (−32.5 cm$^3$/mol$^{-1}$); red diamonds, HClO$_4$ [10] (<4 cm$^3$/mol$^{-1}$); green triangles, HNO$_3$ [10] (−5 cm$^3$/mol$^{-1}$); green diamonds, HClO$_4$ [11] (−14 cm$^3$/mol$^{-1}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
