Sulfate Protonation in Sodium Chloride and Sodium Perchlorate Media

Tuomas Vielma1 ✉ · Glenn Hefter2

Received: 23 February 2022 / Accepted: 31 May 2022 / Published online: 12 July 2022 © The Author(s) 2022

Abstract
The equilibrium (association) constant, \( K_A \), for the first protonation of the sulfate ion in aqueous solution: 
\[ \text{[H}^+(\text{aq}) + \text{SO}_{4}^{2-}(\text{aq}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) \] has been measured at 298.15 K in NaCl and NaClO4 media using glass-electrode potentiometry at five ionic strengths in the range 0.5 \( \leq I/(\text{mol}\cdot\text{dm}^{-3}) \leq 5.0 \). The present \( K_A \) values vary smoothly with \( I \) and are in good agreement with reliable literature data but indicate that the previously reported value of \( K_A \) at \( I = 5 \text{ mol}\cdot\text{dm}^{-3} \) in NaClO4 media is in error.

Keywords Sulfate · Hydrogensulfate · Protonation · Equilibrium constant · Association

1 Introduction
Apart from the self-ionization of water [1], the first protonation of the sulfate ion:

\[ \text{H}^+(\text{aq}) + \text{SO}_{4}^{2-}(\text{aq}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) \] (1)

is undoubtedly the most frequently studied equilibrium in aqueous solution chemistry [2]. Such data are widely employed for chemical speciation modelling of natural waters (marine, fresh, atmospheric) and industrial process solutions, especially in relation to the hydrometallurgical extraction of metals from their ores or wastes.

The association constant \( (K_A) \) corresponding to Eq. 1:

\[ K_A = [\text{HSO}_4^- (\text{aq})]/([\text{H}^+(\text{aq})] \cdot [\text{SO}_{4}^{2-}(\text{aq})]) \] (2)

has, as for most equilibria, been quantified mostly in the presence of relatively high concentrations of supposedly non-interacting ‘swamping’ electrolytes, to minimize variations in the activity coefficients of the interacting species [2, 3], which is essential for accurate stability constant measurements. The electrolyte media most widely employed for this purpose have been sodium perchlorate [NaClO4(aq)] and, to a lesser extent, sodium chloride [NaCl(aq)] [2]. The former is chosen mostly because of its weakly complexing character,
while the latter is of interest because of its perceived relevance to body fluids and other natural solutions [1, 3].

As shown recently [2], despite the popularity of these two salts for the quantification of Eq. 1, the agreement amongst independent determinations of $K_A$ at various ionic strengths ($I$) is only modest, even at 298.15 K. In particular, it has been shown that the numerous $K_A$ values (abstracted from more than 20 papers) measured at finite $I$ in NaClO$_4$(aq) media are rather scattered (see Fig. 4 of [2] and Fig. 3 below). Furthermore, their averaged values do not lie on a smooth curve when plotted against $I$ [2]. While such scatter often occurs amongst genuinely independent measurements of stability constants, it is a little surprising with respect to Eq. 1 given its relatively straightforward nature (no redox or other chemical instabilities; no overlapping reactions; neither too strong nor too weak, etc.) On the other hand, no such conclusions could be drawn regarding $K_A$ values in NaCl(aq) media due to insufficient data [2].

In an effort to lower the uncertainties in this important equilibrium constant, this paper reports a self-consistent set of measurements of the first protonation constant of the sulfate ion, Eq. 1, using H$^+$-responsive glass-electrode potentiometry at five ionic strengths in the range $0.5 \leq I/(\text{mol} \cdot \text{dm}^{-3}) \leq 5$ in both NaCl(aq) and NaClO$_4$(aq) media at 298.15 K.

2 Experimental Section

2.1 Materials

Analytical (AR) grade chemicals were used throughout without further purification; details of purities and sources are given in Table 1. Solutions were prepared volumetrically using calibrated A-grade glassware and high purity water (Ibis Technology, Australia, resistivity $\geq 18$ MΩ·cm) that had been boiled under vacuum for ~60 min to remove carbon dioxide. Acid concentrations were determined by manual titration against commercial Concentrated Volumetric Standard NaOH(aq) with a stated accuracy of ±0.2%, using phenolphthalein indicator. These values were cross-checked by occasional automated strong acid-strong base titrations using a glass electrode. Such titrations were analysed by Gran plots [4] and agreed to within ~0.4%.

Table 1 Sample sources and purities

| Chemical name            | CASRN   | Source        | Mass fraction purity |
|--------------------------|---------|---------------|----------------------|
| Hydrochloric acid        | 7647-01-0 | VWR          | $\geq 0.998$         |
| Perchloric acid          | 7601-90-3 | Merck        | 0.60                 |
| Sodium chloride          | 7647-14-5 | Ajax Finechem | $\geq 0.999$         |
| Sodium hydroxide         | 1310-73-2 | VWR          | $\geq 0.998$         |
| Sodium perchlorate       | 7601-89-0 | ACROS Organics | $\geq 0.99$         |
| Sodium sulfate           | 7757-82-6 | ChemSupply   | $\geq 0.99$         |

$^a$Concentrated volumetric standard

$^b$Analytical grade: the major impurity is water; all other impurities are negligible
2.2 Apparatus and Procedures

Potentiometric titrations were carried out in tall-form pyrex-glass jacketed cells, with machined PTFE lids. Cell temperatures were maintained at 298.15 ± 0.02 K, with a NIST-traceable accuracy of ± 0.05 K, using a refrigerated thermostat-circulator (Julabo, Germany, model F33). A total of four glass electrodes (GEs; Metrohm, Switzerland, Model 6.0101.000) were employed. Individual electrodes were ‘rested’ in 0.005 mol·dm –3 HCl + 0.1 mol·dm −3 NaCl for at least 12 h before a titration. Four Ag–AgCl reference electrodes (REs) of in-house construction were filled with 5 mol·dm −3 NaCl(aq) and used in conjunction with a 5 mol·dm −3 NaCl(aq) salt bridge (SB). The performance of the electrodes was checked by occasional strong acid (HCl or HClO4) + strong base (NaOH) titrations.

Ignoring the galvanic cell sign convention, the cells used in this study can be represented:

\[ \text{RE} \parallel 5.0 \text{ mol} \cdot \text{dm}^{-3} (\text{NaCl}) \parallel \text{HX, NaOH, Na}_2\text{SO}_4, I(\text{NaX})|\text{GE} \]

where the single vertical line represents the GE membrane, the double vertical lines indicate porous glass frits, and \( E_{j1} \) or \( E_{j2} \) are liquid junction (diffusion) potentials (LJPs) that develop across the frits [5]. The quantity \( I(\text{NaX}) \), with \( X^- = \text{Cl}^- \) or \( \text{ClO}_4^- \), denotes a solution of constant ionic strength maintained with appropriate amounts of NaX(aq). Cell potentials were measured to ± 0.1 mV with a high impedance voltmeter of in-house design. Titrations were performed using an automated piston burette (Metrohm, Model 665) with an accuracy of ± 0.1%. Solutions were stirred continuously with a PTFE-encased magnetic bar. All measurements were made on the mol·dm−3 scale.

Assuming the Nernst relationship is applicable, the observed cell potential, \( E_{\text{obs}} \), is given by:

\[ E_{\text{obs}} = E^{\circ} + 59.16 \log_{10} [\text{H}^+] \]  

where \( E^{\circ} \) is a formal cell potential, which includes an activity coefficient term and the LJPs, all of which are assumed to be constant throughout a titration, and 2.3026 \( R T / F = 59.16 \text{ mV} \) is the Nernst slope at 298.15 K [3, 6]. A value of \( E^{\circ} \) was obtained for each titration by in situ calibration using a known \([\text{H}^+] \) in the medium of interest.

Titrations data were processed using the ESTA suite of programs [7, 8]. Association constants were determined by minimizing the objective function \( U \) that quantifies the agreement between the calculated and experimental data:

\[ U = \left( N - n_p \right)^{-1} \sum_{n=1}^{N} \sum_{q=1}^{n_e} n_q^{-1} w_{nq} \left[ Y_{nq}^{\text{obs}} - Y_{nq}^{\text{calc}} \right]^2 \]  

where \( N \) is the total number of titration points, \( n_p \) is the number of parameters to be optimised, \( n_e \) is the number of sensing electrodes in a given titration, \( w_{nq} \) is the weight of the \( q \)th residual at the \( n \)th point, and \( Y_{nq}^{\text{obs}} \) and \( Y_{nq}^{\text{calc}} \) are respectively the observed and calculated variable of the \( q \)th residual at the \( n \)th point. Titrations were optimized using the observed cell potentials \( (Y=E_{\text{obs}}) \) without weighting \((w_{nq} = 1)\).
3 Results and Discussion

The results obtained for $K_A$ in NaCl(aq) and NaClO$_4$(aq) media are listed in Table 2 along with relevant titration information. Satisfactory values of $K_A$ were obtained initially (data not shown) using ‘conventional’ ligand protonation titrations [3, 7, 8]. This involved calibrating of the GE with a known concentration of H$^+$ in the medium of interest followed by addition of a known amount of ‘ligand’ (ie, SO$_2^{-4}$) and titration with OH$^-$. Essentially identical $K_A$ values, but with significantly lower standard deviations, were determined by titrating SO$_2^{-4}$ directly into the in situ calibrating solution. This approach is better for quantifying Eq. 1 because it maximizes variation of the SO$_2^{-4}$/H$^+$ ratio (Table 2) and because the relatively small effect of Eq. 1 on the cell potential is not overwhelmed by the much larger effects of the strong-acid/strong-base reaction (ie, H$^+(aq)$ + OH$^-(aq)$ → H$_2$O). Typical titration curves shown in Fig. 1 demonstrate the magnitude of the observed experimental effects.

The present results and selected literature data are shown as a function of $I$ in Figs. 2 and 3 respectively. In NaCl media (Fig. 2), the present results (black dots) are in excellent agreement at all comparable $I$ with the values of Dickson et al. (orange circles) [9]. Note that the latter were derived by extrapolation of results obtained by high precision hydrogen-electrode potentiometry on the molality (mol·kg$^{-1}$) scale at higher temperatures [9]. Conversion to the molarity (mol·dm$^{-3}$) scale employed densities calculated from Archer’s equation [10]. The present results are, where comparison is possible, in good agreement with the values of Schöön and Wannholt [11], also obtained by GE potentiometry over the range 0.25 ≤ $I$/mol·dm$^{-3}$ ≤ 2. The only other study reporting $K_A$ values as a function of $I$ in NaCl(aq) is the Raman spectroscopic study of Kratsis et al. [12] at 0.5 ≤ $I$/

### Table 2

| $I$/mol·dm$^{-3}$ | $10^3$[H$^+$]$^{a}$ | $10^3$[SO$_2^{-4}$]$^{b}$ | log$_{10}$K$_A$(SD)$^{c}$ | $N_t$/$N_d$
|---|---|---|---|---|
| **NaCl** | | | | |
| 0.50 | 3–5 | 17 | 1.256(11) | 3/153 |
| 1.00 | 3–10 | 33 | 1.106(18) | 3/78 |
| 2.00 | 3–10 | 33 | 1.001(5) | 3/153 |
| 3.00 | 3–10 | 33 | 1.013(9) | 3/153 |
| 5.00 | 6–10 | 33 | 1.145(14) | 3/153 |
| **NaClO$_4$** | | | | |
| 0.50 | 3–5 | 17 | 1.178(16) | 3/153 |
| 1.00 | 3–10 | 33 | 1.112(11) | 3/153 |
| 2.00 | 3–10 | 33 | 1.050(18) | 3/153 |
| 3.00 | 3–10 | 33 | 1.099(21) | 2/102 |
| 5.00 | 6–10 | 17 | 1.354(10) | 2/102 |

Standard uncertainties $u(I) = 0.002$, $u(T) = 0.05$ K, $u_p(p) = 0.01$

*a* Approximate concentration range during the titration(s)

*b* Approximate final concentration

*c* Numbers in parentheses are standard deviations in the last digit of log$_{10}$K$_A$

*d* Number of independent titrations/total number of data points processed
(mol·dm\(^{-3}\)) ≤ 4. Even though this technique is less precise than potentiometry (note the relative size of the error bars) the values obtained, the green triangles in Fig. 2, agree with the present findings almost within the relatively large uncertainties. An alternative explanation for the difference between the present results and those of Kratis et al. is that it might be a medium effect due to the much higher replacement of the swamping electrolyte by sulfate, which is necessitated by the relatively low sensitivity of Raman spectroscopy.

The situation with respect to \(K_A\) values in NaClO\(_4\)(aq) media differs from that in NaCl(aq) because while there are many independent values few are reported as functions of \(I\). Accordingly, Fig. 3 includes the averages of the available data [2] at each \(I\). As noted in the Introduction these average values do not lie on a smooth curve although they are broadly consistent with the present results. Also shown in Fig. 3 are the spectrophotometric values determined by Ashurst and Hancock at \(I/(\text{mol·dm}^{-3}) = 1, 2\) and 5 [13, 14]. While the first two results are
in good agreement with the present values, the last result is significantly larger ($\log_{10} K_A = 1.54$ vs. 1.35). Given the similarity of the behaviour of $\log_{10} K_A$ in the two media (compare Figs. 2 and 3) it seems likely that the value of Ashurst and Hancock in 5 (mol·dm$^{-3}$) (NaClO$_4$) is in error.

For convenience, the present $K_A$ values (Table 2) were fitted with an extended Guggenheim-type equation:

$$\log_{10} K_A = \log_{10} K_A^\circ - \frac{4A_I}{\ln 10} \left( \frac{I^{0.5}}{1 + AI^{0.5}} \right) + BI + CI^{1.5}$$

(5)

where $\log_{10} K_A^\circ = 1.984 \pm 0.013$ [2] and $A_I (= 1.176 \text{ mol}^{-0.5} \text{dm}^{-1.5})$ is the Debye–Hückel slope for activity coefficients at 298.15 K [6]. The quantities $A$, $B$ and $C$ are adjustable parameters with values in NaCl(aq)//NaClO$_4$(aq) media respectively of (1.5536//1.0921) mol$^{-0.5}$·dm$^{-1.5}$, (−0.15974//0.034815) mol$^{-1}$·dm$^3$ and (0.087880//0.046303) mol$^{-1.5}$·dm$^{4.5}$. As can be seen from Figs. 2 and 3, the present results are well-fitted by Eq. 5.

It is interesting to note that the $\log_{10} K_A$ values in the two media differ only slightly (Table 2), with a maximum difference of just 0.2 (unsurprisingly at the highest $I$). This is probably a reflection of the relative strength of the $\text{Na}^+(aq) + \text{SO}_4^{2-}(aq)$ interactions [12, 15] cf. the other ion-ion interactions in these mixtures.

Combination of the present results with the better-quality literature data indicate that the first protonation of $\text{SO}_4^{2-}$ in these two media can now be considered well quantified over a wide range of ionic strengths. However, the same cannot be said of other media, for which almost no systematic data exist [2]. This is especially so with respect to mixed electrolytes, which are the norm in natural waters and industrial process solutions. The accuracy of speciation models for these inherently complicated systems will be enhanced by future determinations of such data.
4 Conclusions

The equilibrium constant for the first protonation of the sulfate ion, SO$_4^{2-}$(aq), has been studied by glass electrode potentiometry in NaCl(aq) and NaClO$_4$(aq) media at ionic strengths $I$(mol·dm$^{-3}$) = 0.5, 1.0, 2.0, 3.0 and 5.0 at $T$ = 298.15 K and 0.1 MPa pressure. The results obtained were well-fitted with a Guggenheim-type equation, are smooth functions of $I$, and agree well with reliable literature data. There is scope for future systematic studies of this equilibrium in single electrolyte solutions and in mixed media.

Acknowledgements This work was funded by Walter Ahlström Foundation, Finnish Research Impact Foundation (TV) and Murdoch University (GH).

Funding Open Access funding provided by University of Oulu including Oulu University Hospital.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Brown, P.L., Ekberg, C.: Hydrolysis of Metal Ions. Wiley, Weinheim, Germany (2016)
2. Hefter, G.T., Guminski, C.: Remarks on the evaluation of thermodynamic data for sulfate ion protona-
tion. J. Solution Chem. 48, 1657–1670 (2019)
3. Rossotti, H.S.: The Study of Ionic Equilibria. Longmans, London (1978)
4. Gran, G.: Determination of the equivalence point in potentiometric titrations. Part II. Analyst 77, 661–
671 (1952)
5. Hefter, G.T.: Calculation of liquid junction potentials for equilibrium studies. Anal. Chem. 54, 2518–
2524 (1982)
6. Robinson, R.S., Stokes, R.H.: Electrolyte Solutions, 2nd edn. Butterworths, London (1970)
7. May, P.M., Murray, K., Williams, D.R.: The use of glass electrodes for the determination of formation
constants. II. Simulation of titration data. Talanta 32, 483–489 (1985)
8. May, P.M., Murray, K., Williams, D.R.: The use of glass electrodes for the determination of formation
constants. III. Optimization of titration data: the ESTA library of computer programs. Talanta 35, 825–830 (1988)
9. Dickson, A.G., Wesolowski, D.J., Palmer, D.A., Mesmer, R.E.: Dissociation constant of bisulfate ion
in aqueous sodium chloride solutions to 250 °C. J. Phys. Chem. 94, 7978–7985 (1990)
10. Archer, D.G.: Thermodynamic properties of NaCl + H$_2$O system. II. Thermodynamic properties of
NaCl(aq), NaCl·2H$_2$O(cr), and phase equilibria. J. Phys. Chem. 21, 793–829 (1992)
11. Schöön, N.H., Wannholt, L.: Determination of the acidity constants for sulfur dioxide and hydrogen
sulfate ion in water solution at different ionic strength (ionic medium NaCl) and at elevated tempera-
ture. Svensk Papperstidning 72, 431–435 (1961)
12. Kratsis, S., Hefter, G.T., May, P.M., Sipos, P.: Thermodynamics of protonation and sodium binding of
sulfate in concentrated NaCl and CsCl solutions studied by Raman spectroscopy. Austral. J. Chem. 53, 363–367 (2000)
13. Ashurst, K.G., Hancock, R.D.: Characterization of inner- and outer-sphere complexes by thermo-
dynamics and absorption spectra. Part 1. Sulphato-complexes of the first-row transition elements. J.
Chem. Soc. Dalton Trans. (1977). https://doi.org/10.1039/dt9770001701
14. The medium is not stated in ref [13] but is listed as NaClO$_4$ in: Ashurst, K. G., Hancock, R. D.: The
thermodynamics of the formation of sulphate complexes of iron(III), cobalt(II), iron(II), manganese(II)
and copper(II) in perchlorate medium, Report 1914, Nat. Inst. Metall., Randburg, South Africa (1977)
15. Buchner, R., Capewell, S.G., Heffer, G.T., May, P.M.: Ion-pair and solvent relaxation processes in aqueous Na$_2$SO$_4$ solutions. J. Phys. Chem. B **103**, 1185–1192 (1999)

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.