



Sulfate Protonation in Sodium Chloride and Sodium Perchlorate Media

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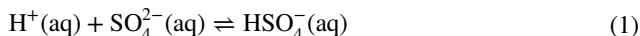
Abstract

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:



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:

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

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,

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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 $\text{NaClO}_4(\text{aq})$ 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 $\text{NaCl}(\text{aq})$ 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 $\text{NaCl}(\text{aq})$ and $\text{NaClO}_4(\text{aq})$ 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 $\geq 18 \text{ M}\Omega\cdot\text{cm}$) 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 $\text{NaOH}(\text{aq})$ with a stated accuracy of $\pm 0.2\%$, 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 $\sim 0.4\%$.

Table 1 Sample sources and purities

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

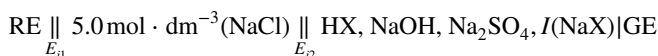
^aConcentrated volumetric standard

^bAnalytical 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 $0.005 \text{ mol}\cdot\text{dm}^{-3} \text{ HCl} + 0.1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl}$ for at least 12 h before a titration. Four Ag–AgCl reference electrodes (REs) of in-house construction were filled with $5 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl(aq)}$ and used in conjunction with a $5 \text{ mol}\cdot\text{dm}^{-3} \text{ NaCl(aq)}$ salt bridge (SB). The performance of the electrodes was checked by occasional strong acid (HCl or HClO_4) + strong base (NaOH) titrations.

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



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 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 $\pm 0.1\%$. Solutions were stirred continuously with a PTFE-encased magnetic bar. All measurements were made on the $\text{mol}\cdot\text{dm}^{-3}$ scale.

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

$$E_{\text{obs}} = E^{\circ'} + 59.16 \log_{10} [\text{H}^+] \quad (3)$$

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 $2.3026 RT/F = 59.16$ 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.

Titration 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:

$$U = (N - n_p)^{-1} \sum_{n=1}^N n_e^{-1} \sum_{q=1}^{n_e} w_{nq} \left[Y_{nq}^{\text{obs}} - Y_{nq}^{\text{calc}} \right]^2 \quad (4)$$

where N is the total number of titration points, n_p is the number of parameters to be optimized, 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}^{obs} and Y_{nq}^{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 NaClO₄(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 in situ calibration of the GE with a known concentration of H⁺ in the medium of interest followed by addition of a known amount of ‘ligand’ (ie, SO₄²⁻) and titration with OH⁻. Essentially identical K_A values, but with significantly lower standard deviations, were determined by titrating SO₄²⁻ directly into the in situ calibrating solution. This approach is better for quantifying Eq. 1 because it maximizes variation of the SO₄²⁻/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) → H₂O). 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 Schön 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 Association constant K_A for the equilibrium: H⁺(aq) + SO₄²⁻(aq) ⇌ HSO₄⁻(aq) as a function of ionic strength I in NaCl(aq) and NaClO₄(aq) media at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa

I /(mol·dm ⁻³)	10 ³ [H ⁺] _T ^{a/} (mol·dm ⁻³)	10 ³ [SO ₄ ²⁻] _T ^{b/} (mol·dm ⁻³)	log ₁₀ K_A (SD) ^c	N_i/N^d
<i>NaCl</i>				
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
<i>NaClO₄</i>				
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 $u_i(I) = 0.002$, $u(T) = 0.05$ K, $u_i(p) = 0.01$

^aApproximate concentration range during the titration(s)

^bApproximate final concentration

^cNumbers in parentheses are standard deviations in the last digit of log₁₀ K_A

^dNumber of independent titrations/total number of data points processed

Fig. 1 Example titration curves in $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4(\text{aq})$ media, with two different initial $\text{H}^+(\text{aq})$ concentrations and one replicate. Solid curves are the calculated changes in the cell potential using the present optimized K_A value (Table 2)

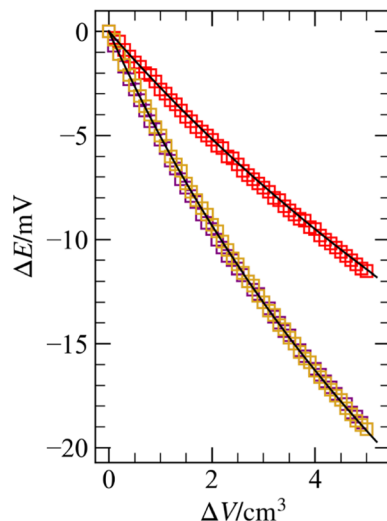
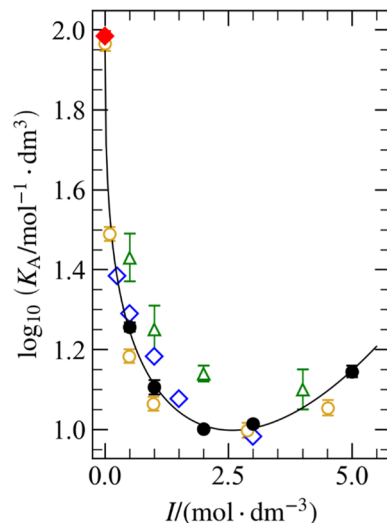


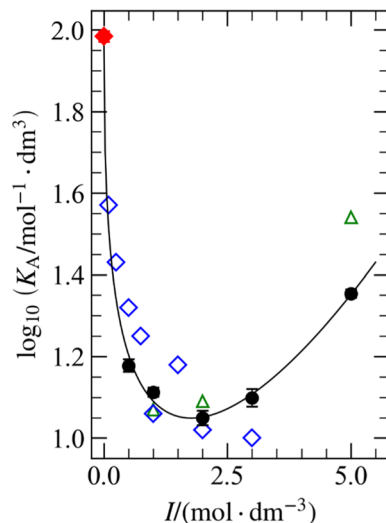
Fig. 2 Association constant K_A for equilibrium (1) in $\text{NaCl}(\text{aq})$ as a function of ionic strength I at $T=298.15 \text{ K}$ and 0.1 MPa pressure. Black dots, present results; yellow circles, Dickson et al. [9]; blue diamonds, Schön and Wanholt [11]; green triangles, Kratsis et al. [12]. The red diamond at $I=0$ is the current recommended value of $\log_{10} K_A^\circ = 1.984 \pm 0.013$ [2]. The solid line is the fit of the present values with Eq. 4 (Color figure online)



$(\text{mol}\cdot\text{dm}^{-3}) \leq 4$. 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 Kratsis 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 $\text{NaClO}_4(\text{aq})$ media differs from that in $\text{NaCl}(\text{aq})$ 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 $I/(\text{mol}\cdot\text{dm}^{-3})=1, 2$ and 5 [13, 14]. While the first two results are

Fig. 3 Association constant K_A for equilibrium (1) in $\text{NaClO}_4(\text{aq})$ as a function of ionic strength I at $T=298.15$ K and 0.1 MPa pressure. Black dots, present results; blue diamonds, average values from various literature sources [2]; green triangles, Ashurst and Hancock [13, 14]. The red diamond at $I=0$ is the current recommended value of $\log_{10} K_A^\circ = 1.984 \pm 0.013$ [2]. The solid line is the fit of the present values with Eq. 4 (Color figure online)



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:

$$\log_{10} K_A = \log_{10} K_A^\circ - \frac{4A_\gamma}{\ln 10} \times \frac{I^{0.5}}{1 + AI^{0.5}} + BI + CI^{1.5} \quad (5)$$

where $\log_{10} K_A^\circ = 1.984 \pm 0.013$ [2] and $A_\gamma (= 1.176 \text{ mol}^{-0.5} \cdot \text{dm}^{-1.5})$ 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 $\text{NaCl}(\text{aq})/\text{NaClO}_4(\text{aq})$ media respectively of (1.5536//1.0921) $\text{mol}^{-0.5} \cdot \text{dm}^{-1.5}$, (-0.15974//0.034815) $\text{mol}^{-1} \cdot \text{dm}^3$ and (0.087880//0.046303) $\text{mol}^{-1.5} \cdot \text{dm}^{4.5}$. 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 $\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ 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 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, $\text{SO}_4^{2-}(\text{aq})$, has been studied by glass electrode potentiometry in $\text{NaCl}(\text{aq})$ and $\text{NaClO}_4(\text{aq})$ media at ionic strengths $I/(\text{mol}\cdot\text{dm}^{-3})=0.5, 1.0, 2.0, 3.0$ 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.

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