# Dissociation constants and speciation in aqueous Li$_2$SO$_4$ and K$_2$SO$_4$ from measurements of electrical conductance to 673 K and 29 MPa

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## Abstract

The electrical conductivities of aqueous solutions of Li$_2$SO$_4$ and K$_2$SO$_4$ have been measured at 523–673 K at 20–29 MPa in dilute solutions for molalities up to $2 \times 10^{-2}$ mol kg$^{-1}$. These conductivities have been fitted to the conductance equation of Turq, Blum, Bernard, and Kunz with a consensus mixing rule and mean spherical approximation activity coefficients. In the temperature interval 523–653 K, where the dielectric constant, $\varepsilon$, is greater than 14, the electrical conductance data can be fitted by a solution model which includes ion association to form $MSO_4^-$, $M_2SO_4^0$, and $HSO_4^-$, where M is Li or K. The adjustable parameters of this model are the first and second dissociation constants of the $M_2SO_4$. For the 673 K and 300 kg m$^{-3}$ state point where the Coulomb interactions are the strongest (dielectric constant, $\varepsilon = 5$), models with more extensive association give good fits to the data. In the case of the Li$_2$SO$_4$ model, including the multi-ion associate, Li$_{16}$(SO$_4$)$_8^0$, gave an extremely good fit to the conductance data.
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## 1. Introduction

A knowledge of the activity coefficients and association constants of alkali sulfates, in particular Li$_2$SO$_4$(aq) and K$_2$SO$_4$(aq), are important in a variety of geochemical and industrial processes. Sulfates represent an important component of the mineral economy and of pollution problems in air and water. There is considerable scientific interest in the mineralogy and geochemistry of sulfate minerals in both high-temperature (igneous and hydrothermal) and low-temperature (weathering and evaporite)

environments. The physical scale of processes affected by aqueous sulfate spans from submicroscopic reactions at mineral–water interfaces to global oceanic cycling and mass balance, and to extraterrestrial applications in the exploration of other planets and their satellites (Alpers et al., 2001). The association of alkali metal sulfates in aqueous solutions at elevated temperatures is also of great importance in many industrial processes such as material transport, solid deposition, and corrosion in electric power plants. Sulfates are common products of hydrothermal waste destruction by supercritical water oxidation.

The data on limiting equivalent sulfate conductance are necessary to predict the diffusion transport of sulfate components in geochemical processes involving fluid–rock interaction (Balashov, 1995).

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One of the most accurate and comprehensive sets of conductivity measurements of aqueous $K_2SO_4$ from 18 up to 306 °C was reported by Arthur Noyes and Arthur Melcher one century ago (Noyes and Melcher, 1907). The initial and final dates of their $K_2SO_4$ experiments are March 14, 1904, and September 29, 1905, respectively. These investigations were continued at ambient temperatures by different authors (Clews, 1935; Jenkins and Monk, 1950; Broadwater and Evans, 1974; Valyashko and Ivanov, 1974; Fedoroff, 1989; Indelli, 1989) and at elevated temperatures (Quist and Marshall, 1966) using conductance measurements, and (Matsushima and Okuwaki, 1988) using e.m.f. measurements. These efforts resulted in the determination of the ion-pair $KSO_4^-$ dissociation constant and limiting equivalent conductance of $SO_4^{2-}$. However, $KSO_4^-$ has not been studied at temperatures near the critical point of water.

The conductivity of aqueous $Li_2SO_4$ was also studied by several authors (Austin and Mair, 1962; Postler, 1970; Valyashko and Ivanov, 1974; Indelli, 1989) but the results are limited to $T \leqslant 200$ °C. There are no previous measurements of association to form the uncharged ion aggregates $K_2SO_4{}^0(aq)$ and $Li_2SO_4{}^0(aq)$.

The conductivities of aqueous $K_2SO_4$ and $Li_2SO_4$ at molalities from 0.05 up to 0.5 mol kg$^{-1}$ and up to 200 °C were measured by Mil'chev and Gorbachev (1958) but their molalities are two high for our method of analysis.

Recently, a new quantitative approach to the analysis of electrical conductivity of aqueous electrolyte solutions was developed by R.H. Wood et al. (Sharygin et al., 2001, 2002; Hnedkovsky et al., 2005). Here, we report new conductivity measurements for $Li_2SO_4(aq)$ and $K_2SO_4(aq)$ in an apparatus with solution flow (Sharygin et al., 2000). Association constants and limiting equivalent conductances are derived for $Li_2SO_4(aq)$ and $K_2SO_4(aq)$ at temperatures from 18 to 400 °C, pressures up to 29 MPa, and water densities from 1000 kg m$^{-3}$ to 300 kg m$^{-3}$.

We found that the model that reproduces most of the experimental data is a model with association to form $MSO_4^-(aq)$ and $M_2SO_4{}^0(aq)$, where M is Li or K, and with ion activities calculated with the Mean Spherical Approximation (MSA). In the case of aqueous $Li_2SO_4$ for the region where the dielectric constant is very low, (water density 300 kg m$^{-3}$), a model with further association to form aggregates $Li_m(SO_4)_s$ with $m + s > 3$ fits the data at the highest molality $2.6 \times 10^{-3}$.

## 2. Experimental

The flow-type, high-temperature, high-pressure conductance apparatus and the associated operating procedures have been previously described in detail (Zimmerman et al., 1995; Gruszkiewicz and Wood, 1997; Sharygin et al., 2001, 2002) and will not be repeated here. The conductance apparatus with platinum–rhodium tubing in the hot zone was used to measure aqueous solutions of $Li_2SO_4$ and $K_2SO_4$ at a given temperature and pressure. The conductance cell consisted of a platinum–rhodium cup which served as an outer electrode and a sapphire insulator with a hole in the center through which the inner electrode passed into the center of the cup. Resistances were measured at frequencies of 1 and 10 kHz using a RCL meter (Fluke Co.; Model PM6304c) with manufacturer's stated accuracy of 0.05% at 1 kHz and 0.1% at 10 kHz. All measured resistances were corrected for the lead resistance. Lead resistances were always less than 0.5% of the solution resistance. The temperature was measured by a platinum resistance thermometer (Hart Scientific; Model 5612) with a stated calibration accuracy of $\pm0.007$ K at 273 K, $\pm0.024$ K at 473 K, and $\pm0.033$ K at 673 K. The solution was introduced inside of the conductance apparatus using an HPLC pump (Waters, Division of Millipore, Inc.; Model 590) which was operated at a constant flow rate of $8.3 \times 10^{-3}$ cm$^3$ s$^{-1}$. The pressure was measured using a Digiquartz pressure transducer (Paro-Scientific, Inc.; Model 760-6K) with an accuracy of $\pm0.01$ MPa. The temperature and pressure were recorded immediately after a stable reading of resistance was achieved, corresponding to a sample plateau.

The cell constant was first determined before all reported measurements by a series of four measurements on dilute aqueous solutions of KCl (with molarities from $10^{-4}$ to $10^{-2}$ mol dm$^{-3}$) at $T = 298.15$. The solutions of KCl used in the calibration of the cell were prepared by mass from certified A.C.S. grade KCl (Fisher Scientific Co.; maximum impurity was mass fraction $10^{-4}$ of Br$^-$) and distilled and deionized water. The salt was dried for 24 h at $T = 573$ K, cooled in a desicator under vacuum, and diluted by mass with conductivity water to the initial molality. All apparent masses were corrected for buoyancy. Using equations given by (Justice, 1983) and (Barthel et al., 1980) for KCl (aq) the cell constant was calculated to be $(0.2025 \pm 0.0004)$ cm$^{-1}$ at 298 K. Calculated cell constants agreed within 0.2% over the complete range of concentrations. The cell constant at elevated temperatures was calculated from the known thermal expansion of the platinum cup, inner electrode, and sapphire insulator. The corrections are small.

Stock solutions of $K_2SO_4$ were prepared from A.C.S. reagent-grade granular potassium sulfate, which was dried overnight in a vacuum oven at $T = 473$ K, cooled under vacuum, and diluted with conductivity water. The solutions were prepared by mass, and all weights were corrected to air buoyancy. Stock solutions of $Li_2SO_4$ were prepared from A.C.S. reagent-grade lithium sulfate monohydrate using the same procedure as described for $K_2SO_4$. The conductivities of all stock solutions were measured at room temperature immediately after all experiments were completed. This showed that the solutions had not changed during the course of the measurement ($\pm0.1\%$). A glass cell with the cell constant equal to 23.705 cm$^{-1}$ was used to measure conductivities of concentrated stock solutions and these conductivities

agreed with literature values to 0.2%. The conductivity water used was first treated using a reverse osmosis system, then passed through one carbon adsorbent and two deionization tanks (Hydro Service and Supplies, Inc.; Picosystem, Model 18). The resulting specific conductance of water was about $2 \times 10^{-5}\,\text{S m}^{-1}$ at $T = 298\,\text{K}$. The solvent conductance was measured at each temperature and pressure.

The experimental conductivities of Li₂SO₄(aq) and K₂SO₄(aq) were corrected for the specific conductivity of impurities in the solvent (water) according to the equation

$$\kappa_\alpha^{\text{crr}} = \kappa_\alpha^{\text{obs}} - \kappa_{\text{solvent}}^{\text{obs}} + \kappa_{\text{w}}, \tag{1}$$

where $\alpha$ is Li₂SO₄ or K₂SO₄; $\kappa_{\text{w}}$, S cm$^{-1}$, is conductivity of pure H₂O calculated from $\kappa_{\text{w}}$ and the equivalent conductances of H$^+$ and OH$^-$. This correction is based on the assumption that the solvent conductance above that due to H$^+$ and OH$^-$ is due to impurities also present in the solutions [see (Sharygin et al., 2001) for details].

The apparent equivalent conductances of Li and K sulfates were defined by expression

$$\Lambda_\alpha = \frac{1000\kappa_\alpha^{\text{crr}}}{2c_\alpha}, \tag{2}$$

where $c_\alpha$, the molar concentration in mol dm$^{-3}$, is

$$c_\alpha = \frac{m_\alpha}{V^*}. \tag{3}$$

The volume of solution per 1 kg of water in dm$^3$ kg$^{-1}$, $V^*$, was calculated from the thermodynamic model of electrolyte solutions [see Section 3]. The Li₂SO₄(aq) and K₂SO₄(aq) experimental data at each temperature and pressure are listed in Tables 1 and 2, respectively.

# 3. Theory

## 3.1. Fitting conductance data

Aqueous solutions of Li₂SO₄ and K₂SO₄ must be treated as mixed electrolytes, since association of sulfate ion with Li$^+$ and K$^+$ ion occurs. Our equation for the conductance of a reacting mixture of electrolytes has three components: (1) a model for the activity coefficients of the ions, so that the equilibrium concentrations of free ions in a mixture of species at a given salt concentration can be calculated from the mass balance relations and the equilibrium constants for the reactions; (2) an equation for the equivalent conductivity of a single strong electrolyte as a function of concentration; (3) a mixing rule that predicts the conductance of a mixture of strong electrolytes from the conductance of the single electrolytes. Recently, Sharygin et al. (2001) have tested this model and shown that it allows the calculation of association constants from conductance measurements containing a mixture of ions. The complete details of the equations used in our model have been published (Sharygin et al., 2001, 2002). Below we will give only a brief discussion of the model.

## 3.2. Multiple ion association

In general, for a 1:2 electrolyte, M₂SO₄, we assume the existence of M$_m$H$_h$(SO₄)$_s$ ion aggregates with charge $(m + h - 2s)$. We characterize the ion equilibria in solution by overall dissociation reactions:

$$\text{M}_m\text{H}_h(\text{SO}_4)_s^{m+n-2s} = m\text{M}^+ + h\text{H}^+ + s\text{SO}_4^{2-}. \tag{4}$$
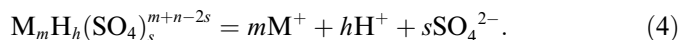
The thermodynamic expression of mass action law of Reaction (4) has the form

$$K_{m,h,s}^{\text{M}} = \frac{a_{\text{M}^+}^m\, a_{\text{H}^+}^h\, a_{\text{SO}_4^{2-}}^s}{a_{\text{M}_m\text{H}_h(\text{SO}_4)_s^{m+h-2s}}}, \tag{5}$$

with $a_{\text{M}^+} = \gamma_{\text{M}^+} m_{\text{M}^+}$ etc., are the molal activities of species in solution, $K_{m,h,s}^{\text{M}}$ is the overall dissociation constant of an ion cluster with cluster index, $m,h,s$; $m_{\text{M}^+}$ is the molality and $\gamma_{\text{M}^+}$ is the molal activity coefficient. The conversion of this constant to the constant with a 1 mol dm$^{-3}$ standard state is given by expression

$$K_{m,h,s}^{c\text{M}} = K_{m,h,s}^{\text{M}}(V^0)^{1-m-h-s}, \tag{6}$$

where $V^0$ is the volume of 1 kg of pure solvent (water).

## 3.3. Activity coefficient models

We have used the mean spherical approximation (Blum and Høye, 1977) (MSA) to calculate activity coefficients. The MSA equation is much more accurate than the Debye–Hückel equation for the activity coefficients of hard spheres in a continuous dielectric medium and it is still an analytic equation. It is more accurate because it conforms to both the Debye–Hückel limiting law at low concentrations and the correct hard sphere repulsion in very concentrated solutions. Both equations apply to a hard sphere ion in a continuous dielectric medium and both equations are rigorously applicable only to the McMillan–Mayer standard state (Friedman and Dale, 1977). In our calculations, we ignored the corrections to the McMillan–Mayer standard state but we did account for the difference in standard states [1 mol dm$^{-3}$ for MSA; see Eq. (6)] and this appears to reduce corrections to the McMillan–Mayer standard state (Sedlbauer and Wood, 2004) so the corrections are probably less than the corrections predicted by Myers et al. (2003) at the highest molality of the two highest temperatures. Other corrections are small. When the usual Debye–Hückel equations are used, the large density changes with concentration are not taken into account and it performs badly near the critical point (Sedlbauer and Wood, 2004).

The activity coefficient at $c = 1$ mol dm$^{-3}$ standard state in the MSA approximation can be expressed in the form of electrostatic (el) and hard sphere (hs) contributions:

$$\ln y_i^{\text{MSA}} = \ln y_i^{\text{el}} + \ln y_i^{\text{hs}}. \tag{7}$$

Table 1
Experimental temperatures ($T/°C$), pressures ($P/MPa$), molalities of $K_2SO_4$ ($m$/mol/kg), and apparent equivalent conductance ($\Lambda$/S cm$^2$ equiv$^{-1}$) of aqueous $K_2SO_4$ [see Eqs. (2) and (3)] and their deviations ($\overline{\Delta\Lambda} = \frac{\Lambda^{Th}-\Lambda}{\Lambda}$) from conductances ($\Lambda^{Th}$ (S cm$^2$ equiv$^{-1}$)) calculated from theoretical conductivities Eq. (18) at average temperatures ($\bar{T}$ °C), pressures ($\bar{P}$ MPa), and densities of water ($\bar{\rho}^0$ kg m$^{-3}$)

| $T$ | $P$ | $m10^3$ | $\Lambda$ | $\overline{\Delta\Lambda}100\%$ |
|---|---|---|---|---|
| $\bar{T} = 250.6$ °C, $\bar{P} = 20.07$MPa, $\bar{\rho}^0 = 815.4$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 4.43$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.13$ | | | | |
| 250.75 | 20.06 | 0.0590 | 961.9 | −0.03 |
| 250.71 | 20.07 | 0.1193 | 948.1 | −0.51 |
| 250.53 | 20.06 | 0.1157 | 935.8 | 0.88 |
| 250.52 | 20.07 | 0.8336 | 876.6 | −0.59 |
| 250.52 | 20.07 | 1.236 | 851.4 | −0.41 |
| 250.52 | 20.07 | 2.912 | 784.0 | 0.09 |
| 250.53 | 20.07 | 5.512 | 720.8 | 1.14 |
| 250.53 | 20.08 | 19.273 | 616.7 | −0.58 |
| | | | | |
| $\bar{T} = 300.23$ °C, $\bar{P} = 20.06$ MPa, $\bar{\rho}^0 = 734.4$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 3.54$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.19$ | | | | |
| 300.20 | 20.03 | 0.0675 | 1089.4 | 0.49 |
| 300.22 | 20.03 | 0.1443 | 1071.8 | 0.55 |
| 300.25 | 20.03 | 0.6936 | 972.0 | −0.33 |
| 300.25 | 20.07 | 1.492 | 886.1 | −0.74 |
| 300.24 | 20.10 | 3.424 | 777.5 | −0.77 |
| 300.24 | 20.08 | 5.512 | 708.8 | 0.30 |
| 300.23 | 20.06 | 19.273 | 569.6 | 0.86 |
| | | | | |
| $\bar{T} = 300.85$ °C, $\bar{P} = 26.03$ MPa, $\bar{\rho}^0 = 743.1$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 3.81$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.16$ | | | | |
| 300.85 | 26.02 | 0.0686 | 1091.9 | −0.18 |
| 300.85 | 26.04 | 0.1564 | 1072.4 | 0.04 |
| 300.85 | 26.06 | 0.7065 | 969.6 | 0.16 |
| 300.85 | 26.09 | 1.388 | 892.2 | 0.008 |
| 300.85 | 26.00 | 7.263 | 659.4 | −0.16 |
| 300.85 | 25.97 | 14.851 | 559.9 | 0.09 |
| | | | | |
| $\bar{T} = 350.96$ °C, $\bar{P} = 25.9$ MPa, $\bar{\rho}^0 = 626.1$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 1.82$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.36$ | | | | |
| 350.93 | 25.92 | 0.0103 | 1219.2 | −0.16 |
| 350.96 | 25.93 | 0.0622 | 1203.8 | 0.39 |
| 350.95 | 25.93 | 0.1690 | 1137.4 | −0.15 |
| 350.96 | 25.94 | 0.8108 | 892.8 | −0.47 |
| 350.97 | 25.90 | 2.571 | 679.4 | 0.38 |
| 350.97 | 25.88 | 11.021 | 464.2 | 0.29 |
| 350.98 | 25.91 | 23.971 | 376.1 | −0.27 |
| | | | | |
| $\bar{T} = 380.3$ °C, $\bar{P} = 25.74$ MPa, $\bar{\rho}^0 = 470.4$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 0.68$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 3.94$ | | | | |
| 379.52 | 25.71 | 0.0106 | 1251.5 | 8.77 |
| 379.80 | 25.73 | 0.0617 | 1182.6 | −1.76 |
| 380.02 | 25.74 | 0.1644 | 975.4 | −3.13 |
| 380.48 | 25.76 | 0.8161 | 596.7 | 2.18 |
| 380.56 | 25.77 | 2.6018 | 416.0 | 2.05 |
| 380.66 | 25.75 | 11.332 | 260.2 | −0.39 |
| 380.72 | 25.74 | 26.101 | 198.0 | −1.26 |
| | | | | |
| $\bar{T} = 400.2$ °C, $\bar{P} = 28.9$ MPa, $\bar{\rho}^0 = 301.6$ kg m$^{-3}$, $\bar{\kappa}_s\,10^6 = 0.23$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 38.83$ | | | | |
| 400.33 | 28.86 | 0.0035 | 1160.2 | 6.7 |
| 400.30 | 28.86 | 0.0261 | 794.7 | −10.0 |
| 400.31 | 28.86 | 0.1294 | 413.8 | −0.6 |
| 400.32 | 28.89 | 0.7626 | 191.0 | 7.3 |
| 400.30 | 28.94 | 2.2234 | 124.4 | 6.1 |
| 399.69 | 29.05 | 5.1224 | 105.3 | −11.0 |

Also the average specific conductivity of experimental water ($\bar{\kappa}_s$/S cm$^{-1}$) and solvent conductivity ratio ($\bar{\kappa}_s/\kappa_w$), where $\kappa_w$ is theoretical conductivity of water (see text) are given.

The MSA expressions (Blum and Høye, 1977; Turq et al., 1995) for the electrostatic and hard sphere parts were discussed in (Sharygin et al., 2002).

The first and simplest choice for the hard sphere diameters of the ions is to use the crystallographic diameters in the equations so that there are no adjustable parameters. The radii of ion clusters $M_mH_h(SO_4)_s$ were calculated from the expressions

$$r_{m,h,s}^M = \sqrt[3]{mr_{M^+}^3 + hr_{H^+}^3 + sr_{SO_4^{2-}}^3}, \tag{8}$$

Table 2

Experimental temperatures ($T$/°C), pressures ($P$/MPa), molalities of Li$_2$SO$_4$ ($m$/mol/kg), and apparent equivalent conductance ($\Lambda$/S cm$^2$ equiv$^{-1}$) of aqueous Li$_2$SO$_4$ [see Eqs. (2) and (3)] and their deviations ($\overline{\Delta\Lambda} = \frac{\Lambda^{Th} - \Lambda}{\Lambda}$) from conductances ($\Lambda^{Th}$/S cm$^2$ equiv$^{-1}$) calculated from theoretical conductivities Eq. (18) at average temperatures ($\bar{T}$/°C), pressures ($\bar{P}$/MPa), and densities of water ($\bar{\rho}^0$/kg m$^{-3}$)

| $T$ | $P$ | $m\ 10^3$ | $\Lambda$ | $\overline{\Delta\Lambda}100$, % |
|---|---|---|---|---|
| $\bar{T} = 24.93$ °C, $\bar{P} = 0.12$ MPa, $\bar{\rho}^0 = 997.0$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 0.65$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 13.3$ | | | | |
| 24.86 | 0.138 | 4.819 | 101.4 | 1.39 |
| 24.86 | 0.138 | 23.093 | 87.63 | 0.60 |
| 24.98 | 0.1013 | 104.85 | 70.81 | −1.41 |
| 25.03 | 0.1013 | 115.1 | 69.75 | −1.65 |
| | | | | |
| $\bar{T} = 250.76$ °C, $\bar{P} = 20.05$ MPa, $\bar{\rho}^0 = 815.1$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 5.16$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.30$ | | | | |
| 250.76 | 20.05 | 0.0683 | 853.6 | 1.10 |
| 250.76 | 20.05 | 0.1460 | 840.7 | 0.06 |
| 250.76 | 20.05 | 0.6063 | 786.4 | −0.70 |
| 250.76 | 20.05 | 1.348 | 732.5 | −0.79 |
| 250.76 | 20.05 | 5.844 | 596.8 | −0.14 |
| 250.76 | 20.05 | 11.650 | 528.1 | 0.63 |
| | | | | |
| $\bar{T} = 296.9$ °C, $\bar{P} = 26.03$ MPa, $\bar{\rho}^0 = 750.1$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 4.36$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.28$ | | | | |
| 295.91 | 26.03 | 0.0747 | 968.5 | 0.29 |
| 296.46 | 26.04 | 0.1534 | 949.5 | −0.08 |
| 297.22 | 26.02 | 0.2675 | 921.8 | −0.30 |
| 298.17 | 26.01 | 0.7122 | 835.7 | 0.14 |
| | | | | |
| $\bar{T} = 299.6$ °C, $\bar{P} = 20.11$ MPa, $\bar{\rho}^0 = 735.7$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 3.99$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.33$ | | | | |
| 299.72 | 20.11 | 0.0683 | 971.2 | 0.45 |
| 299.64 | 20.11 | 0.1470 | 952.5 | −0.18 |
| 299.58 | 20.11 | 0.6875 | 834.3 | −0.32 |
| 299.52 | 20.12 | 1.404 | 746.3 | −0.04 |
| 299.48 | 20.11 | 6.942 | 533.8 | 0.47 |
| 299.46 | 20.11 | 13.912 | 454.6 | −0.27 |
| | | | | |
| $\bar{T} = 303.1$ °C, $\bar{P} = 26.4$ MPa, $\bar{\rho}^0 = 739.6$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 3.80$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.17$ | | | | |
| 303.01 | 26.25 | 0.0205 | 1034.9 | −1.50 |
| 303.05 | 26.28 | 0.0974 | 995.1 | 0.18 |
| 303.11 | 26.33 | 0.3045 | 928.9 | 0.54 |
| 303.14 | 26.37 | 0.4706 | 887.9 | 0.45 |
| 303.18 | 26.41 | 1.033 | 794.8 | −0.06 |
| 303.15 | 26.70 | 3.872 | 605.9 | −0.63 |
| 303.14 | 26.35 | 13.402 | 435.1 | 0.24 |
| | | | | |
| $\bar{T} = 350.98$ °C, $\bar{P} = 25.8$ MPa, $\bar{\rho}^0 = 625.6$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 1.76$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 1.33$ | | | | |
| 350.96 | 25.72 | 0.0104 | 1156.0 | 0.19 |
| 350.97 | 25.74 | 0.0616 | 1104.6 | 0.58 |
| 350.97 | 25.76 | 0.1755 | 983.0 | −0.87 |
| 350.99 | 25.76 | 0.8012 | 703.7 | −0.34 |
| 350.98 | 25.77 | 2.557 | 515.2 | 0.99 |
| 351.00 | 25.85 | 9.827 | 356.8 | 0.22 |
| 350.99 | 25.94 | 23.093 | 278.3 | −0.46 |
| | | | | |
| $\bar{T} = 380.83$ °C, $\bar{P} = 25.74$ MPa, $\bar{\rho}^0 = 463.6$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 0.50$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 3.25$ | | | | |
| 380.88 | 25.76 | 0.0095 | 1235.2 | 1.50 |
| 380.85 | 25.77 | 0.0635 | 977.1 | −3.12 |
| 380.84 | 25.76 | 0.1665 | 744.5 | −0.30 |
| 380.82 | 25.74 | 0.8525 | 449.9 | 2.18 |
| 380.80 | 25.72 | 2.742 | 294.3 | 5.81 |
| 380.82 | 25.72 | 10.382 | 198.2 | −2.70 |
| 380.81 | 25.71 | 23.093 | 147.5 | −2.62 |
| | | | | |
| $\bar{T} = 399.5$ °C, $\bar{P} = 28.77$ MPa, $\bar{\rho}^0 = 303.9$ kg m$^{-3}$, $\bar{\kappa}_s\ 10^6 = 0.26$ S cm$^{-1}$, $\bar{\kappa}_s/\kappa_w = 40.85$ | | | | |
| 399.17 | 28.74 | 0.0089 | 868.1 | 0.48 |
| 399.40 | 28.76 | 0.0602 | 433.8 | −1.30 |
| 399.59 | 28.77 | 0.1602 | 280.8 | 0.84 |
| 399.69 | 28.78 | 0.8346 | 132.9 | 0.002 |
| 399.69 | 28.78 | 2.598 | 53.3 | −0.001 |

Also the average specific conductivity of experimental water ($\bar{\kappa}_s$/S cm$^{-1}$) and solvent conductivity ratio ($\bar{\kappa}_s/\kappa_w$), where $\kappa_w$ is theoretical conductivity of water (see text) are given.

where $r_\alpha$ are the crystallographic radii of corresponding ions (0.6, 1.33, 1.4, and 2.3 Å for $Li^+$, $K^+$, $H_3O^+$, and $SO_4^{2-}$, respectively) (Marcus, 1985).

### 3.4. Determination of solution volume

The volume of solution per 1 kg of solvent (water), $dm^3 kg^{-1}$, was calculated according to (Pitzer, 1991; Sedlbauer et al., 1998)

$$V^* = \frac{1000}{\rho^0} + \sum_i m_i V_i^0 + 1000 A_v \frac{I \ln(1 + b\sqrt{I})}{b}, \tag{9}$$

where $\rho^0$ is the water density (kg m$^{-3}$), $V_i^0$ is standard partial molar volume of $i$th solute at infinite dilution (dm$^3$ mol$^{-1}$), $I$ is ionic strength of solution, $I = \frac{1}{2}\sum m_i z_i^2$, $b = 1.2$ (kg$^{1/2}$ mol$^{-1/2}$). Coefficient $A_v$ (m$^3$ mol$^{-1}$) is defined by equation

$$A_v = 2 A_\phi RT \left( 3 \frac{\partial \ln \varepsilon}{\partial P}_T - \kappa_{H_2O} \right), \tag{10}$$

where $A_\phi$ (kg$^{1/2}$ mol$^{-1/2}$) is the Debye–Hückel slope (Pitzer, 1991) in the formulation,

$$A_\phi = \frac{1}{3}(2\pi N^A \rho^0)^{1/2} \left( \frac{e^2}{4\pi\varepsilon_0\varepsilon k_B T} \right)^{3/2}. \tag{11}$$

At the highest temperatures, the standard partial molar volumes of the ions in solution were approximated by the formula

$$V_i^0 = z_i^2 \frac{V_{Na^+}^0 + V_{Cl^-}^0}{2}, \quad z_i^2 \geqslant 1, \tag{12}$$

For neutral aggregates of ions the approximation,

$$V_i^0 = V_{NaCl}^0; \quad z_i^2 = 0. \tag{13}$$

was used. The calculations of the standard volumes for $V_{Na^+}^0$, $V_{Cl^-}^0$, and $V_{NaCl}^0$ were based on the results of Sedlbauer et al. (1998). This approximation relies on electrostriction effects dominating the partial molar volumes near the critical point. At the experimental molalities, setting the salt volume correction in Eq. (9) to zero made negligible changes at 373–573 K (less than 0.02%) and small changes of 0.1%, 0.2%, and 1.8% at 623, 663, and 673 K, respectively. The approximations in Eqs. (12) and (13) are needed at 673 K. However, at this temperature the maximum changes are still less than the average absolute deviation of the fit (6.9%).

### 3.5. Chemical equilibrium computation

The nonlinear system of mass balance equations and mass action law equations corresponding to the set of independent chemical reactions in aqueous solution was solved by a modified Newton method (Stoer and Bulirsch, 1980). To take into account the activity coefficients and volume corrections the solution of the non-linear chemical system was repeated until the desirable convergence was achieved.

### 3.6. Turq–Blum–Bernard–Kunz conductance model

In the TBBK model (Turq et al., 1995), the Fuoss–Onsager continuity equations were solved directly by a Green's function technique with the MSA pair distribution functions for the unrestricted primitive model (different ionic sizes). The single electrolyte solution consists of two types of free ions—cation (1) and anion (2)—with total conductance given by

$$\Lambda_F = \lambda_1^F + \lambda_2^F, \tag{14}$$

where

$$\lambda_i^F = \lambda_i^0 \left( 1 + \frac{\delta v_i^{el}}{v_i^0} \right) \left( 1 + \frac{\delta X}{X} \right), \tag{15}$$

is the $i$th ion conductance. In the last expression, $\lambda_i^0$ is the limiting equivalent conductance at infinite dilution, $\delta v_i^{el}/v_i^0$ is the free ion electrophoretic velocity effect and $\delta X/X$ is the free ion relaxation force correction. The ion velocity at infinite dilution in electric field $E$ is defined by

$$v_i^0 = e_i E \frac{D_i^0}{k_B T}, \tag{16}$$

where $e_i = z_i e$ is the electric charge of the $i$th ion, $E$ is the electric field, and $D_i^0$ is the diffusion coefficient of the $i$th ion,

$$D_i^0 = \frac{\lambda_i^0 RT}{|z_i|F^2}, \tag{17}$$

where $F$ is the Faraday number.

### 3.7. Mixture model

In this work, we use the same mixing rules which were used by Sharygin and coworkers (Sharygin et al., 2001, 2002) to define the theoretical conductivity, $\kappa$. The consensus equation is for a solution with a molar ionic strength, $I_c$, and MSA shielding parameter, $\Gamma_c$, is
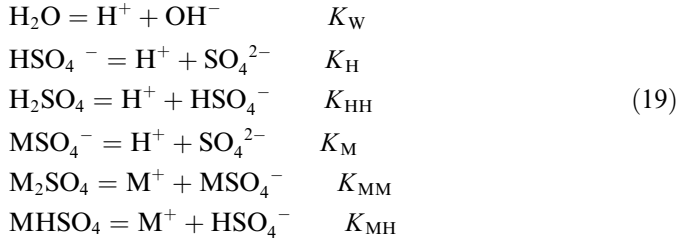
$$\kappa[I_c, \Gamma_c] = N \sum_{M=1}^{N_c} \sum_{X=1}^{N_a} x_M^c x_X^a \Lambda_{MX}[I_c, \Gamma_c], \tag{18}$$

where $N = \sum c_M^c z_M^c = \sum c_X^a |z_X^a|$ is the equivalent concentration, the equivalent fractions of species in solution are given by $x_M^c = c_M^c z_M^c / N$ and $x_X^a = c_X^a |z_X^a| / N$, the sums are over all cations $M$ and all anions $X$. The equivalent conductance of the pure electrolyte, $\Lambda_{MX}[I_c, \Gamma_c]$, is calculated by the TBBK equation at the molar ionic strength of the $I_c = (\sum c_M z_M^2 + \sum c_x z_x^2)/2$ mixture with the shielding parameter $\Gamma_c$ set equal to the shielding parameter of the mixture. Using this shielding parameter may be more accurate than using the shielding parameter of the pure electrolyte as done previously (Sharygin et al., 2001). This speeds up the calculation, and the difference between the two methods is quite small.

## 4. Ion-association model and its auxiliary parameters

### 4.1. Ion-reaction model and constants

Basically, we investigated the following set of independent reactions between ions and ion aggregates:

$$
\begin{aligned}
H_2O &= H^+ + OH^- & K_W \\
HSO_4^- &= H^+ + SO_4^{2-} & K_H \\
H_2SO_4 &= H^+ + HSO_4^- & K_{HH} \\
MSO_4^- &= H^+ + SO_4^{2-} & K_M \\
M_2SO_4 &= M^+ + MSO_4^- & K_{MM} \\
MHSO_4 &= M^+ + HSO_4^- & K_{MH}
\end{aligned}
\tag{19}
$$

where $K_W, K_H, \ldots, K_{MH}$ are the dissociation constants in molal concentration scale, M stands for Li or K. The dissociation constant of water $K_w$ was calculated according to Marshall and Franck (Marshall and Franck, 1981). On the basis of present conductance data we can calculate the $K_{MM}$ and $K_M$ but the second dissociation constant of sulfuric acid ($K_H$) must be known from other work. The $K_H$ is important because it determines the degree of hydrolysis of sulfate ion in aqueous solution. The hydrolysis can be written as linear combination of first two independent reactions in (19)

$$
SO_4^{2-} + H_2O = HSO_4^- + OH^-. \tag{20}
$$

In this work, we have used the new values for $K_H$ and $K_{HH}$ from conductances of aqueous electrolyte mixtures of Na₂SO₄ and H₂SO₄ at temperatures 373–673 K (Hnedkovsky et al., 2005). It was shown that $\log K_H$ at densities 740–1000 kg/m³ (373–573 K) can be described by a linear density function

$$
\log K_H = -18.5 + 16\rho, \tag{21}
$$

and $\log K_H$ at densities 360–730 kg/m³ (573–673 K) is given by a linear density function

$$
\log K_H = -12.1 + 7.6\rho. \tag{22}
$$

The parameter $\rho$ stands for the dimensionless reduced water density and is equal $\rho_{H_2O}/1000 \text{ kg m}^{-3}$.

### 4.2. Limiting equivalent conductances of Li⁺, K⁺, OH⁻, H⁺, HSO₄⁻, LiSO₄⁻ and KSO₄⁻

The experimental data and theoretical calculations (Xiao and Wood, 2000) show for $T < 773$ K and $P < 200$ MPa that within experimental errors the temperature dependence at constant water density of the relative limiting equivalent conductances of different ions are approximately the same. Thus, for two ions $X$ and $Y$ we can write

$$
\frac{1}{\lambda^0[X]}\left(\frac{\partial \lambda^0[X]}{\partial T}\right)_\rho \approx \frac{1}{\lambda^0[Y]}\left(\frac{\partial \lambda^0[Y]}{\partial T}\right)_\rho, \tag{23}
$$

where $\lambda^0[X]$ is a limiting equivalent conductance of X ion. Eq. (23) implies that the ratio of limiting equivalent conductances is a function of water density only. Particularly we must find

$$
\frac{\lambda^0[Y] - \lambda^0[X]}{\lambda^0[X]} \approx f(\rho). \tag{24}
$$

This rule is reasonably accurate at high temperatures where Waldens rule fails. However, Waldens rule predicts that Eq. (24) is also true. We choose X = NaCl because it is the best data set of aqueous conductances. We will refer to $(\lambda^0[Y] - \lambda^0[NaCl])/\lambda^0[NaCl]$ as the reduced limiting equivalent conductance of ion (electrolyte) Y. In this way, since we have a full data set for limiting equivalent conductance of NaCl (aq) as function of water density and temperature, we can describe the conductances of other ions (electrolytes) through Eq. (24).

Two different equations are used to represent the limiting equivalent conductance for sodium chloride, $\Lambda_0[NaCl]$ (cm² S equiv⁻¹), (Wright et al., 1961; Quist and Marshall, 1968; Zimmerman et al., 1995; Gruszkiewicz and Wood, 1997) which is needed to obtain $\lambda^0[Li^+]$ and $\lambda^0[K^+]$ by Eq. (24). In the temperature range 290–520 K and in the water density ($\rho_{H_2O}$) range 800–1000 kg/m³, $\Lambda_0[NaCl]$ can be described with an absolute average deviation (AAD) of 0.25% by the following polynomial dependence of the logarithm of Walden product on the reduced inverse temperature, $t = 1000$ K/$T$, and the logarithm of water density, $d = \ln(\rho_{H_2O}/1000 \text{ kg m}^{-3})$, with water viscosity, $\eta$ (Pa s), taken from (Sengers and Watson, 1986),

$$
\begin{aligned}
\ln(\Lambda_0[NaCl]\eta)^{LT} = &-2.03 - 1.61d - 2.13d^2 \\
&- (0.22 - 0.92d)t + 0.054t^2. 
\end{aligned}
\tag{25}
$$

In the temperature range 520–700 K and in the water density ($\rho_{H_2O}$) range 200–800 kg/m³ or at temperatures 700–800 K and at water densities 500–800 kg/m³, the sodium chloride data of limiting equivalent conductance (Quist and Marshall, 1968; Zimmerman et al., 1995; Gruszkiewicz and Wood, 1997), can be described by the following polynomial dependence of logarithm of Walden product

$$
\begin{aligned}
\ln(\Lambda_0[NaCl]\eta)^{HT} = &-13.4 + 605d^2 - 0.2\kappa + 0.04\kappa^2 \\
&+ (12.8 - 159d - 2010d^2 - 269d^3 - 109d^4)t \\
&+ (277d + 2261d^2 + 350d^3 + 142d^4)t^2 \\
&- (4 + 160d + 1058d^2 + 114d^3 + 47d^4)t^3 \\
&+ (1 + 31d + 176d^2)t^4,
\end{aligned}
\tag{26}
$$

where $\kappa = -\frac{\partial \ln V_{H_2O}}{\partial P}$ (Pa⁻¹) is the compressibility of water. The average absolute deviation from experimental data for this equation is 0.35%.

Then we define

$$
\lambda^0[Na^+] = \Lambda_0[NaCl]t_{Na^+}^0[NaCl], \tag{27}
$$

with $\Lambda_0[NaCl]$ calculated from Eqs. (25) or (26), and the Na⁺ transference number, $t_{Na^+}^0[NaCl]$, from Marshall (Marshall, 1987). The relative difference between experi-

mental data (Zimmerman et al., 1995; Gruszkiewicz and Wood, 1997) for $\Lambda_0[LiCl]$ and $\Lambda_0[NaCl]$, defined by Eq. (26), fits the polynomial function from dimensionless reduced water density ($\rho = \rho_{H_2O}/1000$) in the temperature range 600–670 K

$$\frac{\Lambda_0[LiCl] - \Lambda_0[NaCl]}{\Lambda_0[NaCl]} = \frac{\Delta\lambda^0[Li^+ - Na^+]}{\Lambda_0[NaCl]} = -0.095\rho^2. \quad (28)$$

A similar relation was found for KCl data (Wright et al., 1961; Hwang et al., 1970; Ho and Palmer, 1997; Sharygin et al., 2002) in the temperature range 550–670 K,

$$\frac{\Lambda_0[KCl] - \Lambda_0[NaCl]}{\Lambda_0[NaCl]} = \frac{\Delta\lambda^0[K^+ - Na^+]}{\Lambda_0[NaCl]}$$
$$= 0.28 - 0.86\rho + 0.72\rho^2. \quad (29)$$

The value of $\lambda^0[M^+]$, where $M^+$ is $Li^+$ or $K^+$, for temperature range 520–670 K was calculated by

$$\lambda^0[M^+] = \lambda^0[Na^+] + \Delta\lambda^0[M^+ - Na^+], \quad (30)$$

where $\lambda^0[Na^+]$ was calculated according to Eq. (27) and $\Delta\lambda^0[M^+-Na^+]$ was calculated from Eqs. (26), (28), and (29).

The limiting equivalent conductance of $OH^-$, $\lambda^0[OH^-]$, was calculated from an interpolation of the results of (Wright et al., 1961; Bianchi et al., 1994; Ho and Palmer, 1996; Ho and Palmer, 1997) using Marshall's equation.

The limiting equivalent conductances of $H^+$, $HSO_4^-$, were calculated from the data of (Hnedkovsky et al., 2005). From this work we have for $\lambda^0[HSO_4^-]$

$$\frac{\lambda^0[HSO_4^-] - \Lambda_0[NaCl]}{\Lambda_0[NaCl]} = -0.47 - 0.15\rho, \quad (31)$$

which is valid for density $H_2O$: 300–960 kg m$^{-3}$ (373–673 K). The limiting equivalent conductances of $MSO_4^-$ ion were approximated by the scaling relation

$$\lambda^0[MSO_4^-] = \lambda^0[HSO_4^-]\frac{r_{0,1,1}}{r_{1,0,1}^M}, \quad (32)$$

where the crystallographic radii are calculated using Eq. (8).

## 5. Conductance data and their analysis

### 5.1. Aqueous $K_2SO_4$

The pioneering electrical conductivity data of Arthur Noyes and his coworkers are very accurate and the published presentation of these data is complete and suitable for further analysis (Noyes, 1907). The data for aqueous $K_2SO_4$ are for six temperatures from 18 up to 306 °C; starting from 100 °C the pressures are close to the saturation pressures of vapor–water equilibrium (Noyes and Melcher, 1907). The temperatures were 18 °C, and about 100, 156, 218, 281, and 306 °C. The temperatures above the 100 °C were dictated by use of vapor baths for the conductivity apparatus. Bromobenzene was used as a boiling substance

for 156°C, and naphthalene for 218 °C. Bromonaphthalene and benzophenone were used as boiling substances for the temperatures of 281 and 306 °C.

For each state-point, they measured electrical conductivities of four $K_2SO_4$ aqueous solutions with concentrations (at 4 °C) in miliequivalents per liter: 2, 12.5, 50, and 100. The total number of measured data points for $K_2SO_4$ equals 110; 42 measurements at 18 °C, 16—at each temperature in the range 100–218 °C, and 10—at each of last temperatures: 281 and 306 °C.

The published (Noyes and Melcher, 1907) quantitative analysis of their electrical conductivity data corresponds to the state of electrolyte solutions theory in the beginning of the 20th century and it is very poor compared to contemporary theoretical standards. We fit the Noyes data to the present conductance model with extremely good results (see Table 3). For all state points, we can determine $\log K_K$ and $\lambda^0[SO_4^{2-}]$ with excellent accuracy, and for two last state points we can determine $\log K_{KK}$.

In the following we will discuss the auxiliary parameters of these fits. In the case of Noyes state points 1–4 the $\lambda^0[K^+]$ was calculated by Marshall polynomial function (Marshall, 1987), for the 5th and 6th state points it was calculated through Eqs. (30) and (29). At 18 and 100 °C, the calculated $\lambda^0[K^+]$ exactly correspond to the published values in (Robinson and Stokes, 1959). For 18 °C we used $\lambda^0[H^+] = 315$ S cm$^2$ equiv$^{-1}$ from (Robinson and Stokes, 1959). For all other temperatures the $\lambda^0[H^+]$ was taken from (Hnedkovsky et al., 2005). The $\lambda^0[HSO_4^-]$ and $\lambda^0[KSO_4^-]$ were always calculated through Eqs. (31) and (32). $\log K_H$ and $\log K_{HH}$ were taken from (Hnedkovsky et al., 2005). Our calculations were done in the region where the influence of the reaction governed by $K_{MH}$ was negligible [see Eq. (19)], so $\log K_{KH}$ was given the value 0.

The values of pressure were chosen to agree with the specific volumes of aqueous $K_2SO_4$ solutions reported by (Noyes and Melcher, 1907).

To retrieve the $\lambda_0[SO_4^{2-}]$ and $\log K_K$ at 25 °C we combined the excellent electrical conductivity data set of (Jenkins and Monk, 1950) and (Broadwater and Evans, 1974). The combined data set has 27 data points which belong to interval of $K_2SO_4$ equivalent concentrations $10^{-4}$ to $10^{-3}$. The results of this fit are presented in Table 3. In this fit we used $\lambda^0[H^+] = 349.8$ S cm$^2$ equiv$^{-1}$ from (Robinson and Stokes, 1959). All other auxiliary parameters were calculated in the same manner as it was in the case of Noyes data. The value found for $\lambda^0[SO_4^{2-}] = 79.94(4)$ is very close to the value of 80.02(5) from (Robinson and Stokes, 1959).

The results of the fits of the present electrical conductivity measurements of aqueous $K_2SO_4$ (Table 1) to the conductance model are presented in the last part of Table 3. In this case the limiting equivalent conductances of $K^+$ were always calculated through Eqs. (29) and (30). All other necessary auxiliary parameters were calculated on the basis of the data of (Hnedkovsky et al., 2005) in the same way as it was done for the first two parts of Table 3.

Table 3
K$_2$SO$_4$ (aq): dissociation constants and limiting equivalent conductances for state points (18–400 °C) (see text for details)

| $T$/°C | $P$/MPa | $\rho^0$/kg m$^{-3}$ | $\lambda^0$[K$^+$] | $\lambda^0$[SO$_4^{2-}$] | $\lambda^0$[HSO$_4^-$] | $\lambda^0$[KSO$_4^-$] | Log $K_K$ | Log $K_{KK}$ | AAD[a], % |
|---|---|---|---|---|---|---|---|---|---|
| Fit of the (Noyes and Melcher, 1907) data to the conductance model | | | | | | | | | |
| 18.00 | 0.100 | 998.60 | 63.90 | 67.9(6)[b] | 42.0 | 39.6 | −0.84(4) | — | 0.6 |
| 100.04 | 0.102 | 958.32 | 195.72 | 233.(1) | 141.4 | 133.3 | −1.06(2) | — | 0.2 |
| 156.3 | 0.5675 | 911.04 | 284.28 | 376.(2) | 222. | 209.3 | −1.36(1) | — | 0.2 |
| 218.05 | 2.241 | 842.71 | 393.4 | 522.(13) | 310. | 292.3 | −1.87(4) | — | 0.5 |
| 281.04 | 7.8 | 750.57 | 460.4 | 697.(11) | 399.6 | 376.8 | −2.36(3) | −1.06(4) | 0.2 |
| 305.35 | 9.2 | 700.75 | 495.6 | 748.(22) | 440.9 | 415.7 | −2.65(4) | −1.34(4) | 0.25 |
| Fit of the (Jenkins and Monk, 1950) and (Broadwater and Evans, 1974) data to the conductance model | | | | | | | | | |
| 25.00 | 0.1013 | 997.05 | 73.4 | 79.94(4) | 49.0 | 46.2 | −1.02(1) | — | 0.04 |
| Fit of the present K$_2$SO$_4$ data to the conductance model | | | | | | | | | |
| 250.58 | 20.07 | 815.35 | 415.6 | 558.(10) | 344.9 | 325.1 | −1.82(6) | — | 0.5 |
| 300.23 | 20.06 | 734.4 | 474.9 | 710.(20) | 416.8 | 392.9 | −2.50(4) | — | 0.6 |
| 300.85 | 26.03 | 743.1 | 471.0 | 713.(9) | 411.5 | 387.9 | −2.44(3) | −1.32(9) | 0.1 |
| 350.96 | 25.91 | 626.2 | 562.0 | 865.(33) | 506.1 | 477.1 | −3.18(4) | −1.90(4) | 0.3 |
| 380.25 | 25.74 | 470.4 | 665.7 | 1071.0 | 599.3 | 565.0 | −4.1(2) | −2.8(1) | 2.8 |
| 400.21 | 28.91 | 301.6 | 780.5 | 1207.2 | 660.9 | 623.1 | −5.5(5) | −4.2(1) | 6.9 |

[a] AAD is the average of the absolute relative values of the deviations in percent.
[b] The 95% confidence limits of the last digits are given in parentheses. Numbers without confidence limits are auxiliary data calculated as described in the text.

The volume corrections were made through Eq. (9). At 250–400 °C the standard partial molar volumes of species were calculated either through Eqs. (12) and (13), or through use of Supcrt92 (Johnson et al., 1992) with the same final results. In the temperature range 250–300 °C the volume corrections were close to the volume data of (Obsil et al., 1997).

The equivalent conductances obtained from the fits and calculated through Eqs. (18) and (2) together with the experimental conductance data (Table 1) are shown in Fig. 1 for K$_2$SO$_4$.
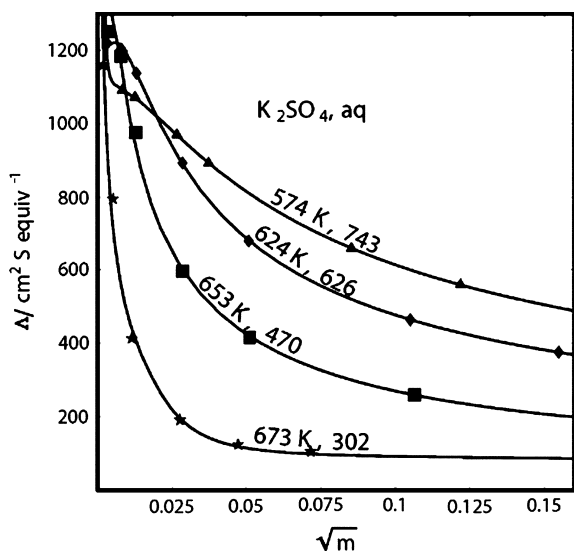


Fig. 1. Plot of experimental and calculated equivalent conductances of aqueous K$_2$SO$_4$. The numbers on the lines following the temperatures correspond to the H$_2$O density in kg m$^{-3}$.

## 5.2. Aqueous Li$_2$SO$_4$

To define the $\lambda^0$[SO$_4^{2-}$] and log $K_{Li}$ at 25 °C we combined the previus electrical conductivity data sets for aqueous Li$_2$SO$_4$ of Indelli (1989) and Postler (1970), with the present data set. This data set has 29 data points belonging to molality interval $5 \times 10^{-3}$ to 0.7. The auxiliary equivalent conductance of Li$^+$ was calculated through the Marshall polynomial function (Marshall, 1987); this value is very close to that published in (Robinson and Stokes, 1959). The necessary volume corrections were done on the basis of the data of (Pearce and Eckstrom, 1937). The fitting (Table 4) is not as accurate as with aqueous K$_2$SO$_4$, because of the much higher concentrations of the solutions (up to 0.7 mol kg$^{-1}$).

The $\lambda^0$[SO$_4^{2-}$], log $K_{Li}$, and log $K_{LiLi}$ found from the fitting of the present electrical conductivity data to the conductance model are represented in the second part of Table 4. The $\lambda^0$[Li$^+$] was always defined from Eqs. (28) and (30). All other auxiliary parameters were calculated from the data of (Hnedkovsky et al., 2005). The conductances resulted from the fits and calculated through Eqs. (18) and (2) together with the experimental conductance data (Table 2) are shown in Fig. 2 for Li$_2$SO$_4$. The volume corrections were made through Eq. (9). The standard partial molar volumes of aqueous species for volume corrections were calculated through Supcrt92 (Johnson et al., 1992). These corrections are in very good correspondence with the experimental data of Abdulagatov and Azizov (2003) who reported densities of aqueous Li$_2$SO$_4$ solutions at 250 and 300 °C ($P = 20$ Mpa). For example, the predicted $V^*$ are 1.22650 dm$^3$ kg$^{-1}$ and 1.35822 dm$^3$ kg$^{-1}$ at state points (250.8 °C, 20.05 MPa) and (299.6 °C, 20.11 MPa) for solutions with highest molality, 0.012 mol and

Table 4
Li$_2$SO$_4$ (aq): dissociation constants and limiting equivalent conductances for state points (25–400 °C) (see text for details)

| T/°C | P/MPa | $\rho^0$/kg m$^{-3}$ | $\lambda^0$[Li$^+$] | $\lambda^0$[SO$_4^{2-}$] | $\lambda^0$[HSO$_4^-$] | $\lambda^0$[LiSO$_4^{2-}$] | Log $K_{Li}$ | Log $K_{LiLi}$ | AAD[a], % |
|---|---|---|---|---|---|---|---|---|---|
| Fit of (Indelli, 1989), (Postler, 1970), and the present data at 25 °C to the conductance model | | | | | | | | | |
| 25 | 0.10 | 997.1 | 38.9 | 80.5(12)[b] | 49.0 | 48.7 | −0.87(5) | — | 0.9 |
| Fit of the present Li$_2$SO$_4$ data to the conductance model | | | | | | | | | |
| 250.76 | 20.05 | 815.1 | 315.7 | 570(15) | 345.1 | 343.1 | −2.09(6) | — | 0.6 |
| 296.94 | 26.03 | 750.1 | 377.5 | 670(20) | 405.6 | 403.2 | −2.6(1) | — | 0.2 |
| 299.57 | 20.11 | 735.7 | 388.6 | 660(20) | 415.7 | 413.2 | −2.62(8) | −1.44(16) | 0.3 |
| 303.11 | 26.38 | 739.6 | 387.5 | 730(40) | 414.6 | 412.2 | −2.7(1) | −1.6(2) | 0.5 |
| 350.98 | 25.79 | 625.6 | 494.1 | 950(90) | 506.5 | 503.5 | −3.62(8) | −2.10(4) | 0.5 |
| 380.83 | 25.74 | 463.6 | 598.5 | 1076.7 | 601.9 | 598.4 | −4.5(2) | −3.05(7) | 2.9 |
| 399.51 | 28.77 | 303.9 | 652.3 | 1203.3 | 659.0 | 655.1 | −5.5(1) | −4.50(6) | 0.5 |

[a] AAD is the average of the absolute relative values of the deviations in percent.
[b] The 95% confidence limits of the last digits are given in parentheses. Numbers without confidence limits are auxiliary data calculated as described in the text.
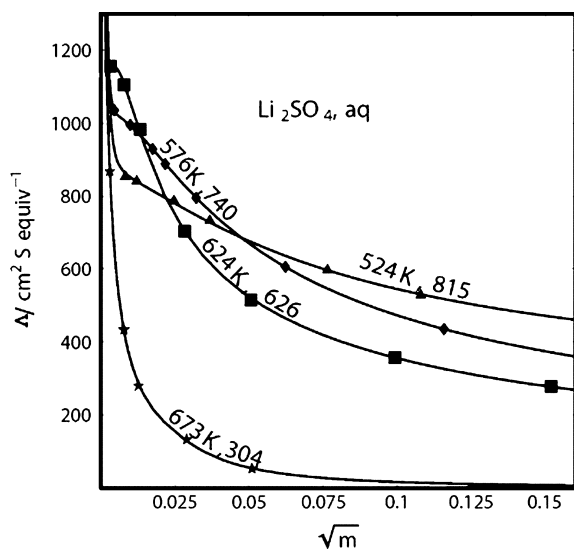


Fig. 2. Plot of experimental and calculated equivalent conductances of aqueous Li$_2$SO$_4$. The numbers on the lines following the temperatures correspond to the H$_2$O density in kg m$^{-3}$.

0.014 mol kg$^{-1}$, respectively (see Table 2). The same volumes $V^*$ are 1.22655 dm$^3$ kg$^{-1}$ and 1.35827 mol kg$^{-1}$ calculated through linear interpolation between H$_2$O and aqueous Li$_2$SO$_4$ with molality 0.0944 mol kg$^{-1}$ from the data of Abdulagatov and Azizov (2003). The difference between the corrections are only slightly above the reported uncertainty (0.03–0.05%) of Abdulagatov and Azizov (2003).

Our model Eq. (19) does not fit the data for Li$_2$SO$_4$ salt at 673 K and 303 kg m$^{-3}$. In this case, we found that models with multi-ion clusters of higher order than Li$_2$SO$_4^0$ could fit the data. The multi-ion associates of the general formula Li$_{2(n+1)}$(SO$_4$)$_{n+1}^0$ were treated in the interval of $n = 1$–14. In this interval the AAD changed from 4.7% ($n = 1$) to 0.8% ($n = 14$) with the minimum value (AAD = 0.5%) for $n = 7$, Li$_{16}$(SO$_4$)$_8^0$ (see Table 4). The nature of the multi-ion cluster found is speculative and combinations of other large clusters of about the same size would probably give reasonable fits to the data. It is likely

a variety of clusters of similar compositions would be present. It is also possible that no large clusters are present and we find them close to the critical point of water because of deficiencies in our activity coefficient model at the highest concentrations. Near the critical point the MSA equation is not accurate because of critical point effects (Levelt Levelt Sengers et al., 1991; Myers et al., 2003).

### 5.3. The limiting equivalent conductance of SO$_4^{2-}$

For water densities less than 620 kg m$^{-3}$ we can not determine $\lambda^0$[SO$_4^{2-}$] from the measurements because of the very low concentration of SO$_4^{2-}$ in the aqueous solution. The linear regression of our SO$_4^{2-}$ equivalent conductance data (Table 3) taken in the form of Eq. (24) gives the relation

$$\frac{\lambda^0[\text{SO}_4^{2-}] - \Lambda_0[\text{NaCl}]}{\Lambda_0[\text{NaCl}]} = -0.373\rho. \tag{33}$$

Adding the $\lambda^0$[SO$_4^{2-}$] data derived from the electrical conductivity of Na$_2$SO$_4$–H$_2$SO$_4$ mixtures (Hnedkovsky et al.,
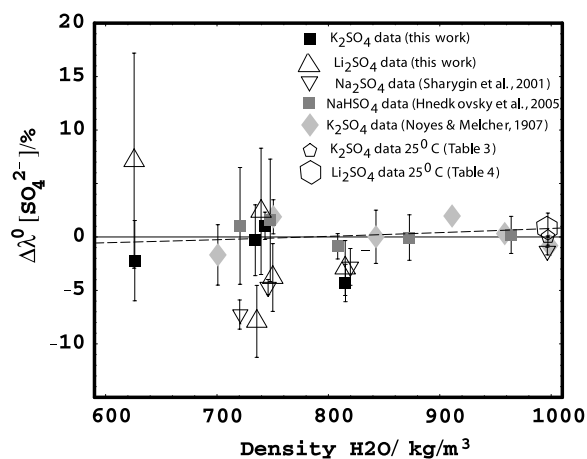


Fig. 3. Plot of the percent deviations of the limiting equivalent conductance of SO$_4^{2-}$ from Eq. (33) versus water density. The dashed line is Eq. (34).

2005) and aqueous $Na_2SO_4$ solutions (Sharygin et al., 2001) to the fit does not change the coefficient of linear regression (33). The percent deviations of different experimental limiting equivalent conductances $SO_4^{2-}$ are represented in Fig. 3.

The linear dependence of $\lambda^0[SO_4^{2-}]$ on water density reported in (Hnedkovsky et al., 2005) is

$$\frac{\lambda^0[SO_4^{2-}] - \Lambda_0[NaCl]}{\Lambda_0[NaCl]} = -0.018 - 0.35\rho. \qquad (34)$$

The differences between Eqs. (33) and (34), are very small, see Fig. 3. Eq. (33) was used in this work to calculate the necessary $\lambda^0[SO_4^{2-}]$ in the region of low $H_2O$ densities.

The $\lambda^0[SO_4^{2-}]$ values derived from the electrical conductivity of aqueous $Li_2SO_4$ are scattered to a greater degree than those derived from either $Na_2SO_4$–$H_2SO_4$ or $K_2SO_4$ data (see Fig. 3).

## 6. Discussion

The logarithms of equilibrium constants and the limiting equivalent conductances can be described by functions of two independent variables: inverse temperature and density of solvent–water (Quist and Marshall, 1968; Marshall and Franck, 1981; Marshall, 1987). The simplest equation has following form

$$\log K = A + \frac{B}{T} + C \log \rho, \qquad (35)$$

the more important term being $C \log\rho$. The $\log K$'s represented in this work are in the temperature range 18–400 °C (290–673 K) with a narrow pressures interval 0.1–28 MPa; see Tables 3 and 4. Because of the high correlation between the experimental density and temperature, we cannot accurately determine both $B$ and $C$ from our data. As a consequence, Eq. (35) should not be used outside the range of our experimental data.

For first dissociation constant of $K_2SO_4$ the fitting gave the relation (see Fig. 4)

$$\log K_{KK} = -3.1 + \frac{1600}{T} + 6.6 \log \rho. \qquad (36)$$

In the case of the second dissociation constant of $K_2SO_4$ it was found that the best linear regression of the Table 3 data satisfies the simple dependence (see Fig. 4)

$$\log K_K = -6.8 + 5.9\rho. \qquad (37)$$

For $Li_2SO_4$ (Table 4) two equations were found for the first and the second dissociation constants, respectively, (see Fig. 4)

$$\log K_{LiLi} = -0.6 + 7.5 \log \rho,$$

$$\log K_{Li} = -2.6 + \frac{500}{T} + 7.4 \log \rho. \qquad (38)$$

The new $\log K$ data for aqueous $K_2SO_4$ and $Li_2SO_4$ are very close to the $\log K_{NaNa}$ and $\log K_{Na}$ from the $Na_2SO_4$ data (Hnedkovsky et al., 2005). To compare the first dissociation constants of all alkali metals (Li, Na, and K) sulfates we plot (Fig. 5) the deviations $\Delta \log K_{MM} = \log K_{MM} - \log K_{KK}$ of these constants from the calculated first dissociation constant of $K_2SO_4$ Eq. (36). The $\log K_{NaNa}$ are taken from the data of Hnedkovsky et al. (2005) and Sharygin et al. (2001). In the last case two constants at 300 °C were calculated through the fits of Sharygin et al. (2001) data to the present conductance model.

A comparison of the second dissociation constants from the previous work with the present results is shown in Fig. 6. The deviations were defined by the equation $\Delta \log K_M = \log K_M - \log K_K$, where $\log K_K$ was calculated according to Eq. (37). Quist et al. (1963) reported a representative set of conductance measurements of aqueous $K_2SO_4$ solutions at 373–1073 K up to 400 MPa. They produced measurements for a set of three aqueous $K_2SO_4$ solutions with molalities $5.03 \times 10^{-4}$, $4.99 \times 10^{-3}$, and $2.2 \times 10^{-3}$ mol/kg and calculated from these data the limiting equivalent conductances $\Lambda_0[K_2SO_4]$ under the assumption that $K_2SO_4$ is fully dissociated in aqueous solutions up
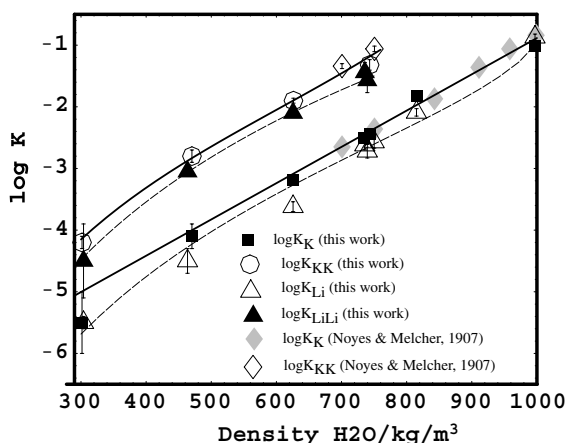


Fig. 4. Plot of the dependences of first and second dissociation constants of $K_2SO_4$ (lines) and $Li_2SO_4$ (dashed lines) with water density. The lines are Eq. (36) at 28 MPa for $\log K_{KK}$ and Eq. (37) at 28 MPa for $\log K_K$. The dashed lines are Eq. (38) at 28 MPa for $\log K_{LiLi}$ and $\log K_{Li}$.
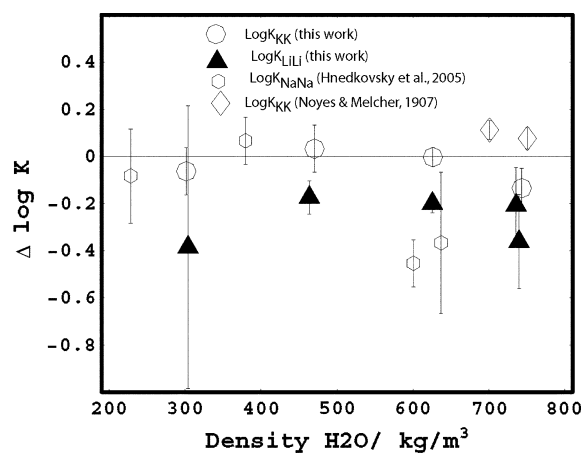


Fig. 5. Plot of the deviations of the first dissociation constants of alkali (Li, Na, and K) sulfates from the line defined by Eq. (36).
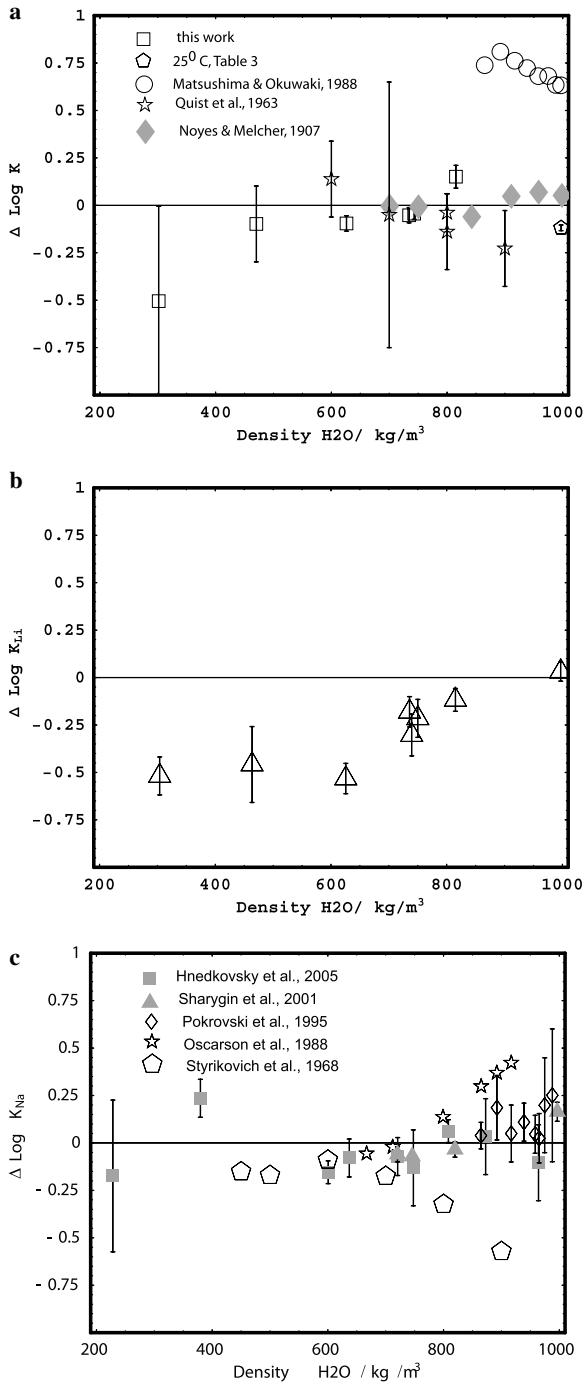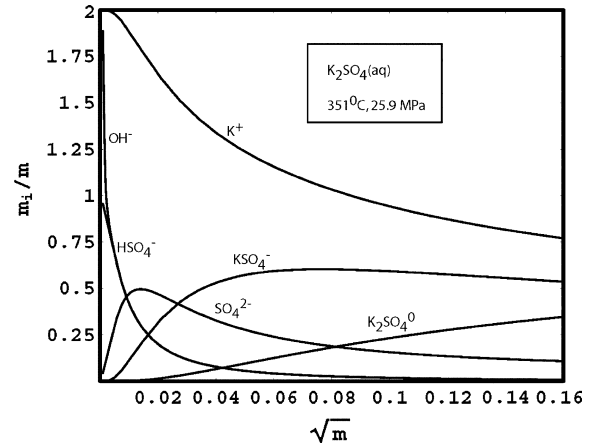
Fig. 7. Plot of the typical speciation in a hydrothermal solution of $K_2SO_4$.
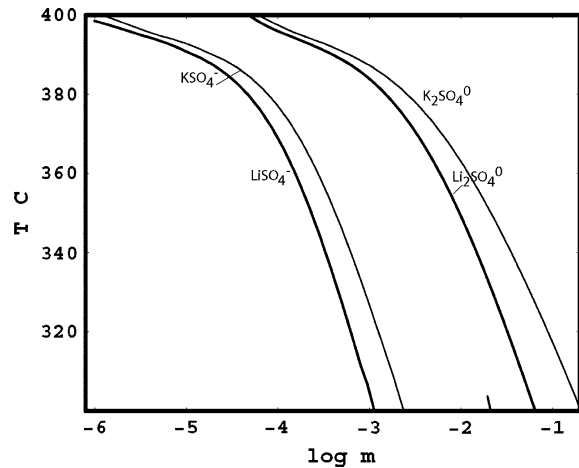


Fig. 8. Plot of the 30% abundance boundaries in salt molality *versus* temperature coordinates for the $MSO_4^-$ and $M_2SO_4^0$ hydrothermal complexes (M = Li or K). The pressure is equal to 28 MPa.

$-2.1(1)$, $-1.7(2)$; $-3.1(2)$, $-2.7(7)$, and $-2.2(2)$, respectively. These recalculated values are presented in Fig. 6. The agreement is excellent. Matsushima and Okuwaki (1988) reported the 2nd dissociation constant of $K_2SO_4$ found from potentiometric measurements at temperatures 298 up to 473 K at water densities from 860 to 1000 kg m$^{-3}$. Their results are above our $\log K_K$ Eq. (37) by 0.6 of logarithmic unit and thus are quite different from all data measured by electrical conductivity.

The $\log K_{Na}$ data measured by different authors (Styrikovich et al., 1968; Oscarson et al., 1988; Pokrovski et al., 1995; Sharygin et al., 2001; Hnedkovsky et al., 2005) are represented through deviations from Eq. (37) in Fig. 6c. The agreement between Pokrovski et al., Sharygin et al., and Hnedkovsky et al., is excellent. The agreement with Styrikovich et al., and Oscarson et al., is not bad.

From Figs. 5 and 6 we conclude that the differences between dissociation constants of $Na_2SO_4$ and $K_2SO_4$ are negligible. For $Li_2SO_4$, $\log K_{KK}$–$\log K_{LiLi}$ is about 0.2 at all densities while $\log K_K$–$\log K_{Li}$ is about 0.6 at low water densities (<600 kg m$^{-3}$) and about 0.1 at 800 kg m$^{-3}$.

Fig. 6. Plot of the deviations the second dissociation constants of alkali sulfates from the line defined by Eq. (37): $\Delta \log K_M = \log K_M - \log K_K$ versus water density for (a) $\log K_K$, (b) $\log K_{Li}$, and (c) $\log K_{Na}$.

to $5 \times 10^{-3}$ mol kg$^{-1}$ at any water density. Our analysis shows that this assumption is not valid at temperatures above 573 K. We fitted the data of Quist et al. (1963) at 573 and 673 K by present model with $\Lambda_0[K_2SO_4] = \lambda^0[K^+] + \lambda^0[SO_4^{2-}]$ according to Eqs. (29), (34), and $\log K$ as adjustable parameters. The fits were reasonable for five state points: at 573 K with water densities 800 and 900 kg m$^{-3}$; and at 673 K with water densities 600, 700, and 800 kg m$^{-3}$. The adjusted values of $\log K_K$ were

The main result of this study is the measurement of $K_{Li}$, $K_{LiLi}$, $K_K$, and $K_{KK}$ in the temperature interval 18–400 °C with water densities from 300 to 1000 kg m$^{-3}$ (see Tables 3, 4, and Figs. 4–6).

The distribution of sulfate species at water density 626.1 kg m$^{-3}$ is shown in Fig. 7 for K$_2$SO$_4$ (aq). At low salt molalities ($m < 4 \times 10^{-4}$), the aqueous solution conductivity is due to the K$^+$, SO$_4^{2-}$, HSO$_4^-$, and OH$^-$ ions. At higher molalities ($m > 4 \times 10^{-4}$), the conductivity is due to the K$^+$, SO$_4^{2-}$, and KSO$_4^-$ ions.

The main characteristic steps in hydrothermal ion association of an aqueous alkali metal sulfate are the formation of MSO$_4^-$ and M$_2$SO$_4^0$ species. On the basis of our results we calculated the 30% abundance boundaries of these species for Li and K sulfates at 28 MPa on a salt molality–temperature diagram (see Fig. 8). The influence of temperature increases drastically above the H$_2$O critical temperature. As an example, at 390 °C, a $10^{-5}$ mol kg$^{-1}$ aqueous solution of Li$_2$SO$_4$ consists of 30% LiSO$_4^-$, and already at $10^{-3}$ mol kg$^{-1}$ the aqueous solution contains 30% Li$_2$SO$_4^0$.

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