

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/273913201>

# Volumetric properties of Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>-NaCl-H<sub>2</sub>O solutions to 523.15 K, 70 MPa

ARTICLE in JOURNAL OF CHEMICAL & ENGINEERING DATA · MARCH 2015

Impact Factor: 2.04 · DOI: 10.1021/je501152a

---

READS

47

3 AUTHORS, INCLUDING:



Denis Zezin

ETH Zurich

13 PUBLICATIONS 88 CITATIONS

SEE PROFILE



Carmen Sanchez-Valle

University of Münster

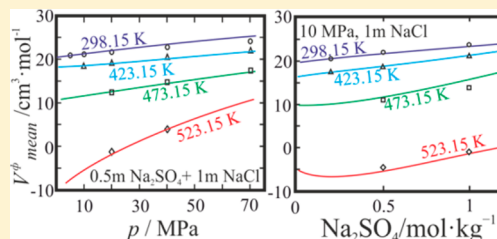
49 PUBLICATIONS 681 CITATIONS

SEE PROFILE

Volumetric Properties of  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  Solutions to 523.15 K, 70 MPaDenis Zezin,<sup>\*,†</sup> Thomas Driesner,<sup>†</sup> and Carmen Sanchez-Valle<sup>‡</sup><sup>†</sup>Institute of Geochemistry and Petrology, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland<sup>‡</sup>Institut für Mineralogie, Universität Muenster, Corrensstrasse 24, 48149 Münster, Germany

## S Supporting Information

**ABSTRACT:** The densities of aqueous solutions in the systems  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  were determined experimentally at temperatures from (298.15 to 523.15) K and pressures up to 70 MPa, and over a wide range of salt concentrations (up to 5 mol·kg<sup>-1</sup> of NaCl and up to 1.2 mol·kg<sup>-1</sup> of  $\text{Na}_2\text{SO}_4$ ). The measurements were conducted in vibrating-tube densimeters permitting density determinations with an accuracy varying from (2.8·10<sup>-5</sup> to 1.0·10<sup>-4</sup>) g·cm<sup>-3</sup> depending on temperature. The Pitzer equation for the apparent molar volume was parametrized on the basis of the newly obtained experimental data and data from literature. The resulting model for binary  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  and ternary  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  solutions can be applied across the entire range of temperatures, pressures, and compositions covered by this study. Most importantly, it is the first model capable of calculating the mean apparent molar volume of the mixed solutes and, consequently, the density of solution in aqueous system  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  at elevated temperatures and pressures. The volumetric properties derived from the parametrized model for mixed electrolyte solutions (i.e., partial molar volume, limiting partial molar volume, and excess molar volume of components) provide an access to quantitative evaluation of the effect of pressure on the activity coefficients of electrolytes in multicomponent aqueous solutions. Calculation of the pressure dependence of a chemical equilibrium is thus much facilitated by the presented models, which can assist in modeling of aqueous systems at elevated temperatures and pressures.



## ■ INTRODUCTION

Sodium sulfate and sodium chloride are key components of many natural waters. Being major dissolved salts in seawater, these electrolytes govern the properties and behavior of fluids and the systems associated with marine water and sediments. The sea-floor hydrothermal system, geothermal fields, and oil-field formation waters may contain significant concentrations of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$ . Precise knowledge of the thermodynamic properties of aqueous fluids involved is essential for successful modeling of physical parameters and chemical processes occurring in these environments. These properties are well established for simple binary salt solutions; however, the properties of mixed electrolyte solutions are not constrained due to lack of experimental data. Thus, the volumetric properties of binary solutions  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  were measured experimentally over a wide range of conditions,<sup>1–28</sup> whereas the data for ternary  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  solutions are only available at limited temperatures (up to 448 K) and at atmospheric pressure only.<sup>7,10,28–33</sup>

With this paper, we continue a series of experimental studies on the volumetric properties of aqueous alkali and alkali earth electrolyte solutions at elevated temperatures and pressures.<sup>34,35</sup> This publication reports the density measurements at temperatures from (298.15 to 523.15) K and pressures up to 70 MPa for the binary  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  system at concentrations from (0.1 to 1.21) mol·kg<sup>-1</sup> and the ternary  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  system at concentrations of NaCl from (0.1 to 5) mol·

kg<sup>-1</sup> and  $\text{Na}_2\text{SO}_4$  from (0.1 to 1) mol·kg<sup>-1</sup>. The experimental measurements are complemented with an accurate model based on the ion interaction approach of Pitzer<sup>36</sup> for calculations of density and molar volumes of binary and ternary aqueous electrolyte solutions.

## ■ EXPERIMENTAL METHOD

The method used in this study is analogous to that described in our previous communications.<sup>34,35</sup> The density difference of the  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  binary solution and the  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  ternary solution with respect to pure water was calculated from the measurements obtained using two vibrating-tube densimeters (a custom-made DMA HP provided by Dr. Hans Stabinger GmbH, and a commercial DMA HP 4100 from Anton Paar). The experimental data were measured at temperatures  $T$  of (298.15, 373.15, 423.15, 473.15, and 523.15) K, pressures  $p$  up to 70 MPa, and molalities up to 5 mol·kg<sup>-1</sup> and 1.2 mol·kg<sup>-1</sup> of NaCl and  $\text{Na}_2\text{SO}_4$ , respectively. All aqueous solutions employed in experimental measurements were prepared by mass dilution from stock solutions of pure salts. The stock solutions were prepared with Milli-Q water (deionized water with resistivity 18.2 MΩ·cm at  $T$  = 298.15 K) and crystalline anhydrous NaCl and  $\text{Na}_2\text{SO}_4$  (Table 1). The

Received: December 19, 2014

Accepted: March 3, 2015

Published: March 12, 2015

Table 1. Sample Information Table

chemical name	source	initial mass fraction purity	treatment
sodium chloride <sup>a</sup>	Fisher Scientific	99.99	dried at 523.15 K for 24 h
sodium chloride <sup>b</sup>	Fisher Scientific	>99.5	"
sodium sulfate <sup>b</sup>	Fisher Scientific	>99.5	"

<sup>a</sup>Used for calibration only. <sup>b</sup>Used for preparation of experimental solutions.

errors on the concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions were less than 0.5 %. Temperature was measured using a platinum resistance thermometer with accuracy of 0.01 K, pressure was measured with accuracy 0.05 % using a pressure transmitter (WIKA, model 891.20.501) calibrated against a Bourdon-type pressure gauge (Heise).

## RESULTS AND DISCUSSION

The density difference between an experimental solution and pure water was obtained from the measured period of vibration of the tube filled with water and reference NaCl solutions in the same manner as described in previous studies.<sup>34,35</sup> The Hill equation of state for water<sup>37</sup> and the consistent Archer equation for aqueous NaCl solution<sup>38</sup> were used for calibration of the densimeters and calculations. Table 2 contains the results of the measurements and calculated density difference  $\Delta\rho$  for experimental solutions in the Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>–NaCl–H<sub>2</sub>O systems. The mean apparent molar volume of electrolyte mixtures,  $V_{\text{mean}}^\phi$ , was calculated from the density of solutions as follows:

$$V_{\text{mean}}^\phi = \frac{1000(\rho_0 - \rho)}{\sum_j m_j \cdot \rho \cdot \rho_0} + \frac{\sum_j m_j \cdot M_j}{\sum_j m_j \cdot \rho} \quad (1)$$

where  $\rho$  and  $\rho_0$  are the density (in g·cm<sup>-3</sup>) of the solution and of pure water, respectively, at the temperature and pressure of interest;  $m_j$  is the concentration (in mol·kg<sup>-1</sup>) and  $M_j$  is the molar weight of Na<sub>2</sub>SO<sub>4</sub> and NaCl.

The results of our measurements for the Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O system are compared to literature data in Figure 1. The data are in good agreement at ambient conditions (Figure 1a); however, the scatter is more significant at elevated temperature and pressure, particularly at low concentrations of Na<sub>2</sub>SO<sub>4</sub> (Figure 1b–e). Most literature data were collected at different temperatures and pressures, thus direct comparison of data at conditions other than ambient can be done only for limited number of data points presented in Figure 1. The data of Trimble,<sup>1</sup> Fabuss et al.,<sup>28</sup> Azizov and Akhundov,<sup>18</sup> and Abramson et al.<sup>19</sup> systematically deviate from the majority of measurements. The data of Al Ghafri et al.<sup>25</sup> show slightly overestimated values of  $V^\phi$ ; a similar deviation was noticed for the CaCl<sub>2</sub>–H<sub>2</sub>O and MgCl<sub>2</sub>–H<sub>2</sub>O systems investigated by these authors.<sup>39</sup>

The behavior of the apparent molar volume of binary Na<sub>2</sub>SO<sub>4</sub> aqueous solution is typical for electrolytes, i.e., it increases with increasing pressure and ionic strength of a solution, whereas the values of  $V^\phi$  decrease upon increasing temperature. Progressively more negative values of limiting apparent molar volume at infinite dilution,  $V_{\text{Na}_2\text{SO}_4}^0$ , are approached with temperature increasing toward the critical temperature of the solvent.

The experimental data for the Na<sub>2</sub>SO<sub>4</sub>–NaCl–H<sub>2</sub>O ternary system are presented in Figure 2. The mean apparent molar volume of the ternary electrolyte mixture decreases with temperature and increases with pressure over the range of conditions investigated (Figure 3). The pressure-related increase of the mean apparent molar volume of the mixtures is much more significant at high temperatures, and can reach the rate of about 0.25 cm<sup>3</sup>·mol<sup>-1</sup> MPa<sup>-1</sup> at  $T = 523.15$  K. These trends of  $V_{\text{mean}}^\phi$  are similar to the behavior of the mixtures of chlorides.<sup>34,35</sup>

A comparison of the data from this study to literature at 298.15 K and 0.1 MPa is shown in Figure 2a–d. A good agreement among the data sets can be observed, with exception of some of the data points from Fabuss et al.<sup>28</sup> The data obtained in this study at elevated temperatures and pressures above ambient are presented in Figure 2e to h. Since this is a unique data set, the consecutive modeling of the volumetric properties of mixtures at elevated temperatures and pressures relies solely on our new measurements.

The results of this study and literature data were used to parametrize a Pitzer model.<sup>36</sup> The approach used in this model assumes that the electrolytes are fully dissociated, although the ion association can be significant.<sup>40–45</sup> On the basis of the calculations of Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O equilibria using the PHREEQC thermodynamic package,<sup>46</sup> it can be estimated that the degree of association in 1 mol·kg<sup>-1</sup> sodium sulfate solutions may reach (20 to 30) % at temperatures between 298 K and 523 K. In addition, hydrolysis is not considered although it could be expected for sulfate solutions of very low concentrations.<sup>44</sup>

**The Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O System.** The apparent molar volume of Na<sub>2</sub>SO<sub>4</sub> in binary aqueous solutions was calculated using the available correlations based on the Pitzer equation and the approach employed by Archer:<sup>47</sup>

$$V^\phi + \frac{v_w}{n_r} = \frac{V(m_r)}{n_r} + \nu z_M z_X \left( \frac{A^\nu}{2b} \right) \ln \{ (1 + bI^{1/2}) / (1 + bI_r^{1/2}) \} + 2\nu_M \nu_X RT \{ mB_{M,X}^\nu(m) - m_r B_{M,X}^\nu(m_r) + \nu_M z_M (m^2 - m_r^2) C_{M,X}^\nu \} \quad (2)$$

where  $v_w$  is the volume of 1 kg of water,  $V(m_r)$  is the volume of a quantity of solution of reference molality  $m_r = 1.5$  mol·kg<sup>-1</sup> which contains 1 kg of water, and  $n_r$  is the number of moles of solute in this quantity of solution,  $A^\nu$  is the Debye–Hückel limiting slope for the apparent molar volume,<sup>48</sup>  $b = 1.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> for 1:1 and 1:2 electrolytes,  $z_M$  and  $z_X$  are the charges of the cation and the anion, respectively,  $\nu_M$  and  $\nu_X$  are the stoichiometric numbers of cations or anions and  $\nu = \nu_M + \nu_X$  is the total number of ions formed upon dissociation,  $m$  is the molal concentration (in mol·kg<sup>-1</sup>) of a solute,  $I$  is the ionic strength of a solution in mol·kg<sup>-1</sup> calculated as  $(1/2) \sum m_i z_i^2$ ,  $R = 8.314472$  cm<sup>3</sup>·MPa·K<sup>-1</sup>·mol<sup>-1</sup> is the gas constant,  $T$  is a temperature in K.  $B_{M,X}^\nu(m)$  and  $C_{M,X}^\nu$  are the temperature- and pressure-dependent volumetric ion interaction parameters. In the case of  $B_{M,X}^\nu(m)$ , the ionic strength dependence of a solution is imposed as follows:

$$B_{M,X}^\nu = \beta_{M,X}^{(0)\nu} + 2\beta_{M,X}^{(1)\nu} [1 - (1 + \alpha I^{1/2}) \times \exp(-\alpha I^{1/2})] (\alpha I^{1/2})^{-2} \quad (3)$$

The volumetric ion interaction parameters are expressed as functions  $f(i, p, T)$ :

Table 2. Results of Experimental Measurements of Density Difference  $\Delta\rho$  of  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  Systems with Respect to Pure Water at Temperature  $T$ , Pressure  $p$ , and Molalities of Components  $m_i^a$ 

$\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$					$\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$				
$T$	$p$	$m(\text{Na}_2\text{SO}_4)$	$10^3 \cdot \Delta\rho$		$T$	$p$	$m(\text{Na}_2\text{SO}_4)$	$10^3 \cdot \Delta\rho$	
K	MPa	mol·kg <sup>-1</sup>	g·cm <sup>-3</sup>		K	MPa	mol·kg <sup>-1</sup>	g·cm <sup>-3</sup>	
298.15	0.1	0.10010	12.690		423.15	10	1.21083	133.864	
298.15	0.1	0.49086	59.282		423.15	20	0.10010	12.372	
298.15	0.1	1.00025	115.553		423.15	20	0.49086	57.415	
298.15	0.1	1.21083	137.353		423.15	20	1.00025	111.864	
298.15	5	0.09999	12.700		423.15	20	1.21083	133.066	
298.15	5	0.49972	60.374		423.15	40	0.10010	12.181	
298.15	5	1.00025	115.496		423.15	40	0.49086	56.722	
298.15	5	1.21083	137.625		423.15	40	1.00025	110.675	
298.15	10	0.09999	12.545		423.15	40	1.21083	131.737	
298.15	10	0.49972	60.139		423.15	70	0.09999	12.036	
298.15	10	1.00025	115.165		423.15	70	0.49972	56.901	
298.15	10	1.21083	137.237		423.15	70	1.00025	109.328	
298.15	20	0.09999	12.564		423.15	70	1.21083	130.159	
298.15	20	0.49972	59.763		473.15	5	0.10010	13.411	
298.15	20	1.00025	114.464		473.15	5	0.49086	60.663	
298.15	20	1.21083	136.426		473.15	5	1.00025	117.430	
298.15	40	0.09999	12.332		473.15	5	1.21083	139.253	
298.15	40	0.49972	59.096		473.15	10	0.10010	13.355	
298.15	40	1.00025	113.230		473.15	10	0.49086	60.414	
298.15	40	1.21083	134.934		473.15	10	1.00025	116.822	
298.15	70	0.09999	12.127		473.15	10	1.21083	138.571	
298.15	70	0.49972	58.051		473.15	20	0.10010	13.150	
298.15	70	1.00025	111.378		473.15	20	0.49086	59.798	
298.15	70	1.21083	132.808		473.15	20	1.00025	115.690	
373.15	5	0.10010	12.162		473.15	20	1.21083	137.292	
373.15	5	0.49086	56.847		473.15	40	0.10010	12.790	
373.15	5	1.00025	111.076		473.15	40	0.49086	58.657	
373.15	5	1.21083	132.606		473.15	40	1.00025	113.858	
373.15	10	0.10010	12.113		473.15	40	1.21083	135.217	
373.15	10	0.49086	56.699		473.15	70	0.10010	12.456	
373.15	10	1.00025	110.826		473.15	70	0.49086	57.595	
373.15	10	1.21083	132.326		473.15	70	1.00025	111.947	
373.15	20	0.10010	11.969		473.15	70	1.21083	132.955	
373.15	20	0.49086	56.319		523.15	5	0.10010	15.112	
373.15	20	1.00025	110.292		523.15	5	0.49086	66.495	
373.15	20	1.21083	131.722		523.15	5	1.00025	127.365	
373.15	40	0.10010	11.867		523.15	5	1.21083	149.935	
373.15	40	0.49086	55.810		523.15	10	0.10010	14.889	
373.15	40	1.00025	109.341		523.15	10	0.49086	65.857	
373.15	40	1.21083	130.581		523.15	10	1.00025	126.067	
373.15	70	0.10010	11.754		523.15	10	1.21083	148.827	
373.15	70	0.49086	55.152		523.15	20	0.10010	14.527	
423.15	5	0.10010	12.493		523.15	20	0.49086	64.521	
423.15	5	0.49972	58.951		523.15	20	1.00025	123.861	
423.15	5	1.00025	112.876		523.15	20	1.21083	146.261	
423.15	5	1.21083	134.272		523.15	40	0.10010	13.928	
423.15	10	0.10010	12.489		523.15	40	0.49086	62.564	
423.15	10	0.49086	57.816		523.15	40	1.00025	120.454	
423.15	10	1.00025	112.512		523.15	40	1.21083	142.454	
$T$	$p$	$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	$10^3 \cdot \Delta\rho$	$T$	$p$	$m(\text{NaCl})$	$m(\text{Na}_2\text{SO}_4)$	$10^3 \cdot \Delta\rho$
K	MPa	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	g·cm <sup>-3</sup>	K	MPa	mol·kg <sup>-1</sup>	mol·kg <sup>-1</sup>	g·cm <sup>-3</sup>
298.15	0.1	0.09995	1.00050	118.468	423.15	10	2.99977	0.09991	118.273
298.15	0.1	0.09998	0.49969	63.589	423.15	10	2.99983	0.50011	155.91
298.15	0.1	0.10038	0.10069	16.801	423.15	10	5.00004	0.09980	169.443
298.15	0.1	0.49963	1.00075	131.183	423.15	20	0.09995	1.00050	115.173
298.15	0.1	0.49971	0.10005	32.074	423.15	20	0.09998	0.49969	61.943

Table 2. continued

Na <sub>2</sub> SO <sub>4</sub> –NaCl–H <sub>2</sub> O									
<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>	<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>
K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>	K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>
298.15	0.1	0.50023	0.50077	77.843	423.15	20	0.10038	0.10069	16.445
298.15	0.1	0.99920	0.99657	146.223	423.15	20	0.49963	1.00075	127.606
298.15	0.1	0.99987	0.50016	94.586	423.15	20	0.49971	0.10005	31.814
298.15	0.1	1.00011	0.10019	50.746	423.15	20	0.50023	0.50077	76.004
298.15	0.1	1.00868	0.19948	62.361	423.15	20	0.99920	0.99657	142.392
298.15	0.1	2.99977	0.09991	118.581	423.15	20	0.99987	0.50016	92.742
298.15	0.1	2.99983	0.50011	157.486	423.15	20	1.00011	0.10019	50.156
298.15	0.1	5.00004	0.09980	170.237	423.15	20	1.00868	0.19948	61.376
298.15	5	0.09995	1.00050	118.733	423.15	20	2.99977	0.09991	117.266
298.15	5	0.09998	0.49969	63.796	423.15	20	2.99983	0.50011	154.79
298.15	5	0.10021	0.09994	16.676	423.15	20	5.00004	0.09980	168.121
298.15	5	0.49963	1.00075	131.568	423.15	40	0.09995	1.00050	113.907
298.15	5	0.49971	0.10005	32.04	423.15	40	0.09998	0.49969	61.196
298.15	5	0.50023	0.50077	78.071	423.15	40	0.10038	0.10069	16.162
298.15	5	0.99920	0.99657	146.485	423.15	40	0.49963	1.00075	126.196
298.15	5	0.99987	0.50016	95.012	423.15	40	0.49971	0.10005	31.25
298.15	5	1.00011	0.10019	50.824	423.15	40	0.50023	0.50077	75.067
298.15	5	2.99977	0.09991	118.632	423.15	40	0.99920	0.99657	140.84
298.15	5	2.99983	0.50011	157.551	423.15	40	0.99987	0.50016	91.59
298.15	5	5.00004	0.09980	170.603	423.15	40	1.00011	0.10019	49.355
298.15	10	0.09995	1.00050	118.321	423.15	40	1.00868	0.19948	60.47
298.15	10	0.09998	0.49969	63.499	423.15	40	2.99977	0.09991	115.608
298.15	10	0.10021	0.09994	16.541	423.15	40	2.99983	0.50011	152.849
298.15	10	0.49963	1.00075	131.103	423.15	40	5.00004	0.09980	165.937
298.15	10	0.49971	0.10005	31.851	423.15	70	0.09995	1.00050	112.565
298.15	10	0.50023	0.50077	77.72	423.15	70	0.09998	0.49969	60.439
298.15	10	0.99920	0.99657	145.905	423.15	70	0.10021	0.09994	15.927
298.15	10	0.99987	0.50016	94.583	423.15	70	0.49963	1.00075	124.683
298.15	10	1.00011	0.10019	50.531	423.15	70	0.49971	0.10005	30.746
298.15	10	2.99977	0.09991	118.153	423.15	70	0.50023	0.50077	74.058
298.15	10	2.99983	0.50011	156.971	423.15	70	0.99920	0.99657	139.091
298.15	10	5.00004	0.09980	169.975	423.15	70	0.99987	0.50016	90.275
298.15	20	0.09995	1.00050	117.692	423.15	70	1.00011	0.10019	48.572
298.15	20	0.09998	0.49969	63.194	423.15	70	2.99977	0.09991	113.728
298.15	20	0.10021	0.09994	16.505	423.15	70	2.99983	0.50011	150.708
298.15	20	0.49963	1.00075	130.418	423.15	70	5.00004	0.09980	163.414
298.15	20	0.49971	0.10005	31.709	473.15	5	0.09995	1.00050	120.826
298.15	20	0.50023	0.50077	77.309	473.15	5	0.09998	0.49969	65.76
298.15	20	0.99920	0.99657	145.214	473.15	5	0.10021	0.09994	17.848
298.15	20	0.99987	0.50016	94.115	473.15	5	0.49963	1.00075	134.377
298.15	20	1.00011	0.10019	50.231	473.15	5	0.49971	0.10005	35.043
298.15	20	2.99977	0.09991	117.474	473.15	5	0.50023	0.50077	81.102
298.15	20	2.99983	0.50011	156.124	473.15	5	0.99920	0.99657	150.404
298.15	20	5.00004	0.09980	168.971	473.15	5	0.99987	0.50016	99.418
298.15	40	0.09995	1.00050	116.34	473.15	5	1.00011	0.10019	55.38
298.15	40	0.09998	0.49969	62.409	473.15	5	2.99977	0.09991	127.551
298.15	40	0.10021	0.09994	16.282	473.15	5	2.99983	0.50011	165.599
298.15	40	0.49963	1.00075	128.961	473.15	5	5.00004	0.09980	181.528
298.15	40	0.49971	0.10005	31.233	473.15	10	0.09995	1.00050	120.336
298.15	40	0.50023	0.50077	76.37	473.15	10	0.09998	0.49969	65.437
298.15	40	0.99920	0.99657	143.518	473.15	10	0.10021	0.09994	17.863
298.15	40	0.99987	0.50016	92.967	473.15	10	0.49963	1.00075	133.757
298.15	40	1.00011	0.10019	49.55	473.15	10	0.49971	0.10005	34.842
298.15	40	2.99977	0.09991	115.903	473.15	10	0.50023	0.50077	80.703
298.15	40	2.99983	0.50011	154.267	473.15	10	0.99920	0.99657	149.653
298.15	40	5.00004	0.09980	166.997	473.15	10	0.99987	0.50016	98.878
298.15	70	0.09995	1.00050	114.496	473.15	10	1.00011	0.10019	55.009
298.15	70	0.09998	0.49969	61.372	473.15	10	2.99977	0.09991	126.721

Table 2. continued

Na <sub>2</sub> SO <sub>4</sub> –NaCl–H <sub>2</sub> O									
<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>	<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>
K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>	K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>
298.15	70	0.10021	0.09994	15.938	473.15	10	2.99983	0.50011	164.613
298.15	70	0.49963	1.00075	126.903	473.15	10	5.00004	0.09980	180.441
298.15	70	0.49971	0.10005	30.625	473.15	20	0.09995	1.00050	119.07
298.15	70	0.50023	0.50077	75.119	473.15	20	0.09998	0.49969	64.688
298.15	70	0.99920	0.99657	141.243	473.15	20	0.10021	0.09994	17.484
298.15	70	0.99987	0.50016	91.398	473.15	20	0.49963	1.00075	132.349
298.15	70	1.00011	0.10019	48.625	473.15	20	0.49971	0.10005	34.213
298.15	70	2.99977	0.09991	113.909	473.15	20	0.50023	0.50077	79.657
298.15	70	2.99983	0.50011	151.779	473.15	20	0.99920	0.99657	148.069
298.15	70	5.00004	0.09980	164.293	473.15	20	0.99987	0.50016	97.612
373.15	5	0.09995	1.00050	114.266	473.15	20	1.00011	0.10019	54.092
373.15	5	0.09998	0.49969	61.257	473.15	20	2.99977	0.09991	124.969
373.15	5	0.10038	0.10069	16.131	473.15	20	2.99983	0.50011	162.657
373.15	5	0.49963	1.00075	126.691	473.15	20	5.00004	0.09980	178.189
373.15	5	0.49971	0.10005	30.939	473.15	40	0.09995	1.00050	117.261
373.15	5	0.50023	0.50077	75.001	473.15	40	0.09998	0.49969	63.521
373.15	5	0.99920	0.99657	141.257	473.15	40	0.10021	0.09994	17.056
373.15	5	0.99987	0.50016	91.491	473.15	40	0.49963	1.00075	130.278
373.15	5	1.00011	0.10019	48.863	473.15	40	0.49971	0.10005	33.378
373.15	5	1.00868	0.19948	59.94	473.15	40	0.50023	0.50077	78.241
373.15	5	2.99977	0.09991	114.641	473.15	40	0.99920	0.99657	145.715
373.15	5	2.99983	0.50011	152.395	473.15	40	0.99987	0.50016	95.781
373.15	5	5.00004	0.09980	165.025	473.15	40	1.00011	0.10019	52.796
373.15	10	0.09995	1.00050	113.972	473.15	40	2.99977	0.09991	122.292
373.15	10	0.09998	0.49969	61.077	473.15	40	2.99983	0.50011	159.611
373.15	10	0.10038	0.10069	16.082	473.15	40	5.00004	0.09980	174.665
373.15	10	0.49963	1.00075	126.433	473.15	70	0.09995	1.00050	115.183
373.15	10	0.49971	0.10005	30.827	473.15	70	0.09998	0.49969	62.238
373.15	10	0.50023	0.50077	74.822	473.15	70	0.10021	0.09994	16.577
373.15	10	0.99920	0.99657	140.89	473.15	70	0.49963	1.00075	127.74
373.15	10	0.99987	0.50016	91.231	473.15	70	0.49971	0.10005	32.203
373.15	10	1.00011	0.10019	48.725	473.15	70	0.50023	0.50077	76.382
373.15	10	1.00868	0.19948	59.793	473.15	70	0.99920	0.99657	142.899
373.15	10	2.99977	0.09991	114.305	473.15	70	0.99987	0.50016	93.689
373.15	10	2.99983	0.50011	152.011	473.15	70	1.00011	0.10019	51.236
373.15	10	5.00004	0.09980	164.585	473.15	70	2.99977	0.09991	119.159
373.15	20	0.09995	1.00050	113.429	473.15	70	2.99983	0.50011	156.22
373.15	20	0.09998	0.49969	60.775	473.15	70	5.00004	0.09980	170.723
373.15	20	0.10038	0.10069	15.943	523.15	5	0.09995	1.00050	131.057
373.15	20	0.49963	1.00075	125.829	523.15	5	0.09998	0.49969	72.604
373.15	20	0.49971	0.10005	30.658	523.15	5	0.10021	0.09994	20.759
373.15	20	0.50023	0.50077	74.437	523.15	5	0.49963	1.00075	145.914
373.15	20	0.99920	0.99657	140.247	523.15	5	0.49971	0.10005	40.913
373.15	20	0.99987	0.50016	90.748	523.15	5	0.50023	0.50077	89.95
373.15	20	1.00011	0.10019	48.427	523.15	5	0.99920	0.99657	164.431
373.15	20	1.00868	0.19948	59.417	523.15	5	0.99987	0.50016	110.728
373.15	20	2.99977	0.09991	113.661	523.15	5	1.00011	0.10019	64.361
373.15	20	2.99983	0.50011	151.225	523.15	5	2.99977	0.09991	144.619
373.15	20	5.00004	0.09980	163.698	523.15	5	2.99983	0.50011	183.731
373.15	40	0.09995	1.00050	112.392	523.15	5	5.00004	0.09980	202.491
373.15	40	0.09998	0.49969	60.164	523.15	10	0.09995	1.00050	129.842
373.15	40	0.10038	0.10069	15.752	523.15	10	0.09998	0.49969	71.928
373.15	40	0.49963	1.00075	124.676	523.15	10	0.10021	0.09994	20.463
373.15	40	0.49971	0.10005	30.272	523.15	10	0.49963	1.00075	144.735
373.15	40	0.50023	0.50077	73.671	523.15	10	0.49971	0.10005	40.2
373.15	40	0.99920	0.99657	138.946	523.15	10	0.50023	0.50077	89.129
373.15	40	0.99987	0.50016	89.821	523.15	10	0.99920	0.99657	162.674
373.15	40	1.00011	0.10019	47.833	523.15	10	0.99987	0.50016	109.424



Table 2. continued

Na <sub>2</sub> SO <sub>4</sub> –NaCl–H <sub>2</sub> O									
<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>	<i>T</i>	<i>p</i>	<i>m</i> (NaCl)	<i>m</i> (Na <sub>2</sub> SO <sub>4</sub> )	10 <sup>3</sup> ·Δ <i>ρ</i>
K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>	K	MPa	mol·kg <sup>−1</sup>	mol·kg <sup>−1</sup>	g·cm <sup>−3</sup>
373.15	40	1.00868	0.19948	58.77	523.15	10	1.00011	0.10019	63.341
373.15	40	2.99977	0.09991	112.392	523.15	10	2.99977	0.09991	142.514
373.15	40	2.99983	0.50011	149.725	523.15	10	2.99983	0.50011	181.5
373.15	40	5.00004	0.09980	162.061	523.15	10	5.00004	0.09980	199.85
373.15	70	0.10038	0.10069	15.56	523.16	20	0.09995	1.00050	127.51
373.15	70	1.00868	0.19948	57.935	523.15	20	0.09998	0.49969	70.415
423.15	5	0.09995	1.00050	116.184	523.15	20	0.10021	0.09994	19.871
423.15	5	0.09998	0.49969	62.508	523.15	20	0.49963	1.00075	142.022
423.15	5	0.10038	0.10069	16.599	523.15	20	0.49971	0.10005	38.966
423.15	5	0.49963	1.00075	128.779	523.15	20	0.50023	0.50077	87.2
423.15	5	0.49971	0.10005	32.221	523.15	20	0.99920	0.99657	159.5
423.15	5	0.50023	0.50077	76.794	523.16	20	0.99987	0.50016	106.955
423.15	5	0.99920	0.99657	143.711	523.15	20	1.00011	0.10019	61.439
423.15	5	0.99987	0.50016	93.724	523.15	20	2.99977	0.09991	138.864
423.15	5	1.00011	0.10019	50.804	523.16	20	2.99983	0.50011	177.505
423.15	5	1.00868	0.19948	62.099	523.15	20	5.00004	0.09980	195.211
423.15	5	2.99977	0.09991	118.67	523.15	40	0.09995	1.00050	123.984
423.15	5	2.99983	0.50011	156.347	523.15	40	0.09998	0.49969	68.135
423.15	5	5.00004	0.09980	169.976	523.15	40	0.10021	0.09994	18.958
423.15	10	0.09995	1.00050	115.884	523.15	40	0.49963	1.00075	137.96
423.15	10	0.09998	0.49969	62.44	523.15	40	0.49971	0.10005	37.128
423.15	10	0.10038	0.10069	16.618	523.16	40	0.50023	0.50077	84.205
423.15	10	0.49963	1.00075	128.385	523.15	40	0.99920	0.99657	154.777
423.15	10	0.49971	0.10005	32.096	523.15	40	0.99987	0.50016	103.267
423.15	10	0.50023	0.50077	76.534	523.15	40	1.00011	0.10019	58.628
423.15	10	0.99920	0.99657	143.295	523.16	40	2.99977	0.09991	133.367
423.15	10	0.99987	0.50016	93.469	523.15	40	2.99983	0.50011	171.465
423.15	10	1.00011	0.10019	50.635	523.15	40	5.00004	0.09980	188.261
423.15	10	1.00868	0.19948	61.45					

<sup>a</sup>*m* is the molality of solute (NaCl or Na<sub>2</sub>SO<sub>4</sub>) in the water solvent; Δ*ρ* represents the measured difference in density of a solution with respect to water. Standard uncertainties *u* are *u*(*T*) = 0.01 K, *u*(*p*) = 0.0005·*p*, *u*(*m<sub>i</sub>*) = 0.005·*m<sub>i</sub>*. The combined uncertainty *U*(Δ*ρ*) = (2.8·10<sup>−5</sup>, 2.9·10<sup>−5</sup>, 3.7·10<sup>−5</sup>, 6.1·10<sup>−5</sup>, and 1.03·10<sup>−4</sup>) g·cm<sup>−3</sup> at *T* = (298.15, 373.15, 423.15, 473.15, and 523.15) K, respectively. The combined uncertainty is based on the standard deviation of the mean density difference of solutions evaluated from the repeated measurements of the solution at every temperature.

$$\beta_{M,X}^{(0)\nu} = f(1, p, T) \quad (4)$$

$$\beta_{M,X}^{(1)\nu} = f(2, p, T) \quad (5)$$

$$C_{M,X}^{\nu} = f(3, p, T) \quad (6)$$

with *f*(*i*, *p*, *T*) represented as

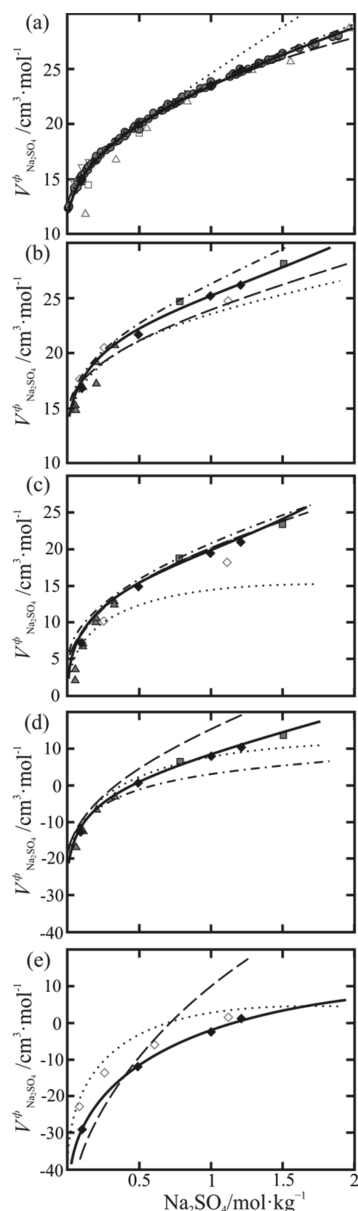
$$\begin{aligned} f(i, p, T) = & b_{i,1} + b_{i,2} \ln\left(\frac{T}{T_r}\right) + b_{i,3} \left[\frac{T - T_r}{T^{\circ}}\right] \\ & + b_{i,4} \left[\frac{T^{\circ}}{620 - T}\right] + b_{i,5} \left[\frac{T^{\circ}}{T - 227}\right] \\ & + 2 \left(\frac{p}{p_0}\right) \left\{ b_{i,6} + b_{i,7} \ln\left(\frac{T}{T_r}\right) + b_{i,8} \left[\frac{T - T_r}{T^{\circ}}\right] \right. \\ & \left. + b_{i,9} \left[\frac{T^{\circ}}{620 - T}\right] + b_{i,10} \left[\frac{T^{\circ}}{T - 227}\right] \right\} \end{aligned} \quad (7)$$

The values of the volume of a quantity of solution at reference molality, *V*(*m<sub>r</sub>*)/*n<sub>r</sub>*, of eq 2 are calculated from the following relation:

$$\begin{aligned} \frac{V(m_r)}{n_r} = & b_{4,1} + b_{4,2} \left(\frac{T}{T_0}\right) + b_{4,3} \left(\frac{T}{T_0}\right)^2 + b_{4,4} \left(\frac{T}{T_0}\right)^3 \\ & + b_{4,5} \left(\frac{p}{p_0}\right) + b_{4,6} \left(\frac{p}{p_0}\right) \left(\frac{T}{T_0}\right) + b_{4,7} \left(\frac{p}{p_0}\right) \left(\frac{T}{T_0}\right)^2 \\ & + b_{4,8} \left(\frac{p}{p_0}\right)^2 + b_{4,9} \left(\frac{p}{p_0}\right)^2 \left(\frac{T}{T_0}\right) \end{aligned} \quad (8)$$

where *T* is a temperature in K, *p* is a pressure in MPa, *T<sub>r</sub>* = 298.15 K, *T<sub>0</sub>* = 1 K, *p<sub>0</sub>* = 1 MPa, and *b<sub>i,j</sub>* are model parameters listed in Table 3. All parameters (here and below) were derived using the IAPWS-95 equation of state for the thermodynamic properties of water<sup>49</sup> and the international formulation for the dielectric properties of water.<sup>48</sup>

The results of the calculations of the apparent molar volume of Na<sub>2</sub>SO<sub>4</sub> in aqueous solutions using the Pitzer model are presented in Figure 1 along with the results of models of Obsil et al.,<sup>17</sup> Phutela and Pitzer (also based on the Pitzer equations),<sup>14</sup> and Appelo et al.<sup>50</sup> Our new parametrization of Pitzer equation performs much better comparing to other models. The models of Phutela and Pitzer and Appelo et al. may be considered for calculations only at temperatures of up



**Figure 1.** Apparent molar volume  $V^{\phi}$  of  $\text{Na}_2\text{SO}_4$  in aqueous solution as a function of concentration. The experimental data (symbols) are compared with the models of Obsil et al.<sup>17</sup> (dotted curves), Phutela and Pitzer (dotted-dashed curves),<sup>14</sup> Appelo et al.<sup>50</sup> (dashed curves), and this study (solid curves) at various temperatures and pressures: (a) 298.15 K, 0.1 MPa; (b) 373.15 K, 10 MPa; (c) 423.15 K, 10 MPa; (d) 473.15 K, 10 MPa; (e) 523.15 K, 40 MPa. Filled black diamonds are used for the data collected in this study; gray filled symbols are used for the data from the literature. Circles in panel (a) represent data from refs 2–7, 10, 11, 13, 16, and 20–25 at 298.15 K; squares, ref 25; triangles, ref 14. Open symbols are used for the data sets from the literature having large deviations (reduced weight assigned in fitting procedure): up triangles, ref 1; down triangles, ref 28; diamonds, ref 18; and squares, ref 19.

to 423 K. Although the model of Obsil et al. reasonably predicts the apparent molar volumes to 473 K, it does not reproduce the experimental results at 423 K and 10 MPa (Figure 1c).

The optimization of parameters for the ion interaction model was done on the basis of the experimental data set from this study (98 points) and the literature data listed above (1228 points). Due to a large deviation, a lower weight in fitting was

assigned for the data sets of Trimble,<sup>1</sup> Fabuss et al.,<sup>28</sup> Azizov and Akhundov,<sup>18</sup> and Abramson et al.<sup>19</sup> (see Table 4; open symbols in Figure 1). The root-mean-square deviation (RMSD) of the modeled values of  $V^{\phi}$  from those determined experimentally is  $0.87 \text{ cm}^3\cdot\text{mol}^{-1}$  (for the refined data set excluding reduced weight data points). It is important to note that the deviation is significantly larger for the solutions of low ionic strength. Thus, the RMSD is  $0.59 \text{ cm}^3\cdot\text{mol}^{-1}$  for solutions at concentration of  $\text{Na}_2\text{SO}_4$  over  $0.1 \text{ mol}\cdot\text{kg}^{-1}$ ; this is to compare with dilute solutions with  $m_{\text{Na}_2\text{SO}_4}$  less than  $0.1 \text{ mol}\cdot\text{kg}^{-1}$  having RMSD of  $1.68 \text{ cm}^3\cdot\text{mol}^{-1}$ . The deviation of the modeled results from the experimental data of the individual data sets is listed in Table 4.

**The  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$ – $\text{H}_2\text{O}$  System.** The mean apparent molar volume of electrolyte mixtures was approximated using the Pitzer approach<sup>36,47</sup> formulated for the apparent molar volume of multicomponent systems:<sup>51</sup>

$$V_{\text{mean}}^{\phi} = V^0 + \frac{1}{\sum m_i} \left[ A^v \left( \frac{I}{b} \right) \ln(1 + bI^{1/2}) + RT \left\{ 2 \sum_c \sum_a m_c m_a [B_{c,a}^v + (\sum_c m_c z_c) C_{c,a}^v] + \sum_c \sum_{c'} m_c m_{c'} (2\theta_{c,c'}^v + \sum_a m_a \psi_{c,c',a}^v) + \sum_a \sum_{a'} m_a m_{a'} (2\theta_{a,a'}^v + \sum_c m_c \psi_{a,a',c}^v) \right\} \right] \quad (9)$$

where  $V^0 = \sum y_i V_i^0$ ,  $y_i$  is the molal fraction of  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  in the mixture,  $V_i^0$  is the apparent molar volume of pure components at infinite dilution,  $m_x$  is the molal concentration (in  $\text{mol}\cdot\text{kg}^{-1}$ ),  $z_x$  is the charge of respective anion  $a$  or cation  $c$ ,  $B_{c,a}^v$  and  $C_{c,a}^v$  are the volumetric parameters obtained from the available correlations for pure binary solutions of electrolytes (this study for the  $\text{Na}_2\text{SO}_4$ – $\text{H}_2\text{O}$  system and ref 35 for the  $\text{NaCl}$ – $\text{H}_2\text{O}$  system). Parameters  $\theta_{a,a'}^v$  and  $\psi_{a,a',c}^v$  are the mixing terms fitted to experimental data for the mixtures, where  $a$  and  $a'$  stand for different anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ). The mixing parameters may comprise both short-range and long-range effects for asymmetric mixing, e.g., for anions of differing charge.<sup>52</sup> In the case when a solution contains electrolytes with a common cation, the second last term of eq 9 (summation over cations) is zero. A temperature and pressure dependence of the mixing terms was introduced along with ionic strength dependence as required for asymmetric mixtures:

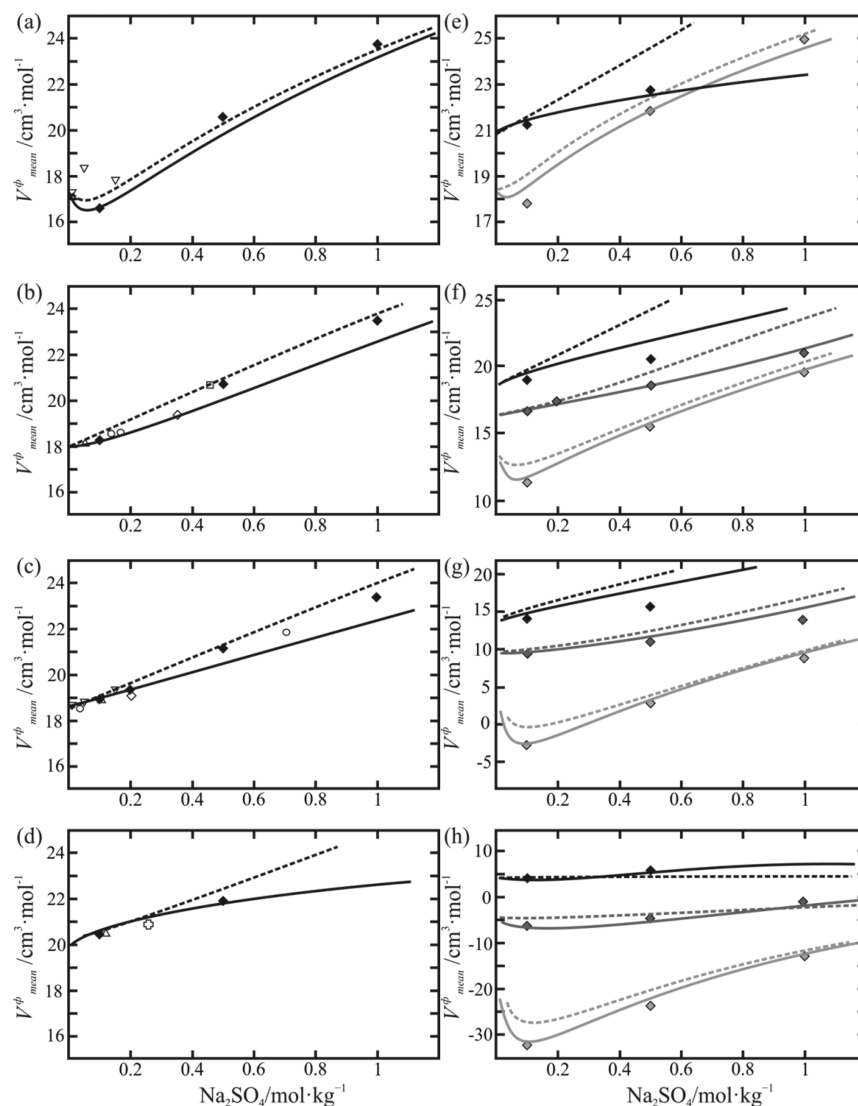
$$\theta_{a,a'}^v = a_{1,1} + (a_{1,2} + a_{1,3}T + a_{1,4}T^2 + a_{1,5}p^2)I^{-1} \quad (10)$$

$$\psi_{a,a',c}^v = a_{2,1} + (a_{2,2} + a_{2,3}T + a_{2,4}T^2 + a_{2,5}p^2)I^{-1} \quad (11)$$

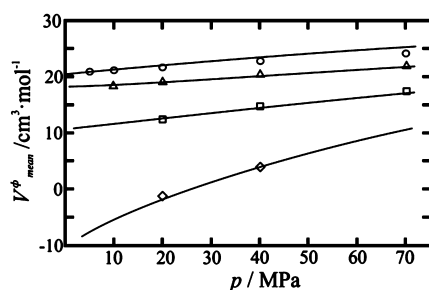
where  $T$  is a temperature in K,  $p$  is a pressure in MPa,  $I$  is the ionic strength of an aqueous solution in  $\text{mol}\cdot\text{kg}^{-1}$ ,  $a_{ij}$  are the parameters for calculation of mixing terms and consequent evaluation of the mean apparent molar volume of  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$  aqueous mixtures (eq 9) at temperatures from (298.15 to 523.15) K and pressures from (0.1 to 70) MPa listed in Table 5.

The optimization of parameters for the mixtures was done on the basis of 299 experimental measurements from this study and 144 data points from the literature (Table 6). Literature data only at  $T < 373.15 \text{ K}$  at  $p = 0.1 \text{ MPa}$  were considered for the fitting. The model error represented by RMSD is  $0.73 \text{ cm}^3$ .





**Figure 2.** Mean apparent molar volume,  $V_{\text{mean}}^{\phi}$ , of  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$  aqueous solute mixtures as a function of  $\text{Na}_2\text{SO}_4$  concentration in a solution. Experimental data from literature (open symbols: up triangle, ref 28; down triangle, ref 29; circle, ref 32; diamond, ref 30; square, ref 31; and cross, ref 7) and this study (filled diamonds) are compared to the results of modeling using a Pitzer-type equation, eq 2 (full lines), and Young's mixing rule, eq 5 (dashed lines), at  $T = 298.15$  K and  $p = 0.1$  MPa (a, at  $m_{\text{NaCl}} = 0.1$  mol·kg $^{-1}$ ; b, at  $m_{\text{NaCl}} = 0.5$  mol·kg $^{-1}$ ; c, at  $m_{\text{NaCl}} = 1$  mol·kg $^{-1}$ , and d, at  $m_{\text{NaCl}} = 3$  mol·kg $^{-1}$ ), and at temperatures 373.15 K (e), 423.15 K (f), 473.15 K (g), and 523.15 K (h),  $p = 10$  MPa, and  $m_{\text{NaCl}} = 0.1$  mol·kg $^{-1}$  (light gray curves and symbols), 1 mol·kg $^{-1}$  (dark gray curves and symbols), and 3 mol·kg $^{-1}$   $\text{NaCl}$  (black curves and symbols).



**Figure 3.** Pressure dependence of  $V_{\text{mean}}^{\phi}$  for the  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$ – $\text{H}_2\text{O}$  system for solutions containing 1 mol·kg $^{-1}$  of  $\text{NaCl}$  and 0.5 mol·kg $^{-1}$  of  $\text{Na}_2\text{SO}_4$ . Symbols represent experimental measurements at different temperatures: circles, 298.15 K; triangles, 423.15 K; squares, 473.15 K; and diamonds, 523.15 K. Curves represent the approximation by a Pitzer equation (see text for details).

mol $^{-1}$  for the data employed. This parametrization of the Pitzer equation based on our new experimental data is the first model capable to calculate the mean apparent molar volume of the mixed solutes and consequently, the density of solutions in aqueous system  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$ – $\text{H}_2\text{O}$  at elevated temperatures and pressures. It shows a generally good performance in describing the  $V_{\text{mean}}^{\phi}$  across the entire range of conditions covered by this experimental study. Figure 2 presents the results of modeling compared to the experimental data for the  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$ – $\text{H}_2\text{O}$  system. The Pitzer model equipped with parameters derived in this study is able to better predict the values of the mean apparent molar volume of solutes comparing to Young's mixing model.<sup>53</sup> The latter one uses the properties of each binary electrolyte constituent of a solution at the same total molality as that of a mixture, and the mean apparent molar volume of the mixture of electrolytes can be calculated as follows:

Table 3. Parameters for Eqs 7 and 8 of the Pitzer Model for  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  Solutions Obtained by Fitting of Experimental Data from This Study and Literature Listed in Table 4

	$i = 1$	$i = 2$	$i = 3$	$i = 4$
$b_{i,1}$	$6.05954 \cdot 10^{-4}$	$1.81948 \cdot 10^{-2}$	$-9.02041 \cdot 10^{-5}$	7.85265
$b_{i,2}$	$-1.33035 \cdot 10^{-2}$	$-1.22328 \cdot 10^{-1}$	$2.23418 \cdot 10^{-3}$	$-9.20087 \cdot 10^{-1}$
$b_{i,3}$	$1.82630 \cdot 10^{-5}$	$4.13138 \cdot 10^{-4}$	$7.54851 \cdot 10^{-8}$	$2.28824 \cdot 10^{-1}$
$b_{i,4}$	$2.40232 \cdot 10^{-1}$	$-4.38235$	$-1.26843 \cdot 10^{-1}$	$-7.31316 \cdot 10^{-2}$
$b_{i,5}$	$-6.77293 \cdot 10^{-2}$	$-1.64437 \cdot 10^{-1}$	$3.42505 \cdot 10^{-2}$	$-6.61264 \cdot 10^{-1}$
$b_{i,6}$	$-5.75614 \cdot 10^{-6}$	$-3.30824 \cdot 10^{-5}$	$-4.63903 \cdot 10^{-6}$	$3.58390 \cdot 10^{-1}$
$b_{i,7}$	$3.61020 \cdot 10^{-4}$	$-2.45357 \cdot 10^{-4}$	$-3.60229 \cdot 10^{-5}$	$-6.66318 \cdot 10^{-2}$
$b_{i,8}$	$-8.08348 \cdot 10^{-7}$	$-1.11329 \cdot 10^{-6}$	$6.77063 \cdot 10^{-8}$	$-1.94421 \cdot 10^{-1}$
$b_{i,9}$	$-1.28047 \cdot 10^{-3}$	$4.58964 \cdot 10^{-2}$	$9.04198 \cdot 10^{-4}$	$6.09792 \cdot 10^{-2}$
$b_{i,10}$	$5.36298 \cdot 10^{-4}$	$-8.40841 \cdot 10^{-3}$	$1.59321 \cdot 10^{-4}$	

Table 4. Summary of Experimental Data on the Density of the  $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  System Used for Fitting of the Pitzer Model (Eqs 2 to 8) and Corresponding Estimates of the Quality of the Fit

ref	no. of points	molality	$T^a$	$p$	weight	RMSD
		$\text{mol} \cdot \text{kg}^{-1}$	K	MPa		$\text{cm}^3 \cdot \text{mol}^{-1}$
1	7	0.06–1.96	298	0.1	0.01/0.5	1.56
2	17	0.07–2.73	298–303	0.1	1	0.17
3	10	0.01–1.47	298	0.1	1	0.40
4	8	0.1–1.96	298	0.1	1	0.30
5	2	0.2–0.84	298	0.1	1	0.18
28	12	0.01–0.15	298–323	0.1	0.2	1.22
8	35	0.05–1	323–473	1.97	1	1.09
6	16	0.03–1.18	298–348	0.1	1	2.26
7	10	1.33	278–318	0.1	1	0.40
9	17	0.002–1	323	0.1	1	1.48
10	76	0.01–0.33	298–323	0.1–80.2	1	0.42
11	65	0.05–1.62	288–318	0.1	1	0.14
12	14	0.035–3.4	313	0.1	1	0.43
13	43	0.05–1.5	288–328	0.1	1	0.67
26	2	0.15–1.13	338–368	0.1	1	0.35
14	108	0.06–0.33	294–475	2–10.2	1	0.96
15	43	0.01–1.53	297–372	0.6	1	0.67
16	40	0.001–0.2	288–308	0.1	1	2.24
17	134	0.005–1	298–523	9.87–30.7	1	1.28
18	200	0.088–1.16	302–573	2.4–39.8	0.2	3.30
19	18	0.15–0.5	298–473	0.1–100	0.2	4.09
20	13	0.01–1.89	298	0.1	1	0.23
21	17	0.5–2.25	283–343	0.1	1	0.35
22	24	0.1–1.85	283–298	0.1	1	0.18
23	5	0.09–0.5	298	0.1	1	0.15
24	168	0.1–1	278–343	0.1	1	0.32
25	124	0.78–1.5	298–473	1.1–68.6	1	0.55
this study	98	0.1–1.21	298–523	0.1–70	1	1.03

<sup>a</sup>Rounded values of  $T$  are listed.Table 5. Parameters of Eqs 10 and 11 for Calculation of Mixing Terms of the Pitzer Model for Ternary Mixtures in  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  System (Eq 9), Obtained by Fitting of Experimental Data from This Study and Literature Listed in Table 6

	$\theta_{\text{Cl}_2\text{SO}_4}^v$ $i = 1$	$\psi_{\text{Na}_2\text{Cl}_2\text{SO}_4}^v$ $i = 2$
$a_{i,1} \cdot 10^4$	−5.03189	−1.77913
$a_{i,2} \cdot 10^2$	−1.29888	1.28991
$a_{i,3} \cdot 10^5$	7.21576	−7.05252
$a_{i,4} \cdot 10^7$	−1.01993	1.04959
$a_{i,5} \cdot 10^7$	0.748483	5.63136

$$V_{\text{mean}}^\phi = \sum_j \frac{m_j V_j^\phi}{\sum_j m_j} \quad (12)$$

where  $m_j$  is the molality of component  $j$  in a mixture, and  $V_j^\phi$  is the apparent molar volume of pure end-member aqueous electrolyte solution ( $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$  and  $\text{NaCl--H}_2\text{O}$ ) at the total molality of a mixture. The RMSD of the mean apparent molar volume of electrolytes calculated using Young's rule from that obtained from experiments is  $1.23 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

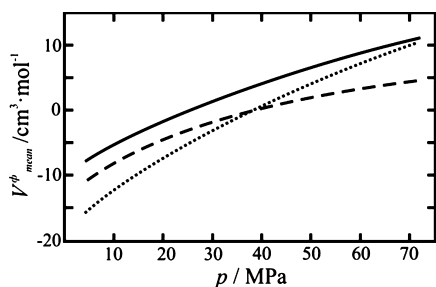
The volumetric behavior of the  $\text{Na}_2\text{SO}_4\text{--NaCl--H}_2\text{O}$  system is similar to that of the mixtures of chlorides,  $\text{CaCl}_2\text{--NaCl--H}_2\text{O}$  and  $\text{MgCl}_2\text{--NaCl--H}_2\text{O}$  as seen in the increase of the

**Table 6.** Summary of Experimental Data on the Density of the Na<sub>2</sub>SO<sub>4</sub>–NaCl–H<sub>2</sub>O System Used for Fitting of the Pitzer Model (Eqs 9 to 11) and Corresponding Estimates of the Quality of the Fit

ref	no. of points	ionic strength	$T^a$	$p$	RMSD
		mol·kg <sup>-1</sup>	K	MPa	cm <sup>3</sup> ·mol <sup>-1</sup>
28	71 (36) <sup>b</sup>	0.13–2.95	298–448	0.1	0.75
7	15	4	273–318	0.1	0.67
29	63 (27) <sup>b</sup>	0.71–3.6	298–423	0.1	0.34
33	7	0.54–1.75	298	0.1	0.12
32	16	1, 3	298	0.1	0.31
30	8	1.5	298	0.1	0.16
31	27	1.95	278–368	0.1	0.58
this study	299	0.4–5.3	298–523	0.1–70	0.80

<sup>a</sup>Rounded values of  $T$  are listed. <sup>b</sup>Numbers in parentheses are the number of points not considered in fitting.

mean apparent molar volume of the solute mixtures with pressure at 523 K (Figure 4). The volume of mixing  $V^{\text{mix}}$  was



**Figure 4.** Mean apparent molar volume of the Na<sub>2</sub>SO<sub>4</sub>–NaCl–H<sub>2</sub>O (solid curve), CaCl<sub>2</sub>–NaCl–H<sub>2</sub>O (dashed curve), and MgCl<sub>2</sub>–NaCl–H<sub>2</sub>O (dotted curve) systems as a function of pressure at 523 K, 1 mol·kg<sup>-1</sup> NaCl, and 0.5 mol·kg<sup>-1</sup> of other electrolyte (Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, or MgCl<sub>2</sub>).

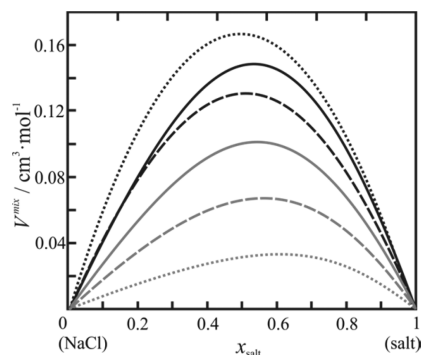
calculated for estimation of the non-idealities of mixed electrolyte solutions. It represents the difference between the molar volume of a solution calculated from the experimental data  $V_{\text{soln}}$  and the molar volume calculated as an ideal mixture of real binary aqueous salt solutions:

$$V^{\text{mix}} = V_{\text{soln}} - [yV_{\text{NaCl}} + (1 - y)V_i] \quad (13)$$

where  $V_i$  is the molar volume of a binary aqueous solution (Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O, CaCl<sub>2</sub>–H<sub>2</sub>O, MgCl<sub>2</sub>–H<sub>2</sub>O, or NaCl–H<sub>2</sub>O) calculated from the Pitzer equations (parametrized in this study and ref 35). Comparison of the volume of mixing of these ternary aqueous solutions also emphasizes the similarity in the mixtures of Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, and MgCl<sub>2</sub> with NaCl (Figure 5).

The partial molar volume  $\bar{V}_i$  and the limiting partial molar volume  $\bar{V}_i^0$  of an individual electrolyte in a mixture were calculated at every experimental point from the newly parametrized Pitzer model according to the following equations:<sup>33</sup>

$$\bar{V}_i = (m_i + m_j) \left( \frac{\partial V_{\text{mean}}^{\phi}}{\partial m_i} \right) + V_{\text{mean}}^{\phi} \quad (14)$$



**Figure 5.** Volume of mixing of ternary aqueous mixtures of Na<sub>2</sub>SO<sub>4</sub> (solid), CaCl<sub>2</sub> (dashed), or MgCl<sub>2</sub> (dotted) with NaCl as a function of mole fraction of solute at 473 K, 5 MPa and 70 MPa (gray and black curves, respectively), and total molality of salts  $\sum m_i = 1 \text{ mol·kg}^{-1}$ .

$$\bar{V}_i^0 = m_{j \neq i} \left( \frac{\partial V_{\text{mean}}^{\phi}}{\partial m_i} \right)_{m_i=0} + V_j^{\phi} \quad (15)$$

where  $V_j^{\phi}$ , the apparent molar volume of the second dissolved component in ternary mixture, was calculated from the Pitzer-type correlations for binary mixtures (this study and ref 35). The values of  $\bar{V}_i$  and  $\bar{V}_i^0$  are presented in Table 1S (Supporting Information). The difference in these molar volumes provides the excess molar volume of a solute in electrolyte mixture, which is an important thermodynamic value constraining the activity coefficient and pressure dependence according to

$$\left( \frac{\partial \ln \gamma_i}{\partial p} \right)_{T,m} = \frac{V_i^{\text{ex}}}{RT} \quad (16)$$

Thus, from the known molar volumes of a component in aqueous mixture derived from the Pitzer model and provided set of equations (eqs 9 to 11 and eqs 14 to 16), one can estimate the variation of the activity coefficients of electrolytes in solution with pressure. This important information permits accurate calculations and modeling of chemical equilibria for aqueous systems containing dissolved sodium chloride and sulfate at elevated temperatures and pressures.

## CONCLUSIONS

This new experimental data on the volumetric properties of binary Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O and ternary Na<sub>2</sub>SO<sub>4</sub>–NaCl–H<sub>2</sub>O solutions were collected for wide ranges of temperature, pressure, and composition. A Pitzer model for the apparent molar volume of aqueous electrolyte solutions was parametrized from the results of this study and the literature data. The validity of these parametrized Pitzer models for binary and ternary aqueous electrolyte solutions expands to temperatures up to 523.15 K and pressures up to 70 MPa. The density of these electrolyte solutions can be accurately calculated. The partial molar volumes and limiting molar volumes of components in multicomponent solutions can be evaluated at any  $p$ – $T$  composition using the set of Pitzer equations and respective derivatives, which in turn, can be used for the evaluation of the excess molar volume of a component in a mixture. The constraints on the variation of the excess volume with pressure permit evaluation of the pressure dependence of the activity coefficients of electrolytes in aqueous solutions. This opens an outstanding opportunity to properly handle the equilibrium calculations for the systems containing complex aqueous

solutions at elevated temperatures and pressures above saturation.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Table 1S, listing the mean apparent molar volume of  $\text{Na}_2\text{SO}_4$ – $\text{NaCl}$  solute mixtures, partial molar volumes, and limiting partial molar volumes of electrolytes in ionic media calculated from the obtained experimental data and the Pitzer model parametrized in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [denis.zezin@erdw.ethz.ch](mailto:denis.zezin@erdw.ethz.ch). Tel.: +41 44 632 80 73.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors sincerely thank Dr. Hans Stabinger for providing the densimeter and encouragement for the project.

## ■ REFERENCES

- (1) Trimble, H. M. The Solubility of Potassium Permanganate in Solutions of Potassium Sulfate and of Sodium Sulfate. *J. Am. Chem. Soc.* **1922**, *44*, 451–460.
- (2) Gibson, R. E. The System Sodium Sulphate–Water: I. The Densities and Specific Volumes of Aqueous Solutions of Sodium Sulfate between 25 and 40°, and the Fictive Volumes of Sodium Sulfate in Solution. *J. Phys. Chem.* **1927**, *31*, 496–510.
- (3) Geffeken, W.; Price, D. Zur Frage Der Konzentrationsabhängigkeit Des Scheinbaren Molvolumens Und Der Scheinbaren Molfraktion in Verdünnten Lösungen. *Z. Phys. Chem.* **1934**, *26*, 81–99.
- (4) Pearce, J.; Eckstrom, H. Vapor Pressures and Partial Molal Volumes of Aqueous Solutions of the Alkali Sulfates at 25°. *J. Am. Chem. Soc.* **1937**, *59*, 2689–2691.
- (5) Dunn, L. A. Apparent Molar Volumes of Electrolytes. Part 1. Some 1–1, 1–2, 2–1, 3–1 Electrolytes in Aqueous Solution at 25 °C. *Trans. Faraday Soc.* **1966**, *62*, 2348–2354.
- (6) Korosi, A.; Fabuss, B. Viscosities of Binary Aqueous Solutions of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$  at Concentrations and Temperatures of Interest in Desalination Processes. *J. Chem. Eng. Data* **1968**, *13*, 548–552.
- (7) Wirth, H.; LoSurdo, A. Temperature Dependence of Volume Changes on Mixing Electrolyte Solutions. *J. Chem. Eng. Data* **1968**, *13*, 226–231.
- (8) Ellis, A. Partial Molal Volumes in High-Temperature Water. Part III. Halide and Oxyanion Salts. *J. Chem. Soc. A* **1968**, *3*, 1138–1143.
- (9) Millero, F. J.; Knox, J. H. Apparent Molal Volumes of Aqueous  $\text{NaF}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$  Solutions at 0° and 50 °C. *J. Chem. Eng. Data* **1973**, *18*, 407–411.
- (10) Chen, C.-T.; Emmet, R. T.; Millero, F. J. The Apparent Molal Volumes of Aqueous Solutions of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{MgSO}_4$  from 0 to 1000 bar at 0, 25, and 50 °C. *J. Chem. Eng. Data* **1977**, *22*, 201–207.
- (11) Lo Surdo, A.; Alzola, E. M.; Millero, F. J. The (p, V, T) Properties of Concentrated Aqueous Electrolytes. I. Densities and Apparent Molar Volumes of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgCl}_2$ , and  $\text{MgSO}_4$  Solutions from 0.1 mol  $\text{kg}^{-1}$  to Saturation and from 273.15 to 323.15 K. *J. Chem. Thermodyn.* **1982**, *14*, 649–662.
- (12) Fleischmann, W.; Mersmann, A. Solubility, Density and Viscosity for Sodium Sulfate–Methanol–Water Systems at 40 °C. *J. Chem. Eng. Data* **1984**, 452–456.
- (13) Isono, T. Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides,  $\text{LaCl}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NaBr}$ ,  $\text{KNO}_3$ ,  $\text{KBr}$ , and  $\text{Cd}(\text{NO}_3)_2$ . *J. Chem. Eng. Data* **1984**, *29*, 45–52.
- (14) Phutela, R. C.; Pitzer, K. S. Densities and Apparent Molar Volumes of Aqueous Magnesium Sulfate and Sodium Sulfate to 473 K and 100 bar. *J. Chem. Eng. Data* **1986**, *31*, 320–327.
- (15) Saluja, P. P. S.; Lemire, R. J.; LeBlanc, J. C. High-Temperature Thermodynamics of Aqueous Alkali-Metal Salts. *J. Chem. Thermodyn.* **1992**, *24*, 181–203.
- (16) Sanchez, M. M.; Dominguez, B.; Raposo, R. R.; Vivo, A. Densities and Molar Volumes of  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  in Ethanol+Water Mixtures at 15, 25, and 35 °C. *J. Chem. Eng. Data* **1994**, 453–456.
- (17) Obšil, M.; Majer, V.; Grolier, J.; Heffer, G. Volumetric Properties Of, and Ion-Pairing In, Aqueous Solutions of Alkali-Metal Sulfates under Superambient Conditions. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4445–4451.
- (18) Azizov, N.; Akhundov, T. The Bulk Properties of the  $\text{Na}_2\text{SO}_4$ – $\text{H}_2\text{O}$  System in a Wide Range of the Parameters of State. *High Temp.* **2000**, *38*, 220–226.
- (19) Abramson, E.; Brown, J.; Slutsky, L. J.; Wiryan, S. Measuring Speed of Sound and Thermal Diffusivity in the Diamond-Anvil Cell. *Int. J. Thermophys.* **2001**, *22*, 405–414.
- (20) Magalhães, M.; Königsberger, E.; May, P. M.; Heffer, G. Heat Capacities of Concentrated Aqueous Solutions of Sodium Sulfate, Sodium Carbonate, and Sodium Hydroxide at 25 °C. *J. Chem. Eng. Data* **2002**, 590–598.
- (21) Kiepe, J.; Rodrigues, A.; Horstmann, S.; Gmehling, J. Experimental Determination and Correlation of Liquid Density Data of Electrolyte Mixtures Containing Water or Methanol. *Ind. Eng. Chem. Res.* **2003**, *42*, 2022–2029.
- (22) Hervello, M.; Sánchez, A. Densities of Univalent Cation Sulfates in Ethanol + Water Solutions. *J. Chem. Eng. Data* **2007**, 752–756.
- (23) Zhuo, K.; Chen, Y.; Wang, W.; Wang, J. Volumetric and Viscosity Properties of  $\text{MgSO}_4/\text{CuSO}_4$  in Sucrose + Water Solutions at 298.15 K. *J. Chem. Eng. Data* **2008**, *53*, 2022–2028.
- (24) Apellat, A.; Manzurola, E.; Orekhova, Z. Thermodynamic Properties of Aqueous Electrolyte Solutions. Volumetric and Compressibility Studies in 0.1 mol· $\text{kg}^{-1}$ , 0.5 mol· $\text{kg}^{-1}$ , and 1.0 mol· $\text{kg}^{-1}$  Sodium Carbonate and Sodium Sulfate Solutions at Temperatures from 278.15 to 323.15 K. *J. Chem. Eng. Data* **2009**, *54*, 2550–2561.
- (25) Al Ghafri, S.; Maitland, G. C.; Trusler, J. P. M.  $\text{SrCl}_2$  (aq),  $\text{Na}_2\text{SO}_4$  (aq),  $\text{NaHCO}_3$  (aq), and Two Synthetic Reservoir Brines at Temperatures between (298 and 473) K, Pressures up to 68.5 MPa, and Molalities up to 3 mol· $\text{kg}^{-1}$ . *J. Chem. Eng. Data* **2013**, *58*, 402–412.
- (26) Connaughton, L.; Hershey, J.; Millero, F. PVT Properties of Concentrated Aqueous Electrolytes: V. Densities and Apparent Molal Volumes of the Four Major Sea Salts from Dilute Solution to Saturation and from 0 to 100 °C. *J. Solution Chem.* **1986**, *15*, 989–1002.
- (27) Mantegazzi, D.; Sanchez-Valle, C.; Reusser, E.; Driesner, T. Thermodynamic Properties of Aqueous Sodium Sulfate Solutions to 773 K and 3 GPa Derived from Acoustic Velocity Measurements in the Diamond Anvil Cell. *J. Chem. Phys.* **2012**, *137*, 224501.
- (28) Fabuss, B.; Korosi, A.; Huq, A. Densities of Binary and Ternary Aqueous Solutions of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$  of Sea Waters, and Sea Water Concentrates. *J. Chem. Eng. Data* **1966**, *11*, 325–331.
- (29) Fabuss, B. M.; Korosi, A.; Othmer, D. F. Viscosities of Aqueous Solutions of Several Electrolytes Present in Sea Water. *J. Chem. Eng. Data* **1969**, *14*, 192–197.
- (30) Millero, F. J.; Sotolongo, S. PVT Properties of Concentrated Aqueous Electrolytes. 7. The Volumes of Mixing of the Reciprocal Salt Pairs  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{NaCl}$ , and  $\text{Na}_2\text{SO}_4$  at 25 °C and  $I = 1.5$  M. *J. Chem. Eng. Data* **1986**, *31*, 470–472.
- (31) Dedick, E. A.; Hershey, J. P.; Sotolongo, S.; Stade, D. J.; Millero, F. J. The PVT Properties of Concentrated Aqueous Electrolytes IX. The Volume Properties of  $\text{KCl}$  and  $\text{K}_2\text{SO}_4$  and Their Mixtures with



NaCl and Na<sub>2</sub>SO<sub>4</sub> as a Function of Temperature. *J. Solution Chem.* **1990**, *19*, 353–374.

(32) Millero, F. J.; Connaughton, L. M.; Vinokurova, F.; Chetirkin, P. V. PVT Properties of Concentrated Aqueous Electrolytes. III. Volume Changes for Mixing the Major Sea Salts at  $I=1.0$  and  $3.0$  at  $25\text{ }^{\circ}\text{C}$ . *J. Solution Chem.* **1985**, *14*, 837–851.

(33) Millero, F.; Lafarriere, A. L.; Chetirkin, P. V. The Partial Molal Volumes of Electrolytes in  $0.725\text{ M}$  Sodium Chloride Solutions at  $25\text{ }^{\circ}\text{C}$ . *J. Phys. Chem.* **1977**, *81*, 1737–1745.

(34) Zezin, D.; Driesner, T.; Sanchez-Valle, C. Volumetric Properties of Mixed Electrolyte Aqueous Solutions at Elevated Temperatures and Pressures. The System KCl–NaCl–H<sub>2</sub>O to  $523.15\text{ K}$ ,  $40\text{ MPa}$ , and Ionic Strength from  $(0.1\text{ to }5.8)\text{ mol}\cdot\text{kg}^{-1}$ . *J. Chem. Eng. Data* **2014**, *59*, 736–749.

(35) Zezin, D.; Driesner, T.; Scott, S.; Sanchez-Valle, C.; Wagner, T. Volumetric Properties of Mixed Electrolyte Aqueous Solutions at Elevated Temperatures and Pressures. The Systems CaCl<sub>2</sub>–NaCl–H<sub>2</sub>O and MgCl<sub>2</sub>–NaCl–H<sub>2</sub>O to  $523.15\text{ K}$ ,  $70\text{ MPa}$ , and Ionic Strength from  $(0.1\text{ to }18)\text{ mol}\cdot\text{kg}^{-1}$ . *J. Chem. Eng. Data* **2014**, *59*, 2570–2588.

(36) Pitzer, K. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.

(37) Hill, P. G. A Unified Fundamental Equation for the Thermodynamic Properties of H<sub>2</sub>O. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1233–1274.

(38) Archer, D. G. Thermodynamic Properties of the NaCl+H<sub>2</sub>O System II. Thermodynamic Properties of NaCl(aq), NaCl·2H<sub>2</sub>O(cr), and Phase Equilibria. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793–829.

(39) Rowland, D.; May, P. M. A Pitzer-Based Characterization of Aqueous Magnesium Chloride, Calcium Chloride and Potassium Iodide Solution Densities to High Temperature and Pressure. *Fluid Phase Equilib.* **2013**, *338*, 54–62.

(40) Kester, D.; Pytkowicz, R. Effect of Temperature and Pressure on Sulfate Ion Association in Sea Water. *Geochim. Cosmochim. Acta* **1970**, *34*, 1039–1051.

(41) Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.

(42) Fisher, F. H.; Fox, A. P. KSO<sub>4</sub><sup>−</sup>, NaSO<sub>4</sub><sup>−</sup>, and MgCl<sup>+</sup> Ion Pairs in Aqueous Solutions up to  $2000\text{ Atm}$ . *J. Solution Chem.* **1977**, *6*, 641–650.

(43) Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. Thermodynamic Quantities for the Interaction of SO<sub>4</sub><sup>2−</sup> with H<sup>+</sup> and Na<sup>+</sup> in Aqueous Solution from  $150\text{ to }320\text{ }^{\circ}\text{C}$ . *J. Solution Chem.* **1988**, *17*, 841–863.

(44) Hnedkovsky, L.; Wood, R. H.; Balashov, V. N. Electrical Conductances of Aqueous Na<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and Their Mixtures: Limiting Equivalent Ion Conductances, Dissociation Constants, and Speciation to  $673\text{ K}$  and  $28\text{ MPa}$ . *J. Phys. Chem. B* **2005**, *109*, 9034–9046.

(45) Djamali, E.; Chen, K.; Cobble, J. W. Standard State Thermodynamic Properties of Completely Ionized Aqueous Sodium Sulfate Using High Dilution Calorimetry up to  $598.15\text{ K}$ . *J. Phys. Chem. B* **2009**, *113*, 11688–11695.

(46) Parkhurst, D. L.; Appelo, C. A. J. Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. *U.S. Geological Survey Techniques and Methods 6—A43*; U.S. Geological Survey: Denver, CO, 2013; 497 pp.

(47) Archer, D. G.; Carter, R. W. Thermodynamic Properties of the NaCl + H<sub>2</sub>O System. 4. Heat Capacities of H<sub>2</sub>O and NaCl(aq) in Cold-Stable and Supercooled States. *J. Phys. Chem. B* **2000**, *104*, 8563–8584.

(48) Fernandez, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. A Formulation for the Static Permittivity of Water and Steam at Temperatures from  $238\text{ to }873\text{ K}$  at Pressures up to  $1200\text{ MPa}$ , Including Derivatives and Debye-Huckel Coefficients. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1125–1166.

(49) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.

(50) Appelo, C. A. J.; Parkhurst, D. L.; Post, V. E. A. Equations for Calculating Hydrogeochemical Reactions of Minerals and Gases such as CO<sub>2</sub> at High Pressures and Temperatures. *Geochim. Cosmochim. Acta* **2014**, *125*, 49–67.

(51) Krumgalz, B. S.; Pogorelsky, R.; Pitzer, K. S. Ion Interaction Approach to Calculations of Volumetric Properties of Aqueous Multiple-Solute Electrolyte Solutions. *J. Solution Chem.* **1995**, *24*, 1025–1038.

(52) Pitzer, K. S. Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; pp 279–434.

(53) Young, T. F.; Smith, M. B. Thermodynamic Properties of Mixtures of Electrolytes in Aqueous Solutions. *J. Phys. Chem.* **1954**, *58*, 716–724.