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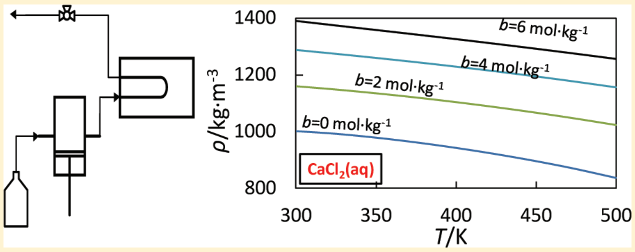
Densities of Aqueous $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), $AlCl_3$(aq), and (0.964 NaCl + 0.136 KCl)(aq) at Temperatures Between (283 and 472) K, Pressures up to 68.5 MPa, and Molalities up to 6 mol·kg^{-1}

Saif Al Ghafri, Geoffrey C. Maitland, and J. P. Martin Trusler*

Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

Ⓢ *Supporting Information*

ABSTRACT: We report the densities of $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), $AlCl_3$(aq), and the mixed salt system [$(1 - x)$NaCl + xKCl](aq), where x denotes the mole fraction of KCl, at temperatures between (283 and 472) K and pressures up to 68.5 MPa. The molalities at which the solutions were studied were (1.00, 3.00, and 5.00) mol·kg^{-1} for $MgCl_2$(aq), (1.00, 3.00, and 6.00) mol·kg^{-1} for $CaCl_2$(aq), (0.67, 0.90, and 1.06) mol·kg^{-1} for KI(aq), (1.06, 3.16, and 6.00) mol·kg^{-1} for NaCl(aq), (1.06, 3.15, and 4.49) mol·kg^{-1} for KCl(aq), (1.00 and 2.00) mol·kg^{-1} for $AlCl_3$(aq), and (1.05, 1.98, 3.15, and 4.95) mol·kg^{-1} for [$(1 - x)$NaCl + xKCl](aq), with $x = 0.136$. The measurements were performed with a vibrating-tube densimeter calibrated under vacuum and with pure water over the full ranges of pressure and temperature investigated. An analysis of uncertainties shows that the relative uncertainty of density varies from 0.03 % to 0.05 % depending upon the salt and the molality of the solution. An empirical correlation is reported that represents the density for each brine system as a function of temperature, pressure, and molality with absolute average relative deviations of approximately 0.02 %. Comparing the model with a large database of results from the literature, we find absolute average relative deviations of 0.03 %, 0.06 %, 0.04 %, 0.02 %, and 0.02 % for the systems $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), and KCl(aq), respectively. The model can be used to calculate density, apparent molar volume, and isothermal compressibility over the full ranges of temperature, pressure, and molality studied in this work. An ideal mixing rule for the density of a mixed electrolyte solution was tested against our mixed salt data and was found to offer good predictions at all conditions studied with an absolute average relative deviation of 0.05 %.



INTRODUCTION

Brines play a significant role in numerous physical, chemical, geothermal, and geochemical processes, often involving high temperatures and/or high pressures, and knowledge of their thermophysical properties, including density, is required to understand fully these diverse applications. Examples in which brine density is important include fluid inclusion studies,[1,2] fluid flow simulation,[3] studies of fluid-rock interactions,[4] CO_2 sequestration,[5,6] and enhanced oil recovery (EOR). In both geological CO_2 storage and CO_2-EOR, the compressibility of brines plays a role in determining the injection rate; consequently this derivative property is also significant. Brines are also used in absorption refrigeration machines and absorption heat pumps, and the thermodynamic properties of aqueous solutions of calcium chloride in particular play a major role in the analysis of such cycles.[7] NaCl and KCl are the major solutes present in natural brines from various geological environments, and accurate density formulations for these saline fluids are a fundamental prerequisite for reliable simulations of fluid flow in geological processes.[8] Density data are also essential in establishing reliable equations of states and calculations of other properties such as isothermal compressibility, isobaric expansibility, dynamic viscosity, interfacial tension, and conversion from molarity to molality.

A critical survey of the available density data for single- and multicomponents brines has been carried out, and in the Supporting Information provided, we tabulate, for each system and experimental study, the ranges of pressure p, temperature T, and molality b as well as the experimental method used and the claimed uncertainty. The published data for $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), $AlCl_3$(aq), and [$(1 - x)$NaCl + xKCl](aq), where x denotes the mole fraction of KCl, appearing in over 100 references.

Many data are available at ambient pressure and temperature over wide ranges of molality. However, there are few published data at elevated pressure and at temperatures above 373.15 K.

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Here we highlight some of the studies that do extend to high pressures or temperatures. For $CaCl_2(aq)$, Safarov et al.[7] studied the range (0.1 to 60) MPa at T = (298.15 to 398.15) K and molality b = (0.184 to 6.007) $mol \cdot kg^{-1}$ using a constant volume piezometer. Gates and Wood[9] studied a wider range of temperature (up to 600 K) with b up to 6.4 $mol \cdot kg^{-1}$ for $p \leq$ 40 MPa. For $MgCl_2(aq)$, Obsil et al.[10] reported densities at T = (298.15 to 623.15) K and b = (0.005 to 3) $mol \cdot kg^{-1}$ at pressures up to 30 MPa. This study covers the widest range of conditions for this system in the literature, but the molality was still restricted to values well below saturation. For the KI(aq) system, the available data are restricted to ambient and near ambient pressures. Swenson and Woolley[11] has covered temperatures of (278.15 to 368.15) K with molality of (0.02 to 7.50) $mol \cdot kg^{-1}$ at a constant pressure of 0.35 MPa. For the NaCl(aq) system, wider ranges of conditions are covered in the literature[12−17] with T = (298.15 to 716.73) K, b = (0.003 to 5.97) $mol \cdot kg^{-1}$, and pressures up to 40.16 MPa. For the KCl(aq) system, few data are reported at high pressures and/or high temperatures. Gates and Wood[18] reported the densities at p = (0.1 to 40.64) MPa and b = (0.059 to 3.012) $mol \cdot kg^{-1}$. However, this range was studied only at T = 298.15 K. Clearly, there is a gap in the literature for this system. There are no data available at pressure $p \neq$ 0.1 MPa and/or $T \neq$ 298.15 K for $AlCl_3(aq)$. Few measurements have been made on ternary or multicomponent brines. The aim of the present study was to expand the available brine density database to wider ranges of p, T, and b.

Due to the gaps in the available data, extensive work has been devoted to modeling the volumetric properties of these aqueous solutions so as to interpolate between the available data and to extrapolate beyond the ranges studied experimentally. Mao and Duan[19] have reviewed the available models and developed a new model for aqueous chloride solutions of the type MCl and MCl_2 where M = (Li, Na, K, Mg, Ca, Sr, and Ba). Their model was parametrized separately for each system and covers wide ranges of conditions. For example for the $MgCl_2(aq)$ system, the ranges are (273 to 543) K, (0.1 to 40) MPa, and (0 to 3) $mol \cdot kg^{-1}$, while for the $CaCl_2(aq)$ system the ranges are (273 to 523) K, (0.1 to 60) MPa, and (0 to 6) $mol \cdot kg^{-1}$. For the NaCl(aq) system the ranges are (273 to 573) K, (0.1 to 100) MPa, and (0 to 6) $mol \cdot kg^{-1}$, while for the KCl(aq) system the ranges are (273 to 543) K, (0.1 to 50) MPa, and (0 to 4.5) $mol \cdot kg^{-1}$. The absolute average relative deviations Δ_{AAD} over the entire range were between 0.020 % and 0.066 %, depending on the system. Safarov et al.[7] used an equation of state[20] to correlate the experimental values for $CaCl_2(aq)$ for T = (298.15 to 398.15) K, p = (0.1 to 60) MPa, and b = (0.18 to 6.01) $mol \cdot kg^{-1}$. The equation was able to reproduce the experimental values with Δ_{AAD} = 0.02 %. Other models have also been reported.[21−32]

In addition numerous empirical correlations have been published for particular brines. For example, Kiepe et al.[33] have developed an empirical correlation method incorporating two adjustable parameters. When applied to the $CaCl_2(aq)$ system, the average absolute deviation was 1.1 $kg \cdot m^{-3}$. However, the correlation covers small ranges of temperature and molality at ambient pressure only. Apelblat and Manzurola[34] fitted density data for KI(aq) to a polynomial function for each given molality at ambient pressure. Most of the available correlation functions[18,35−52] have been fitted only at ambient pressure and/or ambient temperature and cover small ranges of molality.

To summarize the literature, there are significant gaps in the available experimental data in terms of the salts and thermodynamic states that have been investigated, especially with respect to high temperatures, pressures, and molalities. The available models are similarly restricted either by their form or simply by a lack of experimental validation. Hence, there is a need for new experimental data covering wider ranges of pressure, temperature, and molality, so that improved wide-range correlating functions or predictive models can be developed.

In this study, densities ρ were measured for $CaCl_2(aq)$, $MgCl_2(aq)$, KI(aq), NaCl(aq), KCl(aq) $AlCl_3(aq)$, and the mixed brine system (0.864 NaCl + 0.136 KCl)(aq) at temperatures T from (283 to 472) K, pressures p from (0.1 to 68.5) MPa, and various molalities b. We choose the $CaCl_2$ and $MgCl_2$ systems as these salts are significant constituents of carbonate reservoir formation brines, and there are significant gaps in the available data. The mixed salt system was chosen as this mixture is often used as a simple model for sandstone reservoir brine in core-flooding experiments, and a consistent $\rho(T, p, b)$ surface is required for interpreting the data from such experiments. The mole fraction of KCl in this mixture is equivalent to a NaCl/KCl mass ratio of 5:1. Similarly, the KI system was studied as this brine is also used in core-flooding experiments because of its excellent contrast in X-ray imaging. Although the NaCl system is the most well-studied, no single data set covers the full ranges of temperature and pressure considered in this work, and it was therefore considered appropriate to measure this system too. Similar considerations apply to the KCl system. The new data for NaCl(aq) and KCl(aq) were helpful in testing a predictive model for the density of the mixed brine system (0.864 NaCl + 0.136 KCl)(aq). For each salt system investigated, we have parametrized the well-known Tammann−Tait equation[53] so as to fit precisely the density over the entire (p, T, b) ranges investigated.

■ MATERIALS AND METHOD

Chemicals. NaCl ($x \geq$ 0.999), KCl ($x \geq$ 0.99), KI ($x \geq$ 0.995), $CaCl_2$ ($x \geq$ 0.99), $MgCl_2$ ($x \geq$ 0.99), and $AlCl_3$ ($x \geq$ 0.99), where x donates mole fraction purity, were supplied by Sigma Aldrich (UK). The magnesium chloride, aluminum chloride, and calcium chloride were supplied as hexahydrates ($MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$, and $CaCl_2 \cdot 6H_2O$). Anhydrous calcium chloride ($x \geq$ 0.9999) and magnesium chloride ($x \geq$ 0.9999) were supplied by Sigma Aldrich. The magnesium chloride hexahydrate used to prepare the solution with b = 5 $mol \cdot kg^{-1}$ was supplied by VWR (UK) with $x \geq$ 0.99. Deionized water was used for all solutions (Millipore, 18 MΩ·cm at T = 298.15 K).

Apparatus. Among the different methods available for the experimental determination of density at high pressures and temperatures, the vibrating tube densimeter is widely recognized as being a precise, reliable, and relatively rapid technique.[54] This was the technique adopted in this work, and the experimental setup is illustrated in Figure 1. A syringe pump (Quizix, model Q5210) with a maximum service pressure of 70 MPa, and with wetted parts fabricated from brine-resistant Hastelloy C-276, was used to inject the brines and raise the pressure. The pressure was measured using the pressure transducer installed in the syringe pump. The pump was connected to the vibrating tube densimeter through 1.6 mm o.d. Hastelloy C-276 tubing. The densimeter (Anton Paar, DMA HP) is designed to measure the density of liquids and gases at pressures up to 70 MPa and temperatures between (283 and 473) K using a U-shaped vibrating tube of 2 mL total volume. The temperature of the vibrating tube was controlled by an integrated Peltier thermostat to within ± 0.01 K.

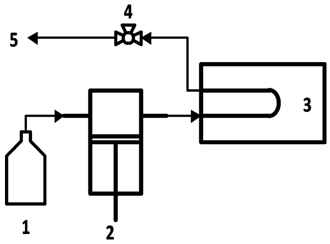

Figure 1. Schematic of the density apparatus. (1) Brine reservoir, (2) syringe pump, (3) vibrating tube densimeter, (4) outlet valve, and (5) waste.

The temperature was measured by means of a Pt100 sensor located in a thermowell in the cellblock. A second calibrated Pt100 temperature sensor (Sensing Device Ltd.) was used to verify the temperature readings. The DMA HP was connected to a master instrument (Anton Paar, DMA 5000 M) which displayed the measured parameters including the period of oscillation with a resolution of 0.01 μs. The outlet of the densimeter was connected via a two-way valve (also fabricated from Hastelloy C-276) to the waste outlet.

Calibration. The pressure transducer was calibrated at pressures in the range (1 to 70) MPa by comparison with a quartz pressure sensor in a pneumatic calibrator (Fluke-DHI model PPCH-G-70M). It is estimated that the expanded uncertainty of the pressure transducer after calibration was 35 kPa (0.05 % of the full scale reading) with a coverage factor $k = 2$.

The platinum resistance thermometer was calibrated at temperatures in the range (273 to 473) K by comparison in a constant-temperature bath with a standard platinum resistance thermometer having an expanded uncertainty of 2 mK in the present temperature range. It is estimated that the expanded uncertainty of the temperature measurements after calibration was 0.05 K with a coverage factor $k = 2$.

The density ρ is related to the period of oscillation τ by the relation

$$\rho(p, T) = A(p, T)\tau^2 - B(p, T) \tag{1}$$

where A and B are parameters that are determined by calibration with fluids of known density. However, as it is difficult to have two fluids with known density over the entire range of pressure and temperature. Lagourette et al.[55] and Sousa et al.[56] proposed eliminating one of the calibration fluids in favor of determining the period of oscillation of the vibrating tube under vacuum, τ_0. The hypothesis of Lagourette et al.[55] is that the ratio A/B depends only upon temperature. Lampreia and Castro[57] proposed an alternative method for relating the period of oscillation to density. In their approach, an analytical method was employed to calculate τ_0 from measurements on two reference fluids rather than the usual experimental determination of this parameter as, they argued, a good vacuum may be hard to achieve. However, in the present work, we followed the method of Lagourette et al.[55] and included tests to verify that an adequate vacuum had been achieved. Calibration was carried out under vacuum at all experimental temperatures and in pure water at every temperature and pressure to be studied. The parameters A and B were thus given by:

$$A(p, T) = \frac{\rho_{\mathrm{w}}(p, T)}{\tau_{\mathrm{w}}^2(p, T) - \tau_0^2(T)} \tag{2}$$

and

$$B(p, T) = \frac{\rho_{\mathrm{w}}(p, T)\tau_0^2(T)}{\tau_{\mathrm{w}}^2(T, p) - \tau_0^2(T)} \tag{3}$$

where $\tau_{\mathrm{w}}(p,T)$ and $\rho_{\mathrm{w}}(p,T)$ are the period of oscillation and the density for calibration with water at given pressure and temperature, and $\tau_0(T)$ is the period of oscillation under vacuum at given temperature. In the present case, ρ_{w} was obtained from the IAPWS-95 equation of state developed by Pruss and Wagner[58] which is associated with a relative standard uncertainty of 0.01 % or less at the pressures and temperatures of this study.

At $T = 298.15$ K and $p = 0.1$ MPa, an alternative calibration was performed using ambient air and water as the reference fluids. When tested in measurements for NaCl(aq) with $b = 4.95\ \mathrm{mol\cdot kg^{-1}}$, the densities obtained were 1168.11 $\mathrm{kg\cdot m^{-3}}$ with the calibration in air and water and 1168.10 $\mathrm{kg\cdot m^{-3}}$ with the calibration in vacuum and water. This was taken as evidence that the vacuum calibration was reliable.

Experimental Procedure. The solutions were prepared gravimetrically on an analytical balance (Mettler Toledo, model PR5003) with 0.001 g resolution. Prior to loading each sample, the solution was stirred to ensure homogeneity and degassed under vacuum. The densimeter was flushed many times with deionized water and dried with air. Then the system was flushed with the degassed brine, and the period of oscillation was recorded after equilibration at $T = 298.15$ K and $p = 1$ MPa. Next, the system was flushed again with the brine, and the measurement of the period of oscillation at $T = 298.15$ K and $p = 1$ MPa was repeated. If the two values matched, the measurements were continued. If not, another sample was injected until consistent values were found. Typically, the temperature was raised in steps of 25 K from $T = (298.15$ to $473.15)$ K and then returned to the initial temperature for a check measurement. The temperature $T = 283.15$ K was also studied for some of the brines. For each isotherm, the pressure values studied were 1 MPa, (10 to 60) MPa in steps of 10 MPa, 68.5 MPa, and a final check measurement at $p = 1$ MPa. No hysteresis was observed going up and down in temperature or in pressure. It was found that the system was very reliable and the period measurements were reproducible within 0.01 μs, which was taken to be the uncertainty of the period of oscillation.

UNCERTAINTY

From eqs 1 to 3, the density is given by

$$\rho = \frac{\rho_{\mathrm{w}}}{\tau_{\mathrm{w}}^2 - \tau_0^2}(\tau^2 - \tau_0^2) \tag{4}$$

Using the guide to the expression of uncertainty in measurements (GUM),[59] the combined standard uncertainty of the density $U(\rho)$ is obtained from the following equation

$$U^2(\rho) = \sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j}u(x_i, x_j) \tag{5}$$

Table 1. Contributions to the Expanded Uncertainty $U(\rho)$ of the Density of $CaCl_2(aq)$ at $T = 472.04$ K, $p = 10.2$ MPa, and Molalities $b = (1.00, 3.00, \text{and } 6.00)$ mol·kg^{-1}, with a Coverage Factor $k = 2$

$b/(\text{mol·kg}^{-1})$	1.00	3.00	6.00
$u(\tau)/\mu s$	0.01	0.01	0.01
$u(\tau_0)/\mu s$	0.01	0.01	0.01
$u(\rho_w)/(\text{kg·m}^{-3})$	0.09	0.09	0.09
$u(T)/K$	0.025	0.025	0.025
$u(p)/\text{MPa}$	0.018	0.018	0.018
$u(b)/(\text{mol·kg}^{-1})$	0.001	0.003	0.006
$(\partial\rho/\partial\tau)/(\text{kg·m}^{-3}·\mu s^{-1})$	4.79	4.84	4.90
$(\partial\rho/\partial\tau_0)/(\text{kg·m}^{-3}·\mu s^{-1})$	0.48	1.24	2.05
$(\partial\rho/\partial\tau_w)/(\text{kg·m}^{-3}·\mu s^{-1})$	−5.27	−6.09	−6.96
$(\partial\rho/\partial T)/(\text{kg·m}^{-3}·\text{K}^{-1})$	−0.98	−0.81	−0.69
$(\partial\rho/\partial p)/(\text{kg·m}^{-3}·\text{MPa}^{-1})$	0.57	0.44	0.35
$(\partial\rho/\partial b)/(\text{kg}^2·\text{m}^{-3}·\text{mol}^{-1})$	83.54	66.19	40.15
$U(\rho)/(\text{kg·m}^{-3})$	0.30	0.49	0.58

where x_i and x_j represent the input variables, $(\partial f/\partial x_i)$ is the sensitivity coefficient of the input variable x_i, $u(x_i, x_j)$ is the covariance $(i \neq j)$ or the variance $(i = j)$ for variables x_i and x_j, and $u^2(x)$ is the variance of x. By neglecting the covariance effects and combining eqs 4 and 5, the expanded uncertainty is obtained as

$$U^2(\rho) = k^2\Big[\left(\frac{\tau^2 - \tau_0^2}{\tau_w^2 - \tau_0^2}\right)^2 u^2(\rho_w) + \left(\frac{2\rho_w\tau}{\tau_w^2 - \tau_0^2}\right)^2 u^2(\tau) + \left(\frac{2\rho_w\tau_0}{(\tau_w^2 - \tau_0^2)^2}(\tau_w^2 - \tau_0^2)\right)^2 u^2(\tau_0) + \left(\frac{-2\rho_w\tau_w}{(\tau_w^2 - \tau_0^2)^2}(\tau^2 - \tau_0^2)\right)^2 u^2(\tau_w) + \left(\frac{\partial\rho}{\partial T}\right)_{p,b}^2 u^2(T) + \left(\frac{\partial\rho}{\partial p}\right)_{T,b}^2 u^2(p) + \left(\frac{\partial\rho}{\partial b}\right)_{T,p}^2 u^2(b)\Big] \quad (6)$$

where k is the coverage factor. The quantities considered are ρ_w, τ_w, τ_0, τ, T, p, and b. Examples of the various contributions to the uncertainty are given in Table 1 for $CaCl_2(aq)$ at $T = 472.04$ K, $p = 10.2$ MPa, and three different molalities. The results are very similar for all brines. The uncertainty increases as temperature and molality increase but decreases as pressure increases; hence, the largest uncertainty occurs at the highest temperature, highest molality, and lowest pressure.

The uncertainties in temperature, pressure, and oscillation period have been discussed above. The remaining experimental uncertainty is that associated with the molality of the brine which is influenced by weighing errors, salt purity, and especially, the water content of the salt. The relative uncertainty in b associated with weighing was always below 0.01 %. In the case of the hexahydrated salts, we assumed that there were exactly six water molecules per salt unit. To test for the effects of any impurities and possible variations in the water content of these hexahydrates, further solutions of $CaCl_2$ and $MgCl_2$ were prepared from anhydrous salts with specified mole-fraction purity $x \geq 0.9999$. These salts were provided in sealed glass ampules, and the solutions were prepared gravimetrically immediately after opening them. The densities of these solutions were measured at ambient pressure and $T = 298.15$ K using an Anton Paar DMA 5000 densimeter calibrated at that temperature in air and pure water. The results were $\rho = 1380.20$ kg·m^{-3} for $CaCl_2(aq)$ at $b = 5.81$ kg·m^{-3} and $\rho = 1296.41$ kg·m^{-3} for $MgCl_2(aq)$ at $b = 4.98$ mol·kg^{-1}. To compare these data with the values obtained in our measurements on solutions prepared from $CaCl_2·6(H_2O)$ and $MgCl_2·6(H_2O)$, we made use of the corresponding correlations of our experimental $\rho(T, p, b)$ results discussed below. The values obtained were 1380.06 kg·m^{-3} for the $CaCl_2$ solution and 1296.59 kg·m^{-3} for the $MgCl_2$ solution. Thus the relative differences were 0.010 % and 0.014 %, which are smaller than the uncertainties of the correlations involved in these comparisons. Based on this comparison, we estimate the relative standard uncertainty of molality to be 0.05 % which for $CaCl_2(aq)$ at $T = 298.15$ K, $p = 0.1$ MPa, and $b = 6$ mol·kg^{-1} corresponds to a relative uncertainty in ρ of 0.015 %. Taking all factors into account, the final expanded relative uncertainty of the density varies from 0.03 % to 0.05 %, and for the sake of simplicity, we ascribe the larger uncertainty to all of the results.

■ RESULTS AND DISCUSSIONS

$CaCl_2(aq)$, $MgCl_2(aq)$, KI(aq), NaCl(aq), KCl(aq), and (0.864 NaCl + 0.136 KCl)(aq) solutions were measured at temperatures from (298.15 to 473.15) K, pressure of (1 to 68.5) MPa, and molalities of (1, 3, and 6) mol·kg^{-1} for $CaCl_2$ (aq), (1, 3, and 5) mol·kg^{-1} for $MgCl_2(aq)$, (0.669, 0.900, and 1.063) mol·kg^{-1} for KI(aq), (1, 3, and 6) mol·kg^{-1} for $CaCl_2(aq)$, (0.67, 0.90, and 1.06) mol·kg^{-1} for KI(aq), (1.06, 3.16, and 6.00) mol·kg^{-1} for NaCl(aq), (1.06, 3.15, and 4.49) mol·kg^{-1} for KCl(aq), and (1.05, 1.98, 3.15, and 4.95) mol·kg^{-1} for (0.864 NaCl + 0.136 KCl)(aq). Some of these brines were also measured at $T = 283.15$ K. The $AlCl_3(aq)$ solution was measured at pressures of (1 to 68.5) MPa and molalities of (1 and 2) mol·kg^{-1}. However this solution was only measured at $T = (298.15 \text{ to } 373.15)$ K. This is because, at higher temperatures, the solutions were found to be reactive, possibly undergoing hydrolysis-precipitation of aluminum as discussed by Bottero et al.,[60,61] and the results obtained became erratic within one or two hours in the cell; severe corrosion was later discovered necessitating replacement of the vibrating tube. Experimental results are given in Tables 2 to 8.

■ CORRELATION

The experimental data were initially fitted for each given molality and temperature with the Tammann−Tait equation[53] as follows

$$\rho(T, p, b) = \rho_{\text{ref}}(T, b)\left[1 - C(b) \ln\left\{\frac{B(T, b) + p}{B(T, b) + p_{\text{ref}}(T)}\right\}\right]^{-1} \quad (7)$$

Here, ρ_{ref} is the density at a reference pressure $p_{\text{ref}}(T)$, which we take to be the vapor pressure of pure water at the given temperature, and B and C are parameters. The vapor pressure

Table 2. Densities ρ of $CaCl_2(aq)$ at Temperatures T, Pressures p, and Molalities b^a

p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$
b = 1.00 mol·kg^{-1}							
T = 283.15 K		T = 298.12 K		T = 323.07 K		T = 348.04 K	
1.05	1087.02	1.05	1082.37	1.05	1072.02	1.05	1058.99
10.02	1090.65	10.02	1085.93	10.02	1075.48	10.02	1062.51
19.97	1094.63	19.97	1089.70	19.97	1079.27	19.97	1066.31
29.90	1098.56	29.90	1093.48	29.90	1082.99	29.90	1070.05
39.83	1102.39	39.83	1097.27	39.83	1086.62	39.83	1073.75
49.76	1106.11	49.76	1100.95	49.76	1090.10	49.76	1077.29
59.68	1109.84	59.68	1104.52	59.68	1093.62	59.68	1080.87
68.12	1113.04	68.12	1107.46	68.12	1096.56	68.12	1083.78
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.05	1043.73	1.05	1026.22	1.05	1006.80	1.05	985.31
10.02	1047.42	10.02	1030.11	10.02	1011.09	10.02	989.96
19.97	1051.39	19.97	1034.38	19.97	1015.62	19.97	995.04
29.90	1055.27	29.90	1038.38	29.90	1020.00	29.90	999.90
39.83	1059.05	39.83	1042.42	39.83	1024.30	39.83	1004.57
49.76	1062.77	49.76	1046.36	49.76	1028.53	49.76	1009.07
59.68	1066.34	59.68	1050.19	59.68	1032.62	59.68	1013.53
68.12	1069.39	68.12	1053.29	68.12	1036.00	68.12	1017.15
T = 472.96 K				b = 3.00 mol·kg^{-1}			
10.02	966.77	T = 298.12 K		T = 323.07 K		T = 348.04 K	
19.97	972.43	1.05	1225.07	1.05	1212.47	1.05	1198.77
29.90	977.79	10.02	1228.17	10.02	1215.47	10.02	1201.83
39.83	983.04	19.97	1231.30	19.97	1218.73	19.97	1205.15
49.76	988.08	29.90	1234.60	29.90	1221.98	29.90	1208.41
59.68	992.91	39.83	1237.81	39.83	1225.08	39.83	1211.58
68.12	996.86	49.76	1240.96	49.76	1228.11	49.76	1214.64
		59.68	1244.00	59.68	1231.21	59.68	1217.80
		68.12	1246.57	68.12	1233.72	68.12	1220.39
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.05	1184.12	1.05	1167.99	1.05	1150.79	1.05	1132.22
10.02	1187.20	10.02	1171.26	10.02	1154.33	10.02	1135.97
19.97	1190.58	19.97	1174.82	19.97	1158.03	19.97	1139.99
29.90	1193.94	29.90	1178.23	29.90	1161.68	29.90	1143.88
39.83	1197.14	39.83	1181.65	39.83	1165.21	39.83	1147.62
49.76	1200.38	49.76	1184.96	49.76	1168.72	49.76	1151.30
59.68	1203.46	59.68	1188.20	59.68	1172.12	59.68	1154.99
68.12	1206.10	68.12	1190.88	68.12	1174.94	68.12	1157.94
T = 472.96 K				b = 6.00 mol·kg^{-1}			
10.02	1116.32	T = 298.12 K		T = 323.07 K		T = 348.04 K	
19.97	1120.67	1.05	1388.00	1.05	1372.06	1.05	1356.18
29.90	1124.82	10.02	1390.67	10.02	1374.67	10.02	1358.90
39.83	1129.01	19.97	1393.43	19.97	1377.58	19.97	1361.82
49.76	1132.99	29.90	1396.28	29.90	1380.48	29.90	1364.67
59.68	1136.86	39.83	1399.14	39.83	1383.27	39.83	1367.55
68.12	1140.04	49.76	1401.93	49.76	1385.94	49.76	1370.29
		59.68	1404.61	59.68	1388.68	59.68	1373.09
		68.12	1406.89	68.12	1390.90	68.12	1375.40
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.05	1340.35	1.05	1324.03	1.05	1307.39	1.05	1290.23
10.02	1343.09	10.02	1326.81	10.02	1310.40	10.02	1293.23
19.97	1346.07	19.97	1329.91	19.97	1313.54	19.97	1296.61
29.90	1349.03	29.90	1332.86	29.90	1316.63	29.90	1299.83
39.83	1351.92	39.83	1335.87	39.83	1319.70	39.83	1303.02
49.76	1354.76	49.76	1338.78	49.76	1322.71	49.76	1306.09
59.68	1357.57	59.68	1341.67	59.68	1325.64	59.68	1309.22
68.12	1359.88	68.12	1344.00	68.12	1328.12	68.12	1311.73
T = 472.96 K							
10.02	1275.65						
19.97	1279.19						

Table 2. continued

p	ρ	p	ρ	p	ρ	p	ρ
MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}
T = 472.96 K							
29.90	1282.53						
39.83	1285.96						
49.76	1289.19						
59.68	1292.45						
68.12	1295.04						

[a] Expanded uncertainties are: $U(\rho)$ = 0.30 kg·m^{-3} at b = 1 mol·kg^{-1}; $U(\rho)$ = 0.49 kg·m^{-3} at b = 3 mol·kg^{-1}; $U(\rho)$ = 0.58 kg·m^{-3} at b = 6 mol·kg^{-1}.

Table 3. Densities ρ of $MgCl_2(aq)$ at Temperatures T, Pressures p, and Molalities b[a]

p	ρ	p	ρ	p	ρ	p	ρ
MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}
			b = 1.00 mol·kg^{-1}				
T = 283.15 K		T = 298.12 K		T = 323.07 K		T = 348.04 K	
1.05	1074.73	1.05	1070.86	1.05	1061.56	1.05	1049.32
10.02	1078.32	10.02	1074.43	10.02	1065.03	10.02	1052.80
19.97	1082.31	19.97	1078.17	19.97	1068.73	19.97	1056.56
29.90	1086.21	29.90	1081.96	29.90	1072.46	29.90	1060.31
39.83	1090.04	39.83	1085.70	39.83	1076.00	39.83	1063.92
49.76	1093.73	49.76	1089.34	49.76	1079.49	49.76	1067.47
59.68	1097.42	59.68	1092.83	59.68	1082.98	59.68	1070.97
68.12	1100.57	68.12	1095.78	68.12	1085.82	68.12	1073.88
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.05	1034.76	1.05	1017.83	1.05	999.03	10.02	982.73
10.02	1038.36	10.02	1021.72	10.02	1003.28	19.97	987.82
19.97	1042.33	19.97	1025.91	19.97	1007.77	29.90	992.59
29.90	1046.17	29.90	1029.97	29.90	1012.16	39.83	997.27
39.83	1049.91	39.83	1033.96	39.83	1016.47	49.76	1001.73
49.76	1053.59	49.76	1037.86	49.76	1020.62	59.68	1006.15
59.68	1057.17	59.68	1041.60	59.68	1024.61	68.12	1009.73
68.12	1060.13	68.12	1044.71	68.12	1027.95		
T = 472.96 K							
10.02	960.31						
19.97	965.92						
29.90	971.25						
39.83	976.50						
49.76	981.41						
59.68	986.20						
68.12	990.10						
			b = 3.00 mol·kg^{-1}				
T = 283.15 K		T = 298.12 K		T = 323.07 K		T = 348.04 K	
1.10	1200.48	1.10	1194.98	1.10	1185.53	1.10	1174.63
10.10	1203.26	10.10	1197.76	10.10	1188.36	10.10	1177.48
20.10	1206.45	20.10	1200.84	20.10	1191.36	20.10	1180.55
30.10	1209.48	30.10	1203.93	30.10	1194.33	30.10	1183.56
40.10	1212.45	40.10	1206.91	40.10	1197.32	40.10	1186.60
50.10	1215.49	50.10	1209.79	50.10	1200.25	50.10	1189.47
60.10	1218.46	60.10	1212.66	60.10	1203.13	60.10	1192.42
68.60	1220.98	68.60	1215.18	68.60	1205.42	68.60	1194.89
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.10	1162.60	1.10	1149.22	1.10	1134.62	1.10	1118.93
10.10	1165.51	10.10	1152.27	10.10	1137.91	10.10	1122.27
20.10	1168.64	20.10	1155.47	20.10	1141.36	20.10	1126.00
30.10	1171.77	30.10	1158.76	30.10	1144.67	30.10	1129.62
40.10	1174.82	40.10	1162.02	40.10	1147.96	40.10	1133.07
50.10	1177.87	50.10	1165.10	50.10	1151.23	50.10	1136.51
60.10	1180.77	60.10	1168.09	60.10	1154.39	60.10	1139.92
68.60	1183.21	68.60	1170.63	68.60	1157.07	68.60	1142.62

Table 3. continued

p	ρ	p	ρ	p	ρ	p	ρ
MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}
T = 472.96 K							
10.10	1105.72						
20.10	1109.63						
30.10	1113.50						
40.10	1117.27						
50.10	1120.96						
60.10	1124.60						
68.60	1127.48						
b = 5.00 mol·kg^{-1}							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
1.05	1298.01	1.05	1288.53	1.05	1278.25	1.05	1267.42
10.02	1300.39	10.02	1290.86	10.02	1280.63	10.02	1269.83
19.97	1302.84	19.97	1293.39	19.97	1283.18	19.97	1272.48
29.90	1305.37	29.90	1295.97	29.90	1285.71	29.90	1275.12
39.83	1307.91	39.83	1298.44	39.83	1288.26	39.83	1277.64
49.76	1310.34	49.76	1300.80	49.76	1290.69	49.76	1280.15
59.68	1312.81	59.68	1303.27	59.68	1293.17	59.68	1282.60
68.12	1314.82	68.12	1305.22	68.12	1295.26	68.12	1284.68
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
1.05	1255.66	1.05	1243.30	1.05	1230.19	10.02	1219.23
10.02	1258.16	10.02	1245.98	10.02	1232.81	19.97	1222.30
19.97	1260.88	19.97	1248.69	19.97	1235.76	29.90	1225.27
29.90	1263.46	29.90	1251.46	29.90	1238.61	39.83	1228.28
39.83	1266.15	39.83	1254.16	39.83	1241.42	49.76	1231.18
49.76	1268.74	49.76	1256.84	49.76	1244.17	59.68	1234.02
59.68	1271.25	59.68	1259.41	59.68	1246.88	68.12	1236.38
68.12	1273.36	68.12	1261.60	68.12	1249.11		

[a] Expanded uncertainties are: $U(\rho)$ = 0.30 kg·m^{-3} at b = 1 mol·kg^{-1}; $U(\rho)$ = 0.48 kg·m^{-3} at b = 3 mol·kg^{-1}; $U(\rho)$ = 0.58 kg·m^{-3} at b = 5 mol·kg^{-1}.

Table 4. Densities ρ of KI (aq) at Temperatures T, Pressures p, and Molalities b[a]

p	ρ	p	ρ	p	ρ	p	ρ
MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}	MPa	kg·m^{-3}
b = 0.669 mol·kg^{-1}							
T = 283.15 K		T = 298.12 K		T = 323.07 K		T = 348.04 K	
1.05	1078.98	1.05	1074.75	1.05	1064.04	1.05	1049.72
10.02	1083.16	10.02	1078.81	10.02	1067.95	10.02	1053.73
19.97	1087.75	19.97	1083.04	19.97	1072.19	19.97	1057.99
29.90	1092.18	29.90	1087.37	29.90	1076.42	29.90	1062.23
39.83	1096.51	39.83	1091.56	39.83	1080.45	39.83	1066.38
49.76	1100.74	49.76	1095.69	49.76	1084.42	49.76	1070.32
59.68	1104.92	59.68	1099.67	59.68	1088.30	59.68	1074.35
68.12	1108.52	68.12	1103.00	68.12	1091.53	68.12	1077.66
T = 372.99 K		T = 397.97 K		T = 422.94 K		T = 447.94 K	
1.05	1032.60	1.05	1012.71	1.05	990.31	1.05	965.35
10.02	1036.79	10.02	1017.19	10.02	995.34	10.02	970.94
19.97	1041.30	19.97	1022.06	19.97	1000.61	19.97	976.95
29.90	1045.73	29.90	1026.71	29.90	1005.73	29.90	982.65
39.83	1050.01	39.83	1031.29	39.83	1010.72	39.83	988.10
49.76	1054.18	49.76	1035.78	49.76	1015.55	49.76	993.34
59.68	1058.24	59.68	1040.10	59.68	1020.17	59.68	998.49
68.12	1061.64	68.12	1043.65	68.12	1024.00	68.12	1002.64
T = 472.96 K							
10.02	944.19						
19.97	950.96						
29.90	957.40						
39.83	963.57						
49.76	969.44						
59.68	975.11						

Table 4. continued

p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
$T = 472.96$ K							
68.12	979.68						
$b = 0.900$ mol·kg^{-1}							
$T = 298.12$ K		$T = 323.07$ K		$T = 348.04$ K		$T = 372.99$ K	
1.05	1100.27	1.05	1088.99	1.05	1074.24	1.05	1056.80
10.02	1104.27	10.02	1092.94	10.02	1078.29	10.02	1061.02
19.97	1108.67	19.97	1097.21	19.97	1082.62	19.97	1065.55
29.90	1112.93	29.90	1101.41	29.90	1086.89	29.90	1070.01
39.83	1117.15	39.83	1105.46	39.83	1091.06	39.83	1074.32
49.76	1121.30	49.76	1109.41	49.76	1095.03	49.76	1078.51
59.68	1125.31	59.68	1113.37	59.68	1099.04	59.68	1082.50
68.12	1128.62	68.12	1116.58	68.12	1102.03	68.12	1085.89
$T = 397.97$ K		$T = 422.94$ K		$T = 447.94$ K			
1.05	1036.96	1.05	1014.85	1.05	990.56		
10.02	1041.47	10.02	1019.62	10.02	996.18		
19.97	1046.32	19.97	1024.97	19.97	1002.22		
29.90	1050.95	29.90	1030.16	29.90	1007.94		
39.83	1055.56	39.83	1035.28	39.83	1013.36		
49.76	1060.02	49.76	1040.03	49.76	1018.68		
59.68	1064.32	59.68	1044.78	59.68	1023.80		
68.12	1067.94	68.12	1048.68	68.12	1027.98		
$b = 1.063$ mol·kg^{-1}							
$T = 283.15$ K		$T = 298.12$ K		$T = 323.07$ K		$T = 348.04$ K	
1.05	1122.95	1.05	1117.90	1.05	1106.19	1.05	1091.20
10.02	1127.11	10.02	1121.98	10.02	1110.17	10.02	1095.23
19.97	1131.70	19.97	1126.32	19.97	1114.52	19.97	1099.65
29.90	1136.20	29.90	1130.67	29.90	1118.76	29.90	1103.95
39.83	1140.54	39.83	1134.96	39.83	1122.89	39.83	1108.16
49.76	1144.78	49.76	1139.11	49.76	1126.88	49.76	1112.21
59.68	1149.02	59.68	1143.14	59.68	1130.86	59.68	1116.30
68.12	1152.59	68.12	1146.49	68.12	1134.11	68.12	1119.62
$T = 372.99$ K		$T = 397.97$ K		$T = 422.94$ K		$T = 447.94$ K	
1.05	1073.46	1.05	1053.24	1.05	1030.64	1.05	1005.63
10.02	1077.72	10.02	1057.79	10.02	1035.74	10.02	1011.23
19.97	1082.29	19.97	1062.77	19.97	1041.07	19.97	1017.26
29.90	1086.83	29.90	1067.47	29.90	1046.25	29.90	1022.96
39.83	1091.17	39.83	1072.16	39.83	1051.30	39.83	1028.47
49.76	1095.44	49.76	1076.71	49.76	1056.19	49.76	1033.81
59.68	1099.61	59.68	1081.09	59.68	1060.87	59.68	1038.97
68.12	1103.03	68.12	1084.70	68.12	1064.81	68.12	1043.19
$T = 472.96$ K							
10.02	984.84						
19.97	991.38						
29.90	997.97						
39.83	1004.20						
49.76	1010.14						
59.68	1015.81						
68.12	1020.40						

[a]Expanded uncertainties are: $U(\rho) = 0.29$ kg·m^{-3} at $b = 0.67$ mol·kg^{-1}; $U(\rho) = 0.31$ kg·m^{-3} at $b = 0.90$ mol·kg^{-1}; $U(\rho) = 0.31$ kg·m^{-3} at $b = 1.63$ mol·kg^{-1}.

of water was obtained from the auxiliary equation given by Wagner and Pruss:[58]

$$\ln p_{\mathrm{ref}}(T)/p_{\mathrm{c}} = (T_{\mathrm{c}}/T)[\sigma_1\varphi + \sigma_2\varphi^{1.5} + \sigma_3\varphi^3 + \sigma_4\varphi^{3.5} + \sigma_5\varphi^4 + \sigma_6\varphi^{7.5}] \quad (8)$$

where $T_{\mathrm{c}} = 647.10$ K is the critical temperature, $p_{\mathrm{c}} = 22.064$ MPa is the critical pressure, and $\varphi = (1 - T/T_{\mathrm{c}})$. Initially, optimal values of ρ_{ref}, B, and C were found by minimizing the sum square of the differences between the experimental and the calculated values of density for each isotherm and molality. It was found that the parameters obtained (ρ_{ref}, B, and C) could be represented over the full ranges of pressure, temperature,

Table 5. Densities ρ of $[(1 - x)\mathrm{NaCl} + x\mathrm{KCl}](\mathrm{aq})$ with $x = 0.136$ at Temperatures T, Pressures p, and Molalities b[a]

p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
			$b = 1.05$ mol·kg^{-1}				
$T = 283.15$ K		$T = 298.12$ K		$T = 323.07$ K		$T = 348.04$ K	
1.05	1043.91	1.05	1039.58	1.05	1029.20	1.05	1015.69
10.02	1047.73	10.02	1043.32	10.02	1032.84	10.02	1019.39
19.97	1051.89	19.97	1047.29	19.97	1036.81	19.97	1023.43
29.90	1056.06	29.90	1051.20	29.90	1040.67	29.90	1027.31
39.83	1060.03	39.83	1055.12	39.83	1044.44	39.83	1031.24
49.76	1063.89	49.76	1058.94	49.76	1048.10	49.76	1034.88
59.68	1067.81	59.68	1062.65	59.68	1051.77	59.68	1038.60
68.12	1071.08	68.12	1065.77	68.12	1054.74	68.12	1041.64
$T = 372.99$ K		$T = 397.97$ K		$T = 422.94$ K		$T = 447.94$ K	
1.05	999.54	1.05	981.06	1.05	960.34	1.05	937.36
10.02	1003.46	10.02	985.22	10.02	964.96	10.02	942.49
19.97	1007.66	19.97	989.73	19.97	969.88	19.97	948.00
29.90	1011.73	29.90	994.12	29.90	974.59	29.90	953.24
39.83	1015.75	39.83	998.35	39.83	979.23	39.83	958.29
49.76	1019.66	49.76	1002.52	49.76	983.70	49.76	963.22
59.68	1023.46	59.68	1006.54	59.68	988.02	59.68	967.97
68.12	1026.61	68.12	1009.83	68.12	991.58	68.12	971.82
$T = 472.96$ K							
10.02	917.64						
19.97	923.91						
29.90	929.85						
39.83	935.62						
49.76	941.09						
59.68	946.40						
68.12	950.72						
			$b = 1.98$ mol·kg^{-1}				
$T = 298.12$ K		$T = 323.07$ K		$T = 348.04$ K		$T = 372.99$ K	
0.92	1073.46	0.92	1062.21	0.92	1048.37	0.92	1032.50
9.92	1076.94	9.92	1065.64	9.92	1051.92	9.92	1036.21
19.92	1080.78	19.92	1069.40	19.92	1055.75	19.92	1040.20
29.92	1084.52	29.92	1073.08	29.92	1059.53	29.92	1044.24
39.92	1088.21	39.92	1076.77	39.92	1063.22	39.92	1048.05
49.92	1091.80	49.92	1080.31	49.92	1066.81	49.92	1051.76
59.92	1095.29	59.92	1083.80	59.92	1070.37	59.92	1055.37
68.42	1098.34	68.42	1086.65	68.42	1073.33	68.42	1058.46
$T = 397.97$ K		$T = 422.94$ K		$T = 447.94$ K		$T = 472.96$ K	
0.92	1014.52	0.92	994.44	0.92	972.49	9.92	953.84
9.92	1018.48	9.92	998.81	9.92	977.23	19.92	959.59
19.92	1022.74	19.92	1003.42	19.92	982.40	29.92	965.06
29.92	1026.84	29.92	1007.90	29.92	987.31	39.92	970.41
39.92	1030.96	39.92	1012.29	39.92	992.12	49.92	975.50
49.92	1034.94	49.92	1016.57	49.92	996.72	59.92	980.43
59.92	1038.81	59.92	1020.69	59.92	1001.24	68.42	984.46
68.42	1042.00	68.42	1024.12	68.42	1004.93		
			$b = 3.15$ mol·kg^{-1}				
$T = 298.12$ K		$T = 323.07$ K		$T = 348.04$ K		$T = 372.99$ K	
0.92	1113.08	0.92	1100.94	0.92	1086.80	0.92	1070.97
9.92	1116.33	9.92	1104.19	9.92	1090.12	9.92	1074.45
19.92	1119.88	19.92	1107.71	19.92	1093.72	19.92	1078.26
29.92	1123.39	29.92	1111.16	29.92	1097.30	29.92	1082.01
39.92	1126.85	39.92	1114.67	39.92	1100.82	39.92	1085.59
49.92	1130.25	49.92	1118.08	49.92	1104.22	49.92	1089.17
59.92	1133.50	59.92	1121.33	59.92	1107.60	59.92	1092.70
68.42	1136.42	68.42	1124.04	68.42	1110.43	68.42	1095.56
$T = 397.97$ K		$T = 422.94$ K		$T = 447.94$ K		$T = 472.96$ K	
0.92	1053.46	0.92	1034.07	0.92	1013.19	9.92	994.68
9.92	1057.19	9.92	1038.17	9.92	1017.60	19.92	999.91

Table 5. continued

p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
19.92	1061.17	19.92	1042.46	19.92	1022.35	29.92	1005.05
29.92	1065.09	29.92	1046.70	29.92	1026.97	39.92	1009.93
39.92	1068.93	39.92	1050.91	39.92	1031.42	49.92	1014.65
49.92	1072.73	49.92	1054.81	49.92	1035.74	59.92	1019.26
59.92	1076.36	59.92	1058.75	59.92	1039.97	68.42	1022.96
68.42	1079.37	68.42	1062.00	68.42	1043.40		
b = 4.95 mol·kg^{-1}							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.92	1168.01	0.92	1154.75	0.92	1140.17	0.92	1124.41
9.92	1170.96	9.92	1157.75	9.92	1143.25	9.92	1127.60
19.92	1174.22	19.92	1161.03	19.92	1146.65	19.92	1131.16
29.92	1177.43	29.92	1164.27	29.92	1149.94	29.92	1134.67
39.92	1180.64	39.92	1167.54	39.92	1153.21	39.92	1138.06
49.92	1183.74	49.92	1170.65	49.92	1156.41	49.92	1141.34
59.92	1186.74	59.92	1173.70	59.92	1159.59	59.92	1144.61
68.42	1189.37	68.42	1176.22	68.42	1162.24	68.42	1147.28
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.92	1107.25	0.92	1088.67	0.92	1068.86	9.92	1052.13
9.92	1110.73	9.92	1092.44	9.92	1072.83	19.92	1056.87
19.92	1114.41	19.92	1096.37	19.92	1077.20	29.92	1061.38
29.92	1118.04	29.92	1100.22	29.92	1081.38	39.92	1065.92
39.92	1121.63	39.92	1104.04	39.92	1085.48	49.92	1070.19
49.92	1125.14	49.92	1107.79	49.92	1089.45	59.92	1074.41
59.92	1128.57	59.92	1111.39	59.92	1093.35	68.42	1077.83
68.42	1131.38	68.42	1114.39	68.42	1096.53		

[a] Expanded uncertainties are: $U(\rho)$ = 0.26 kg·m^{-3} at b = 1.05 mol·kg^{-1}; $U(\rho)$ = 0.29 kg·m^{-3} at b = 1.98 mol·kg^{-1}; $U(\rho)$ = 0.33 kg·m^{-3} at b = 3.15 mol·kg^{-1}; $U(\rho)$ = 0.39 kg·m^{-3} at b = 4.95 mol·kg^{-1}.

Table 6. Densities ρ of NaCl(aq) at Temperatures T, Pressures p, and Molalities b[a]

p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
b = 1.06 mol·kg^{-1}							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1038.78	0.90	1028.45	0.90	1014.93	0.90	998.89
9.90	1042.49	9.90	1032.10	9.90	1018.61	9.90	1002.77
19.90	1046.61	19.90	1036.09	19.90	1022.67	19.90	1007.00
29.90	1050.58	29.90	1039.95	29.90	1026.61	29.90	1011.16
39.90	1054.45	39.90	1043.77	39.90	1030.49	39.90	1015.15
49.90	1058.27	49.90	1047.49	49.90	1034.25	49.90	1019.09
59.90	1061.93	59.90	1051.10	59.90	1037.94	59.90	1022.88
68.40	1065.11	68.40	1054.12	68.40	1041.08	68.40	1026.09
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	980.42	0.90	959.71	0.90	936.49	9.90	916.86
9.90	984.60	9.90	964.31	9.90	941.64	19.90	923.12
19.90	989.13	19.90	969.29	19.90	947.14	29.90	929.00
29.90	993.51	29.90	974.04	29.90	952.41	39.90	934.76
39.90	997.76	39.90	978.60	39.90	957.55	49.90	940.22
49.90	1002.02	49.90	983.20	49.90	962.42	59.90	945.52
59.90	1006.01	59.90	987.46	59.90	967.35	68.40	949.91
68.40	1009.32	68.40	991.15	68.40	971.22		
b = 3.16 mol·kg^{-1}							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1111.08	0.90	1098.80	0.90	1084.57	0.90	1068.60
9.90	1114.33	9.90	1102.10	9.90	1087.94	9.90	1072.14
19.90	1117.89	19.90	1105.63	19.90	1091.54	19.90	1075.95
29.90	1121.40	29.90	1109.07	29.90	1095.09	29.90	1079.61
39.90	1124.91	39.90	1112.54	39.90	1098.65	39.90	1083.24

Table 6. continued

p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
49.90	1128.21	49.90	1115.90	49.90	1101.95	49.90	1086.77
59.90	1131.46	59.90	1119.20	59.90	1105.34	59.90	1090.25
68.40	1134.29	68.40	1121.87	68.40	1108.22	68.40	1093.16
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	1051.16	0.90	1031.93	0.90	1010.87	9.90	993.19
9.90	1054.84	9.90	1036.08	9.90	1015.28	19.90	998.47
19.90	1058.92	19.90	1040.37	19.90	1020.13	29.90	1003.47
29.90	1062.79	29.90	1044.51	29.90	1024.61	39.90	1008.45
39.90	1066.63	39.90	1048.68	39.90	1029.15	49.90	1013.17
49.90	1070.44	49.90	1052.68	49.90	1033.43	59.90	1017.78
59.90	1074.07	59.90	1056.58	59.90	1037.71	68.40	1021.53
68.40	1077.08	68.40	1059.82	68.40	1041.14		
b = 6.00 $mol \cdot kg^{-1}$							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1194.53	0.90	1180.58	0.90	1165.53	0.90	1149.58
9.90	1197.36	9.90	1183.46	9.90	1168.53	9.90	1152.70
19.90	1200.44	19.90	1186.57	19.90	1171.76	19.90	1156.09
29.90	1203.47	29.90	1189.69	29.90	1174.98	29.90	1159.48
39.90	1206.51	39.90	1192.73	39.90	1178.07	39.90	1162.74
49.90	1209.49	49.90	1195.77	49.90	1181.15	49.90	1165.95
59.90	1212.31	59.90	1198.70	59.90	1184.21	59.90	1169.00
68.40	1214.78	68.40	1201.09	68.40	1186.78	68.40	1171.60
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	1132.48	0.90	1114.20	0.90	1094.62	9.90	1078.20
9.90	1135.74	9.90	1117.84	9.90	1098.38	19.90	1082.67
19.90	1139.35	19.90	1121.56	19.90	1102.62	29.90	1087.01
29.90	1142.80	29.90	1125.33	29.90	1106.53	39.90	1091.28
39.90	1146.27	39.90	1128.98	39.90	1110.46	49.90	1095.39
49.90	1149.66	49.90	1132.56	49.90	1114.27	59.90	1099.39
59.90	1152.86	59.90	1136.03	59.90	1118.04	68.40	1102.68
68.40	1155.61	68.40	1138.92	68.40	1121.10		

[a] Expanded uncertainties are: $U(\rho)$ = 0.26 $kg \cdot m^{-3}$ at b = 1.06 $mol \cdot kg^{-1}$; $U(\rho)$ = 0.33 $kg \cdot m^{-3}$ at b = 3.16 $mol \cdot kg^{-1}$; $U(\rho)$ = 0.41 $kg \cdot m^{-3}$ at b = 6.00 $mol \cdot kg^{-1}$.

Table 7. Densities ρ of KCl(aq) at Temperatures T, Pressures p, and Molalities b[a]

p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$	p MPa	ρ $kg \cdot m^{-3}$
b = 1.06 $mol \cdot kg^{-1}$							
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1044.20	0.90	1034.14	0.90	1020.74	0.90	1004.76
9.90	1047.96	9.90	1037.83	9.90	1024.46	9.90	1008.64
19.90	1052.02	19.90	1041.82	19.90	1028.51	19.90	1012.91
29.90	1056.08	29.90	1045.67	29.90	1032.50	29.90	1017.11
39.90	1060.00	39.90	1049.58	39.90	1036.42	39.90	1021.10
49.90	1063.86	49.90	1053.35	49.90	1040.18	49.90	1025.08
59.90	1067.62	59.90	1057.01	59.90	1043.91	59.90	1028.91
68.40	1070.84	68.40	1060.07	68.40	1047.14	68.40	1032.17
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	986.31	0.90	965.57	0.90	942.89	9.90	923.68
9.90	990.53	9.90	970.25	9.90	948.08	19.90	929.93
19.90	995.11	19.90	975.13	19.90	953.62	29.90	935.86
29.90	999.53	29.90	979.97	29.90	958.88	39.90	941.62
39.90	1003.82	39.90	984.63	39.90	963.97	49.90	947.07
49.90	1008.02	49.90	989.18	49.90	968.88	59.90	952.36
59.90	1012.10	59.90	993.52	59.90	973.66	68.40	956.79
68.40	1015.46	68.40	997.11	68.40	977.57		

Table 7. continued

p / MPa	ρ / $kg{\cdot}m^{-3}$	p / MPa	ρ / $kg{\cdot}m^{-3}$	p / MPa	ρ / $kg{\cdot}m^{-3}$	p / MPa	ρ / $kg{\cdot}m^{-3}$
			$b = 3.15\ mol{\cdot}kg^{-1}$				
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1124.07	0.90	1112.58	0.90	1098.82	0.90	1083.32
9.90	1127.47	9.90	1115.91	9.90	1102.28	9.90	1086.89
19.90	1131.16	19.90	1119.53	19.90	1105.97	19.90	1090.74
29.90	1134.81	29.90	1123.11	29.90	1109.59	29.90	1094.53
39.90	1138.35	39.90	1126.71	39.90	1113.24	39.90	1098.25
49.90	1141.90	49.90	1130.16	49.90	1116.68	49.90	1101.91
59.90	1145.28	59.90	1133.60	59.90	1120.15	59.90	1105.38
68.40	1148.20	68.40	1136.35	68.40	1123.07	68.40	1108.37
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	1065.90	0.90	1046.73	0.90	1025.62	9.90	1007.94
9.90	1069.71	9.90	1050.87	9.90	1030.11	19.90	1013.25
19.90	1073.82	19.90	1055.23	19.90	1034.96	29.90	1018.38
29.90	1077.73	29.90	1059.51	29.90	1039.57	39.90	1023.39
39.90	1081.65	39.90	1063.66	39.90	1044.09	49.90	1028.19
49.90	1085.49	49.90	1067.79	49.90	1048.45	59.90	1032.84
59.90	1089.26	59.90	1071.77	59.90	1052.77	68.40	1036.57
68.40	1092.30	68.40	1075.00	68.40	1056.27		
			$b = 4.49\ mol{\cdot}kg^{-1}$				
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1168.21	0.90	1156.09	0.90	1142.21	0.90	1126.88
9.90	1171.42	9.90	1159.30	9.90	1145.43	9.90	1130.26
19.90	1174.92	19.90	1162.77	19.90	1148.98	19.90	1133.92
29.90	1178.38	29.90	1166.16	29.90	1152.52	29.90	1137.58
39.90	1181.79	39.90	1169.63	39.90	1155.93	39.90	1141.11
49.90	1185.09	49.90	1172.93	49.90	1159.38	49.90	1144.58
59.90	1188.28	59.90	1176.14	59.90	1162.56	59.90	1147.95
68.40	1191.12	68.40	1178.80	68.40	1165.39	68.40	1150.77
T = 397.97 K		T = 422.94 K		T = 447.94 K		T = 472.96 K	
0.90	1109.90	0.90	1091.46	0.90	1071.39	9.90	1054.54
9.90	1113.48	9.90	1095.41	9.90	1075.50	19.90	1059.47
19.90	1117.40	19.90	1099.54	19.90	1080.06	29.90	1064.17
29.90	1121.12	29.90	1103.53	29.90	1084.38	39.90	1068.85
39.90	1124.86	39.90	1107.49	39.90	1088.62	49.90	1073.32
49.90	1128.56	49.90	1111.34	49.90	1092.74	59.90	1077.68
59.90	1132.08	59.90	1115.08	59.90	1096.73	68.40	1081.18
68.40	1135.00	68.40	1118.18	68.40	1100.10		

[a] Expanded uncertainties are: $U(\rho) = 0.26\ kg{\cdot}m^{-3}$ at $b = 1.06\ mol{\cdot}kg^{-1}$; $U(\rho) = 0.35\ kg{\cdot}m^{-3}$ at $b = 3.15\ mol{\cdot}kg^{-1}$; $U(\rho) = 0.39\ kg{\cdot}m^{-3}$ at $b = 4.49\ mol{\cdot}kg^{-1}$.

and molality for each brine system by means of the following relations:

$$[\rho_{\mathrm{ref}}(T, b) - \rho_0(T)]/(\mathrm{kg{\cdot}m^{-3}}) = \sum_{i=1}^{i=3} \alpha_{i0}[b/(\mathrm{mol{\cdot}kg^{-1}})]^{(i+1)/2} + \sum_{i=1}^{i=3}\sum_{j=1}^{j=3} \alpha_{ij}[b/(\mathrm{mol{\cdot}kg^{-1}})]^{(i+1)/2}(T/T_c)^{(j+1)/2} \qquad (9)$$

$$B(T, b)/\mathrm{MPa} = \sum_{i=0}^{i=1}\sum_{j=0}^{j=3} \beta_{ij}[b/(\mathrm{mol{\cdot}kg^{-1}})]^{i}(T/T_c)^{j} \qquad (10)$$

$$C(b) = \gamma_0 + \gamma_1[b/(\mathrm{mol{\cdot}kg^{-1}})] + \gamma_2[b/(\mathrm{mol{\cdot}kg^{-1}})]^{3/2} \qquad (11)$$

In eq 9, $\rho_0(T)$ is the density of saturated liquid water given by the auxiliary equation of Wagner and Pruss[58] as follows:

$$\rho_0(T)/\rho_c = 1 + c_1\varphi^{1/3} + c_2\varphi^{2/3} + c_3\varphi^{5/3} + c_4\varphi^{16/3} + c_5\varphi^{43/3} + c_6\varphi^{110/3} \qquad (12)$$

The coefficients in eqs 10 and 11 pertaining to pure water were optimized in a fit of eq 7 to densities computed from the IAPWS-95 equation of state[58] at all temperatures and pressures considered experimentally. Thus these coefficients were the same for every brine considered. The relative deviations of the density of pure water from this fit were all within ± 0.02 %. In Table 9 we give the parameters σ_i, c_i, β_{0i}, and γ_0 required for pure water.

Table 8. Densities ρ of $AlCl_3$(aq) at Temperatures T, Pressures p, and Molalities b[a]

p MPa	ρ kg·m^{-3}	p MPa	ρ kg·m^{-3}	p MPa	ρ kg·m^{-3}	p MPa	ρ kg·m^{-3}
			b = 1.00 mol·kg^{-1}				
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1105.53	0.90	1096.76	0.90	1085.66	0.90	1072.64
9.90	1108.79	9.90	1099.96	9.90	1088.98	9.90	1075.97
19.90	1112.30	19.90	1103.44	19.90	1092.48	19.90	1079.63
29.90	1115.82	29.90	1106.84	29.90	1096.02	29.90	1083.19
39.90	1119.28	39.90	1110.31	39.90	1099.44	39.90	1086.72
49.90	1122.69	49.90	1113.67	49.90	1102.74	49.90	1090.20
59.90	1125.95	59.90	1116.93	59.90	1106.07	59.90	1093.58
68.40	1128.83	68.40	1119.60	68.40	1108.86	68.40	1096.34
			b = 2.00 mol·kg^{-1}				
T = 298.12 K		T = 323.07 K		T = 348.04 K		T = 372.99 K	
0.90	1212.19	0.90	1203.26	0.90	1192.82	0.90	1181.64
9.90	1214.96	9.90	1206.02	9.90	1196.00	9.90	1184.73
19.90	1217.92	19.90	1209.01	19.90	1199.11	19.90	1187.90
29.90	1220.94	29.90	1211.90	29.90	1202.10	29.90	1191.11
39.90	1223.85	39.90	1214.88	39.90	1205.07	39.90	1194.19
49.90	1226.72	49.90	1217.80	49.90	1207.92	49.90	1197.22
59.90	1229.57	59.90	1220.60	59.90	1210.85	59.90	1200.14
68.40	1232.02	68.40	1222.88	68.40	1213.26	68.40	1202.66

[a] Expanded uncertainties are: $U(\rho)$ = 0.30 kg·m^{-3} at b = (1 and 2) mol·kg^{-1}.

Table 9. Coefficients α_i, β_{0j}, γ_0, and σ_i for Pure Water in Equations 8 to 12

c_1	c_2	c_3	c_4	c_5	c_6
1.992741	1.099653	−0.510839	−1.754935	−45.517035	674694.450000
β_{00}	β_{01}	β_{02}	β_{03}	γ_0	σ_1
−1622.40	9383.80	−14893.80	7309.10	0.11725	−7.859518
σ_2	σ_3	σ_4	σ_5	σ_6	
1.844083	−11.786650	22.680741	−15.961872	1.801225	

The remaining parameters in eqs 9 to 11 were optimized in a surface fit with eq 7 for each brine, considering simultaneously all temperatures and pressures. The coefficients α_{ij}, β_{ij}, and γ_i obtained are given in Table 10. For each brine, we computed the absolute average relative deviation (Δ_{AAD}), average relative deviation (Δ_{Bias}), and maximum absolute relative deviation (Δ_{MAD}) from eq 7. These statistical measures are defined as follows:

$$\Delta_{AAD} = \frac{1}{N}\sum_{i}^{N}\left|\frac{\rho_i^{exp} - \rho_i^{cal}}{\rho_i^{exp}}\right| \tag{13}$$

$$\Delta_{Bias} = \frac{1}{N}\sum_{i}^{N}\frac{\rho_i^{exp} - \rho_i^{cal}}{\rho_i^{exp}} \tag{14}$$

$$\Delta_{MAD} = \mathrm{Max}\left(\sum_{i}^{N}\left|\frac{\rho_i^{exp} - \rho_i^{cal}}{\rho_i^{exp}}\right|\right) \tag{15}$$

The values Δ_{AAD}, Δ_{Bias}, and Δ_{MAD} are given in Table 10; they compare favorably with the relative uncertainty of the data. In Figure 2, we plot the relative deviations of the experimental densities from eq 7.

■ MIXED BRINE

A simple model for predicting the density of a mixed brine may be obtained with the assumption that the excess volume of mixing single salt solutions at specified (p, T, b) is zero.[27] With this approach, the density ρ_m of a mixed electrolyte solution at given (p, T, b) is related to the densities of single electrolyte solutions from which it may be formed as follows:

$$\rho_m(p, T, b) = \left[\sum_i x_i(1 + bM_i)\right]\left[\sum_i \{x_i(1 + bM_i)/\rho_i(p, T, b)\}\right]^{-1} \tag{16}$$

Here, x_i is the mole fraction of electrolyte i in the mixed salt, M_i is the molar mass of salt i, and ρ_i is the density of the single electrolyte solution at the pressure, temperature, and molality of the mixed electrolyte solution.

This equation was applied to predict the density of the mixed electrolyte solution (0.864 NaCl + 0.136 KCl)(aq) at temperatures from (283.15 to 473.15) K, pressures up to 68.5 MPa, and total molalities of (1.05, 1.98, 3.15, and 4.95) mol·kg^{-1}. The densities of the single solutions, NaCl(aq) and KCl(aq), were obtained from the correlations developed in this work for those brines. The predicted densities were then compared with the experimental values, and the relative

Table 10. Coefficients α_{ij}, β_{ij}, and γ_i and Statistical Parameters Absolute Average Relative Deviation (Δ_{AAD}), Average Relative Deviation (Δ_{Bias}), and Maximum Absolute Relative Deviation (Δ_{MAD}) for $CaCl_2$(aq), $MgCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), [0.864NaCl + 0.136KCl](aq), and $AlCl_3$(aq) in Equations 8 to 12

	NaCl(aq)	$CaCl_2$ (aq)	$MgCl_2$(aq)	KI(aq)	(0.864NaCl + 0.136KCl)(aq)	KCl(aq)	$AlCl_3$(aq)
α_{10}	2863.158	2546.760	2385.823	8657.149	3452.312	2332.802	1326.366
α_{11}	−46844.356	−39884.946	−38428.112	−94956.477	−58732.356	−39637.418	−310263.216
α_{12}	120760.118	102056.957	99526.269	167497.772	154450.565	104801.288	443804.244
α_{13}	−116867.722	−98403.334	−97041.399	−74952.063	−152574.650	−104266.828	0.000
α_{14}	40285.426	33976.048	33841.139	−8734.207	53700.479	37030.556	0.000
α_{20}	−2000.028	−1362.157	−1254.938	−14420.621	−2900.592	−1287.572	−1804.785
α_{21}	34013.518	22785.572	21606.295	137360.624	51539.478	23543.994	527875.006
α_{22}	−88557.123	−59216.108	−56988.274	−184940.639	−137384.642	−63846.097	−755878.487
α_{23}	86351.784	57894.824	56465.943	−11953.289	137291.425	65023.561	0.000
α_{24}	−29910.216	−20222.898	−19934.064	79847.960	−48772.381	−23586.370	0.000
α_{30}	413.046	217.778	192.534	7340.083	712.600	206.032	727.779
α_{31}	−7125.857	−3770.645	−3480.374	−66939.345	−12852.805	−4003.757	−218520.857
α_{32}	18640.780	9908.135	9345.908	81446.737	34456.168	11128.162	312961.409
α_{33}	−18244.074	−9793.484	−9408.904	23983.386	−34603.469	−11595.475	0
α_{34}	6335.275	3455.587	3364.018	−49031.473	12343.593	4295.498	0
β_{10}	241.57	307.24	358.00	241.84	188.98	211.49	0
β_{11}	−980.97	−1259.10	−1597.10	−1030.61	−722.33	−888.16	0
β_{12}	1482.31	2034.03	2609.47	1548.15	1063.85	1400.09	0
β_{13}	−750.98	−1084.94	−1383.91	−754.36	−525.66	−732.79	0
γ_1	−0.00134	−0.00493	−0.00789	−0.01026	−0.00123	−0.00170	−0.04236
γ_2	0.00056	0.00231	0.00142	0.00842	0.00059	0.00083	0.01319
$10^2\Delta_{AAD}$	0.005	0.004	0.004	0.005	0.005	0.005	0.008
$10^2\Delta_{Bias}$	−0.0001	−0.0002	−0.0002	−0.0002	0.0000	−0.0002	−0.0003
$10^2\Delta_{MAD}$	0.016	0.016	0.016	0.019	0.020	0.016	0.033

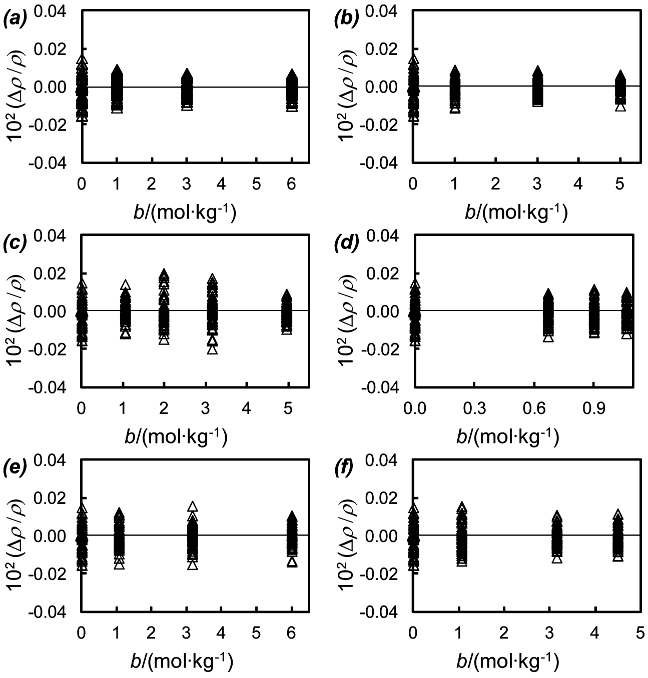

Figure 2. Deviations $\Delta\rho$ of experimental densities ρ from eq 7 as a function of molality b: (a) $CaCl_2$(aq); (b) $MgCl_2$(aq); (c) [0.864NaCl + 0.136KCl](aq); (d) KI(aq); (e) NaCl(aq); (f) KCl(aq).

deviations are plotted in Figure 3a. The agreement is within ± 0.05 %, and this suggests that eq 16 is reliable over extended ranges of temperature, pressure, and molality.

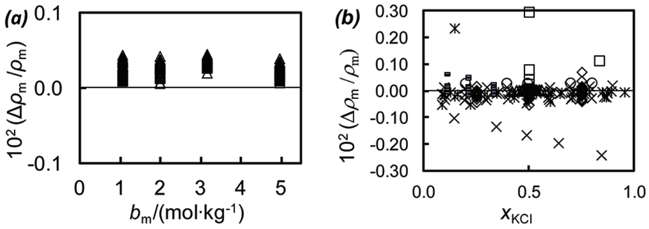

Figure 3. Deviation $\Delta\rho_m$ of densities ρ_m for the mixed brine [$(1 - x)$ NaCl + xKCl] from eqs 7 and 13: (a) this work, as a function of molality b_m; (b) literature data at p = 0.1 MPa and different temperatures as function of x. △, Miller et al.,[62] T = 298.15 K, x = 0.42 to 0.58; ◇, Zhang and Han,[63] T = 298.15 K, x = 0.25 to 0.75; ×, Dedick et al.,[45] T = (278.15 to 368.15) K, x = 0.10 to 0.90; ∗, Kumar,[64] T = 298.15 K, x = 0.09 to 0.95; ○, Millero et al.,[68] T = 298.15 K, x = 0.20 to 0.80; □, Goldsack and Franchetto,[66] T = 298.15 K, x = 0.50 to 0.83; -, Fabuss et al.,[67] T = (298.15 to 348.15) K, x = 0.10 to 0.32.

■ LITERATURE COMPARISON

To further test the correlations developed in this study, comparisons have been made with the available literature data for the salt systems investigated. There are a large number of literature sources. As discussed above, many of the available data pertain to near-ambient conditions of temperature and pressure, but wide ranges of molality are covered. The total number of the density data points considered was 1668 for NaCl(aq), 899 for $CaCl_2$(aq), 693 for KCl(aq), 506 for $MgCl_2$(aq), and 334 for KI(aq). The deviations Δ_{AAD}, Δ_{Bias}, and Δ_{MAD} from eq 7 for each literature source are detailed in the Supporting Information, together with the number of data points and the temperature, pressure, and molality ranges for each.

The average absolute deviation from all literature sources considered are 0.03 %, 0.06 %, 0.04 %, 0.02 %, and 0.02 % for the systems $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), and KCl(aq) respectively. These values indicate generally good agreement between our results and those available in the literature. Also presented in the Supporting Information are deviation plots for the literature data from the correlations developed in this work.

There are a few literature data available for $[(1 - x)\text{NaCl} + x\text{KCl}]$(aq) solution at $p = 0.1$ MPa, $T = (298.15$ to $368.15)$ K and various molalities and mole fractions x. Figure 3b compares the densities obtained from eq 16, with eq 7 for each single-electrolyte solution, with those reported in the literature[45,62−67] for different mole fractions of KCl at $p = 0.1$ MPa and $T = (298.15$ to $368.15)$ K. Most of the data fall well within ± 0.1 %.

■ CONCLUSION

The density values of aqueous solutions of $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), $AlCl_3$(aq), and the mixed salt system (0.864 NaCl + 0.136 KCl)(aq) were measured at temperatures between (283.15 and 473.15) K, pressures up to 68.5 MPa, and various molalities. The expanded relative uncertainties at 95 % confidence are approximately 0.05 % for all of the brines studied.

Correlation models were developed for the density of each brine system with relative uncertainties of 0.05 % at 95 % confidence. These are valid in the temperature range (298.15 to 473.15) K and at pressures up to 68.5 MPa for all brines studied except in the case of $AlCl_3$(aq) where the temperature is restricted to the range (298.15 to 373.15) K. The correlations are valid for all molalities up to (5.0, 6.0, 1.06, 6.0, 4.5, 2.0, and 4.95) $\text{mol}\cdot\text{kg}^{-1}$ for $MgCl_2$(aq), $CaCl_2$(aq), KI(aq), NaCl(aq), KCl(aq), $AlCl_3$(aq), and (0.864 NaCl + 0.136 KCl)(aq), respectively. The correlations were shown to be in good agreement with the available literature data for the brines studied.

A model based on the assumption of zero excess volume of mixing at any given (T, p, b) was tested on predictions of the density of (0.864 NaCl + 0.136 KCl)(aq) and was found to agree with the experimental data to within ± 0.05 %. We suggest that the same model may be useful for the density of other mixed brine systems.

The data and models presented in this paper may be used to obtain derivative properties such as apparent molar volume and compressibility over the (T, p, b) ranges investigated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Available literature sources for the densities of single-salt and mixed-salt aqueous solutions (Tables S1 and S2) and deviations for the densities of the studied systems (Table S3); relative deviations of densities for the present model (Figures S1 to S5) and densities of NaCl−KCl solution as a function of molality (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: m.trusler@imperial.ac.uk.

Notes

The authors declare no competing financial interest.

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