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# Solid – Liquid Equilibria in Aqueous Solutions of Tris, Tris-NaCl, Tris-TrisHCl, and Tris-(TrisH)<sub>2</sub>SO<sub>4</sub> at Temperatures From 5 °C to 45 °C

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**ABSTRACT:** The substance Tris (or THAM, 2-amino-2-hydroxymethyl-1,3-propanediol) is used in the preparation of pH buffer solutions for applications in natural water chemistry, including seawater. The development of a chemical speciation model of buffer solutions containing Tris, TrisH<sup>+</sup>, and the major ions of seawater is desirable so that the effects of changes in the composition and concentration of the medium on pH can be calculated. The Pitzer activity coefficient equations, commonly used in such speciation models, describe the thermodynamic properties of solutions in terms of interactions between dissolved ions and uncharged solute species. To determine some of these interactions we have measured solubilities of Tris<sub>(s)</sub> in water and aqueous solutions of NaCl, TrisHCl, and (TrisH)<sub>2</sub>SO<sub>4</sub>, and the solubility of NaCl<sub>(s)</sub> in aqueous Tris<sub>(aq)</sub>, from 5 °C to 45 °C. We report measurements of the water activities of Tris solutions at 293.5 K to high supersaturation with respect to the solid. Using the Pitzer equations, we compare our results to literature data yielding stoichiometric dissociation constants of TrisH<sup>+</sup> in aqueous NaCl, and electromotive forces of cells containing dissolved Tris, TrisHCl, and NaCl.

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3 Values of parameters for the interactions of Tris with the ions  $\text{TrisH}^+$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  at 25 °C are  
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5 determined.  
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## 9 1. INTRODUCTION

11 The compound Tris, together with its conjugate acid  $\text{TrisH}^+$ , is used in aqueous buffer solutions for the  
12 calibration of pH measurements in natural waters, including seawater.<sup>1</sup> The thermodynamic  $pK_a$  for the  
13 acid dissociation  $\text{TrisH}_{(\text{aq})}^+ \leftrightarrow \text{H}_{(\text{aq})}^+ + \text{Tris}_{(\text{aq})}$  has been determined experimentally by Bates and Hetzer<sup>2</sup>  
14 for temperatures in the range 0 °C to 50 °C, and the values (e.g., 8.07 at 25 °C) make it suitable for  
15 buffering of solutions in the pH range 7 – 9. Solutions of equimolar Tris and  $\text{TrisH}^+$  in artificial  
16 seawater, which contains the ions  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , are used to define the pH scale  
17 used for measuring the acidity of seawater over the range of salinities 5 to 40, and for temperatures from  
18 0 °C to 45 °C.<sup>3, 4</sup> This concentration-based 'total' pH scale ( $\text{pH} = -\log_{10}([\text{H}^+] + [\text{HSO}_4^-])$ ) is applicable  
19 only to saline waters containing the major ions of seawater in the ratios found in the open ocean, and it  
20 is desirable for several reasons to develop a chemical speciation model of  $\text{TrisH}^+$  dissociation in salt  
21 solutions: (1) to more accurately extend the pH scale to low salinity waters; (2) to be able to calculate  
22 the pH of buffers for saline waters whose stoichiometry differs from that of open ocean seawater; and  
23 (3) to address metrological concerns regarding the link between the total pH scale and SI base units.<sup>5</sup>  
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41 Gallego-Urrea and Turner<sup>6</sup> have summarised the application of a Pitzer-based<sup>7</sup> speciation model to  
42 describe solute and solvent activities in solutions containing Tris buffer and artificial seawater at 25 °C.  
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44 There are also several models for acid-base equilibria in artificial seawater based on the Pitzer  
45 formulation.<sup>8-10</sup> In these models the variations of solute and solvent activity coefficients, and other  
46 thermodynamic properties, are described in terms of interactions between pairs and triplets of solute  
47 species.<sup>7</sup> The values of the interaction parameters, which are functions of both temperature and pressure,  
48 are determined from thermodynamic measurements that yield (directly or indirectly) values of activities  
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3 or their differentials with respect to  $T$  or  $P$ . Examples of such data, from which activities can be  
4 determined, include isopiestic measurements of water activity, electromotive forces (EMFs) of  
5 electrochemical cells, solute or solvent vapour pressures, and solubilities of solids.  
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10 Osmotic coefficients have been measured at 25 °C for solutions of Tris,<sup>11</sup> TrisHCl,<sup>11</sup> and  
11 (TrisH)<sub>2</sub>SO<sub>4</sub><sup>12</sup> and stoichiometric values of the  $K_a$  of TrisH<sup>+</sup> ( $K_a^* = mH^+ \cdot mTris/mTrisH^+$ , where  $m$   
12 denotes molality), have been measured in various chloride solutions by Millero et al.<sup>13</sup> Gallego-Urrea  
13 and Turner<sup>6</sup> have used these and other data to derive Pitzer parameters for the interaction of Tris and  
14 TrisH<sup>+</sup> with seawater ions. The resulting Pitzer thermodynamic model for equimolal Tris buffers in  
15 artificial seawater showed significant offsets from the experimental EMFs reported by DelValls and  
16 Dickson<sup>3</sup> for these solutions.  
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21 With the aim of developing a speciation model of pH of Tris buffers in saline waters, we have  
22 measured solubilities of Tris<sub>(s)</sub> in water and aqueous solutions of NaCl, TrisHCl, and (TrisH)<sub>2</sub>SO<sub>4</sub>, and  
23 the solubility of NaCl<sub>(s)</sub> in Tris<sub>(aq)</sub>, at temperatures from 5 °C to 45 °C. We also report new measurements  
24 of the water activities of aqueous Tris solutions at 293.5 K to high supersaturation with respect to the  
25 solid phase.  
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30 The results at 25 °C are compared with EMF and other literature data that yield activities of Tris and  
31 TrisH<sup>+</sup>, and we have obtained preliminary values of Pitzer model parameters for the interaction of Tris  
32 with the ions Na<sup>+</sup>, TrisH<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> from the solubility measurements.  
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## 36 37 38 39 40 41 42 43 44 45 **2. EXPERIMENTAL METHODS**

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48 In all the experiments ultrapure water obtained from a Milli-Q<sup>®</sup> water purification system (Merck  
49 group), with a resistivity of 18.2 M Ω ·cm and total organic carbon <5 ppb, was used. Ultrapure  
50 (≥99.9%) NaCl and Tris, TRIS hydrochloride (TrisHCl), and Tris hemisulphate ((TrisH)<sub>2</sub>SO<sub>4</sub>) were  
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3 purchased from VWR International and dried at 110 °C during 48 h before use (Table 12). All the  
4 samples were prepared gravimetrically using a 1 mg precision balance (Sartorius, model AS). The  
5 linearity of the balance from a calibration certificate (3 mg) allowed us to obtain the uncertainty of the  
6 weights using the formula:  $3/(3)^{0.5} = \pm 1.73$  mg. This contribution has been counted twice (tare and gross  
7 weight), giving an uncertainty of  $\pm 2.45$  mg. Using a coverage factor ( $k$ ) of 2, an uncertainty of  $\pm 4.9$  mg  
8 is obtained, which applying error propagation results in an expanded uncertainty ( $U(m)$ , 0.95 level of  
9 confidence) for the stock solution concentrations of  $\pm 8 \cdot 10^{-5}$  mol kg<sup>-1</sup>.

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19 **2.1 Tris Solubility in Aqueous NaCl, TrisHCl, and (TrisH)<sub>2</sub>SO<sub>4</sub>.** Stock solutions of NaCl (~5 mol  
20 kg<sup>-1</sup>), TrisHCl (~4 mol kg<sup>-1</sup>) and (TrisH)<sub>2</sub>SO<sub>4</sub> (~2 mol kg<sup>-1</sup>) were prepared by accurate weighing of the  
21 respective salts. Buoyancy corrections were made to all weighings, including those made in order to  
22 determine solubilities, using the equations presented in Dickson et al.<sup>14</sup>

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In each experiment 8–9 glass flasks containing about 200–300 cm<sup>3</sup> of background electrolyte, and  
excess solid Tris, were introduced into a water bath with constant temperature control ( $\pm 0.2$  °C), and  
were magnetically stirred at the selected temperature (in the range 5 °C to 45 °C). The water bath  
consisted in a 20 L plastic container isolated with 2 cm panels of polystyrene. A steady flow of  
temperature-controlled water was supplied to the water bath using a re-circulating chiller (Fisherbrand  
FBC 720) as shown in Figure 1. The flasks with the solutions were prepared by diluting salt stock  
solutions to final molalities of: (a) NaCl – 0, 1, 2, 3, 4 and 5 mol kg<sup>-1</sup>; (b) TrisHCl – 0, 0.5, 1, 2, 3 and 4  
mol kg<sup>-1</sup>; and (c) (TrisH)<sub>2</sub>SO<sub>4</sub> – 0, 0.25, 1, 1.5 and 2 mol kg<sup>-1</sup>. The flasks containing 4 mol kg<sup>-1</sup> aqueous  
NaCl, and 1 and 3 mol kg<sup>-1</sup> aqueous TrisHCl, were prepared in duplicate. In addition, a flask containing  
pure water with no added salts was used as control. During the equilibrations the flasks were stoppered  
to prevent evaporation of water. The attainment of equilibrium was tested in one experiment at 25 °C  
containing excess solid Tris and 5 mol kg<sup>-1</sup> of NaCl in which aliquots were withdrawn every 24 h, and

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3 measured to check for variations in Tris concentrations over time. In this case, 48 h were enough to  
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5 attain equilibrium; but because longer times can be expected for lower temperatures we decided to wait  
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7 for at least 12 days to ensure equilibrium between solid and liquid phases at all temperatures and  
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9 solution compositions studied.

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12 Typically, the experiments were started at 25 °C and, once finished, the temperature was increased in 5  
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14 °C intervals. Afterwards, the temperature was set to 20 °C, and subsequent experiments followed a  
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16 decreasing trend until the lowest temperature was achieved. No significant differences were observed  
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18 between measured Tris solubilities for which the experimental temperatures had been approached from  
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20 either higher or lower temperatures.  
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24 In the experiments containing TrisHCl and (TrisH)<sub>2</sub>SO<sub>4</sub> the same flasks were used for the whole range  
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26 of temperatures. For the experiments containing NaCl in the range 5 °C to 20 °C a different set of flasks  
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28 were used to ensure a proper agitation; these flasks contained identical background electrolyte molalities  
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30 but lower amounts of solid Tris than were used for the experiments in the range 25 °C to 45 °C.  
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34 Once equilibrium was reached, samples were withdrawn from each flask in triplicate or duplicate (for  
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36 the flasks containing the same background electrolyte concentration) using a pre-heated glass syringe  
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38 with a 0.2 µm Minisart RC filter (Sartorius Stedim Biotech) attached, to remove any particles of solid  
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40 Tris suspended in the solution. These samples, generally weighing 5-10 g, were then diluted and the  
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42 concentration of Tris quantified by potentiometric titrations. At least two samples, of about 35 g each,  
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44 from each diluted solution were then weighed and placed in a 50 cm<sup>3</sup> water-jacketed cell maintained at a  
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46 constant 25 ± 0.1 °C using a temperature-controlled bath (Julabo Labortechnik F25). These samples  
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48 were titrated against ~0.5 mol kg<sup>-1</sup> HCl (Optima Grade, Fisher Scientific) added from an automatic  
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50 burette (Metrohm Dosimat 665) and maintained under N<sub>2</sub> bubbling. Densities of the aqueous HCl at the  
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52 laboratory temperature of 22 °C were taken from the critical evaluation of Clegg and Wexler.<sup>15</sup> The  
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3 EMF measurements were made with a glass pH and a reference electrode (Thermo Scientific Orion  
4 Ross) both connected to a pH-meter (Thermo Orion 720A+). The burette and pH-meter were computer-  
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6 controlled using a Matlab script. The HCl solution was previously standardised by titration of known  
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8 amounts of sodium tetraborate decahydrate (borax) supplied by Sigma-Aldrich. The equivalence points  
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10 of the titrations of the Tris in the samples from the test solutions were determined using the Gran's plot  
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12 approach,<sup>16</sup> and the molalities of the Tris in the solutions calculated from these results. Four to six  
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14 measurements were made of the Tris molality in each flask.  
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19 **2.2 NaCl Solubility in Aqueous Tris.** Two Tris stock solutions of 2.5 and 4.5 mol kg<sup>-1</sup> concentration  
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21 were prepared from weighed amounts of solid Tris and water. Each of these stock solutions was used to  
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23 prepare flasks containing an excess of solid NaCl over its expected solubility, and the fixed molalities of  
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25 Tris: 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mol kg<sup>-1</sup> (1 and 2 mol kg<sup>-1</sup> flasks prepared in duplicate) for experiments  
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27 from 5 °C to 20 °C; and 0, 0.5, 1.0, 2.0, 3.5 and 4.5 mol kg<sup>-1</sup> for experiments from 25 °C to 45 °C (1.0  
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29 and 3.5 mol kg<sup>-1</sup> flasks were prepared in duplicate). In the same way as for the other experiments, the  
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31 flasks were placed in a water bath with constant temperature control ( $\pm 0.2$  °C), and were magnetically  
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33 stirred for at least 12 days at each temperature to ensure equilibrium. Samples were withdrawn from  
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35 each flask in triplicate (where there was only a single flask containing a particular Tris molality) or  
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37 duplicate (where there were two such flasks) using a pre-heated glass syringe with a filter attached as  
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39 described earlier. Immediately after sampling, the samples (each of 10-18 g of solution) were diluted  
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41 and the concentration of chloride determined by titration following a modification of Volhard's  
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43 method.<sup>17</sup> The procedure was as follows: at least two samples (of 8-9 g) from each of the diluted  
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45 primary solution samples were weighed and placed in a glass cell together with approximately 3.5 g of  
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47 HNO<sub>3</sub> (purity  $\geq 65\%$ , Fluka), 38 g of ultrapure water, 2 cm<sup>3</sup> of chloroform (Carl Roth, >99.9%), and 0.4  
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49 cm<sup>3</sup> of NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (Acros Organics, +99%). An accurately weighed mass of about 10.1 g of  
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3 AgNO<sub>3</sub> (0.1 M volumetric solution, Fisher Scientific) was also added to the glass cell. A density of  
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5 1.0119 g·cm<sup>-3</sup> for 0.1 M AgNO<sub>3</sub> at the laboratory temperature (22 °C) was used to determine the amount  
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7 of silver. This density was calculated from the apparent molar volume of AgNO<sub>3</sub> at 25 °C in a 0.1 M  
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9 solution<sup>18</sup> and the molar volume of water at 22 °C.

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12 These samples were titrated against KSCN (0.1 N standardized solution, Alfa Aesar) added from an  
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14 automatic burette (Dosimat 665, Metrohm) until a colour change was observed, from pale white-yellow  
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16 to dark red, once all the silver ions added had reacted to form a silver thiocyanate precipitate, and the  
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18 excess of thiocyanate bound to Fe<sup>3+</sup> to form a red complex. At least four measurements were made of  
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20 the NaCl molality in each flask.  
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24 **2.3 Water Activities of Supersaturated Tris Solutions.** A description of the experimental method  
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26 is presented in the Appendix.  
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### 31 32 **3. RESULTS**

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34 The averaged measured solubilities for each solution composition, including those of Tris and NaCl  
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36 in pure water, are listed in Tables 1 to 6. The standard uncertainties ( $u$ ) for our measurements were  
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38 calculated as  $(\sum(x - \bar{x})^2/(n - 1))^{0.5}$  where  $x$  are the measured sample values,  $\bar{x}$  is the sample mean and  $n$   
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40 the sample size.  
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44 **3.1 Solubilities in Pure Water.** The solubility of Tris in water (Table 1) has been measured over  
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46 the temperature range 15 °C to 40 °C by several groups, and is compared with our results in Figure 2.  
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48 The combined data can be represented by the following equation, obtained by a weighted fit:  
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$$51 \ln(m_{\text{Tris(sat.)}}) = (1.75317 \pm 0.0013) - (1974.42 \pm 12.0)(1/T - 1/T_r) \quad (1)$$

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3 where  $m_{\text{Tris}}(\text{sat.})$  (mol kg<sup>-1</sup>) is the molality of Tris in the saturated solution,  $T$  (K) is temperature, and  $T_r$   
4 is the reference temperature of 298.15 K. The plot of deviations from eq 1 is shown in the inset to  
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7 Figure 2. The mean absolute deviation of all measurements from the fitted line is 0.099 mol kg<sup>-1</sup>.  
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10 The solubilities of NaCl in pure water determined in this work are listed in Table 2. Measurements  
11 in the literature up to 1983 have been critically evaluated by Cohen-Adad et al.,<sup>19</sup> and represented by  
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13 the following function  $Y$ :  
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$$16 \quad Y(x) = 2\ln(x/(1+x)) \quad (2)$$

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21 where  $x$  is the mole fraction of NaCl in the saturated solution, calculated as  $m_{\text{NaCl}}/(m_{\text{NaCl}} \cdot M_s +$   
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23  $1000/M_w)$  where prefix  $m$  denotes molality,  $M_s$  is the molar mass of NaCl (58.44 g mol<sup>-1</sup>) and  $M_w$  is  
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25 the molar mass of water (18.0153 g mol<sup>-1</sup>). The dependence of  $Y$  on temperature, from 273 K to 1073  
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27 K, is given by:  
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$$30 \quad Y(x) = Y(x_0) + A \cdot (1/T - 1/T_0) + B \cdot \ln(T/T_0) + C \cdot (T - T_0) \quad (3)$$

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34 where  $T_0$  is 273.15K, the mole fraction  $x_0$  at the same temperature is 0.09896,  $A$  is equal to 99.14456,  
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37  $B$  is equal to -1.53935, and  $C$  equals 0.00724959. Solubilities of NaCl in water can also be calculated  
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39 from the thermodynamic evaluations by Archer of NaCl<sub>(s)</sub><sup>20</sup> and NaCl – H<sub>2</sub>O solutions,<sup>21</sup> which are  
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41 particularly relevant to this study because the Pitzer activity coefficient equations<sup>7</sup> were used to  
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43 represent solvent and solute activities in the aqueous solutions.  
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47 Solubilities of NaCl in pure water measured in this study are shown in Figure 3 together with values  
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49 calculated using eq 3 above, and from the work of Archer.<sup>20, 21</sup> It is clear that the variation of solubility  
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51 with temperature is slight – only a 2.5% increase from 0 °C to 45 °C. Our results agree quite well with  
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53 the critical evaluation of Cohen-Adad et al.<sup>19</sup> up to about 30 °C. At 25 °C their equation yields a  
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55 solubility of 6.156 mol kg<sup>-1</sup>, and the thirty nine measurements that Cohen-Adad et al. fitted at this  
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3 temperature have a mean value of  $6.1536 \pm 0.024$  mol kg<sup>-1</sup>. Our own value is  $6.135 \pm 0.0067$  mol kg<sup>-1</sup>,  
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5 which agrees satisfactorily. However, at higher temperatures our measured solubilities are lower: by -  
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7 0.37% at 35 °C, and -0.67% at 45 °C. Insufficient equilibration time in the experiments does not  
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9 appear to be the reason for this, because solubilities at 35 °C were measured twice, in one case the  
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11 previous equilibration having been at a lower temperature, and in the other case a higher temperature.  
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13 The two results are  $6.1742 \pm 0.0067$  mol kg<sup>-1</sup> and  $6.1734 \pm 0.0023$  mol kg<sup>-1</sup>, which agree well.  
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17 **3.2 Solubilities in Mixtures.** Measured solubilities of NaCl in aqueous Tris are listed Table 3, and  
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19 those of Tris in aqueous solutions of NaCl, TrisHCl, and (TrisH)<sub>2</sub>SO<sub>4</sub> in Tables 4 to 6, respectively.  
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21 The overall behaviour observed is that the solubility of Tris is reduced, relative to that in pure water at  
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23 the same temperature, in aqueous NaCl and aqueous (TrisH)<sub>2</sub>SO<sub>4</sub> (salting out) but increased slightly in  
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25 aqueous TrisHCl (salting in). We note that this is qualitatively the same as is observed for NH<sub>3</sub>  
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27 solubilities in NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and NH<sub>4</sub>Cl solutions.<sup>22</sup> Sodium chloride is salted out in aqueous Tris  
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29 solutions (Table 3), as would be expected from the corresponding results for Tris solubilities in  
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31 NaCl<sub>(aq)</sub>.  
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35 The only data with which these results can be compared directly are solubilities of Tris in aqueous  
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37 NaCl at 25 °C inferred from density measurements (see Figure 1 and Table 4 of Taha and Lee<sup>23</sup>). The  
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39 data of Taha and Lee are compared with our own in Figure 4. There is generally good agreement,  
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41 except at the highest NaCl molalities for which our measurements suggest that there might be a slight  
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43 increase in Tris solubility (this tendency is also shown at other temperatures, see section 5.1.4). The  
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45 uncertainties in the data of Taha and Lee<sup>23</sup> for Tris solubility are not stated, but seem likely to be  
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47 greater than for our measurements because of the indirect way in which they are obtained.  
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We have represented our measurements using simple fitted equations as follows. First, the results listed in Tables 1 and 2 for Tris and NaCl solubilities (and excluding other data) in pure water were described by an equation of the same form as eq 1:

$$\ln(mS_{(\text{sat.})}^{\circ}) = a_0 + a_1(1/T - 1/T_r) \quad (4)$$

where  $mS_{(\text{sat.})}^{\circ}$  (mol kg<sup>-1</sup>) is the molality of the solute S in a saturated solution in pure water, and  $T$  and  $T_r$  have the same meanings as for eq 1. The values of the coefficients  $a_0$  and  $a_1$  for the two solutes are listed in Table 7.

The following equation is used to represent the solubilities ( $mS_{(\text{sat.})}$ ) of Tris in aqueous TrisHCl, (TrisH)<sub>2</sub>SO<sub>4</sub>, and NaCl, and of NaCl in aqueous Tris solutions:

$$\ln(mS_{(\text{sat.})}) = \ln(mS_{(\text{sat.})}^{\circ}) + b_0 \cdot m[1 + b_1(1/T - 1/T_r)] + b_2 \cdot m^c \quad (5)$$

where  $\ln(mS_{(\text{sat.})}^{\circ})$  is given by eq 4 above,  $m$  (mol kg<sup>-1</sup>) is the molality of the salt that is the background medium,  $b_{0-2}$  are fitted coefficients, and  $c$  is a constant that is assigned a value of 1.5 or 2 depending on the system. The values of the coefficients for all the systems measured are listed in Table 7. Note that the use of eq 4, with coefficients  $a_0$  and  $a_1$ , in eq 5 means that fitted solubilities of Tris represent our measurements only and do not include solubilities in pure water measured in the other studies listed in Table 1.

Figure 5 shows the measured and fitted solubilities of Tris in aqueous TrisHCl and (TrisH)<sub>2</sub>SO<sub>4</sub>. In both cases the solubilities have a nearly linear relationship with the salt molality, and slopes that change slightly with temperature. Solubilities of Tris in aqueous NaCl, shown in Figure 6, have a more complex relationship with salt molality: the relationship is clearly non-linear, and an extra coefficient ( $b_2$ ) is required in eq 5. The results at all molalities of NaCl, at 40 °C and 45 °C, do not appear to be fully consistent with the data for lower temperatures, and are poorly represented. We note

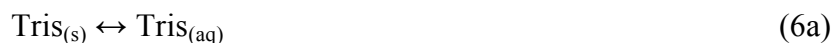
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3 that it is difficult to keep the glass-sampling syringe at temperatures higher than 40 °C for the long  
4 period of time sometimes required for sampling (ca. 1-2 min.), which could affect the solubility  
5 measurements at the highest temperatures as described above.  
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10 Solubilities of NaCl in aqueous Tris are shown in Figure 7. They vary only slightly with Tris  
11 molality, and are relatively more scattered than the other results. There is a clear dependence of the  
12 slope of the relationship between solubility and Tris molality with temperature, and the data for 25 °C  
13 to 40 °C suggest that there is a salting in effect at the highest Tris molalities. However, the results for  
14 45 °C are not fully consistent with this (the measured solubilities decrease almost linearly with Tris  
15 molality).  
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24 **3.3 Water Activities of Supersaturated Tris Solutions.** We have also measured water activities of  
25 Tris solutions, to extremely high concentrations, using a kinetic technique in which micron sized  
26 droplets are evaporated in an environment of controlled relative humidity.<sup>24</sup> These new experimental  
27 data are relevant to the analysis of Tris solubilities at temperatures above 25 °C, because the values of  
28 the water activities of aqueous Tris are currently known only at 25 °C up to saturation at that  
29 temperature (about 5.7 mol kg<sup>-1</sup>). The results of these experiments are presented in the Appendix.  
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#### 38 4. THEORY

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40 The equilibrium between pure solid phase Tris and its saturated solution is given by:  
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$$45 K_S(\text{Tris}) = m_{\text{Tris}} \cdot \gamma_{\text{Tris}} \quad (6b)$$

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49 where  $m_{\text{Tris}}$  is the molality of Tris,  $\gamma_{\text{Tris}}$  is its molality-based activity coefficient, and  $K_S$  (mol kg<sup>-1</sup>) is  
50 the equilibrium constant which is a function of temperature and pressure. The corresponding  
51 equilibrium for NaCl is:  
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$$K_S(\text{NaCl}) = m\text{Na}^+ m\text{Cl}^- \cdot \gamma_{\text{Na}} \gamma_{\text{Cl}} \quad (7b)$$

where  $m\text{Na}^+$  and  $m\text{Cl}^-$  are the molalities of the two ions in the solution saturated with respect to solid NaCl,  $\gamma_{\text{Na}}$  and  $\gamma_{\text{Cl}}$  are their activity coefficients, and  $K_S(\text{NaCl})$  ( $\text{mol}^2 \text{kg}^{-2}$ ) is the equilibrium constant.

The variation of the Tris and NaCl solubilities with the composition of the solution medium reflects changes in the activity coefficients in the above equations. These can be expressed using the Pitzer equations<sup>7</sup> in terms of interactions between the species present. The Pitzer model expression for the activity coefficient of an uncharged solute N in a solution of a single electrolyte  $M_{v^+}X_{v^-}$  is:

$$\begin{aligned} \ln(\gamma_N) = & 2mN \cdot \lambda_{N,N} + 3mN^2 \cdot \mu_{N,N,N} + 2mM^{z^+} \cdot \lambda_{N,M} + 2mX^{z^-} \cdot \lambda_{N,X} \\ & + mM^{z^+} \cdot mX^{z^-} \cdot \zeta_{N,M,X} + 6mN \cdot mM^{z^+} \cdot \mu_{N,N,M} + 6mN \cdot mX^{z^-} \cdot \mu_{N,N,X} \end{aligned} \quad (8)$$

where parameters  $\lambda_{N,N}$  and  $\mu_{N,N,N}$  describe the self-interactions of solute N, and  $\lambda_{N,M}$  and  $\lambda_{N,X}$  the interactions with cation  $M^{z^+}$  and anion  $X^{z^-}$ , respectively. In addition, there are parameters for higher order interactions of solute N with the cation and anion together ( $\zeta_{N,M,X}$ ), and two molecules of solute N with the cation ( $\mu_{N,N,M}$ ), and with the anion ( $\mu_{N,N,X}$ ). Because of the constraint of electroneutrality the interactions with single ions can only be determined in combination, and not individually. For this reason it is conventional to set the parameter for the interaction with one ion to zero,<sup>22, 25</sup> and we do this here for  $\text{Cl}^-$  so that both  $\lambda_{\text{Tris},\text{Cl}}$  and  $\mu_{\text{Tris},\text{Tris},\text{Cl}}$  are set to zero.

The expression for the mean activity coefficient of NaCl ( $\gamma_{\text{NaCl}}$ , given by  $\ln(\gamma_{\text{NaCl}}) = (1/2)[\ln(\gamma_{\text{Na}}) + \ln(\gamma_{\text{Cl}})]$ ) in a solution also containing an uncharged solute N can be written:

$$\begin{aligned} \ln(\gamma_{\text{NaCl}}) = & -A^\phi [I^{1/2}]/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2}) \\ & + m\text{NaCl} (2\beta_{\text{NaCl}}^{(0)} + \beta_{\text{NaCl}}^{(1)}[\exp(-\alpha I^{1/2}) + g(\alpha I^{1/2})]) \\ & + m\text{NaCl}^2 (3C_{\text{NaCl}}^{(0)} + 2C_{\text{NaCl}}^{(1)}[\exp(-\omega I^{1/2}) + 2h(\omega I^{1/2})]) \\ & + mN \cdot \lambda_{N,\text{Na}} + mN \cdot m\text{NaCl} \cdot \zeta_{N,\text{Na},\text{Cl}} + (3/2)mN^2 \cdot \mu_{N,N,\text{Na}} \end{aligned} \quad (9)$$

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3 where  $A^\phi$  is the Debye Hückel constant<sup>26</sup> (0.391475 at 25 °C and 1 atm pressure),  $I$  (mol kg<sup>-1</sup>) is the  
4 ionic strength of the solution, prefix  $m$  denotes molality, and quantities  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^{(0)}$ , and  $C^{(1)}$  are  
5 parameters for the interaction of Na<sup>+</sup> with Cl<sup>-</sup> ions (determined from measurements of solute and  
6 solute activities in pure aqueous NaCl solutions). The quantities  $\alpha$  (2.0) and  $\omega$  (2.5) are constants, and  
7 the functions  $g(x)$  and  $h(x)$  are given by:  
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$$14 \quad g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \quad (10)$$

$$15 \quad h(x) = \{6 - [6 + x(6 + 3x + x^2)]\exp(-x)\}/x^4 \quad (11)$$

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20 The elements of eq 9 for the Na<sup>+</sup> – Cl<sup>-</sup> interactions can be derived from the equations in Appendix I of  
21 Clegg et al.<sup>27</sup> for the general case of a mixture of electrolytes containing an arbitrary number of ions.  
22 Generalised expressions for the activity coefficients of neutral (i.e., uncharged) solutes, and for the  
23 contributions of ion-neutral interactions to the activity coefficients of ions, are given by Pitzer.<sup>7</sup>  
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30 The existence of three common parameters in eq 9, and in eq 8 for the interaction of uncharged  
31 solute N and Na<sup>+</sup> and Cl<sup>-</sup> ions, implies that the effect of dissolved NaCl on Tris solubility, and vice  
32 versa, can be determined from measurements of the solubility of either component in a solution of the  
33 other. It also means that where both have been measured, as in the present study, the results can be  
34 tested for mutual consistency. More broadly, it is possible to compare the results with any  
35 thermodynamic measurement yielding solute or solvent activities from which values of the same  
36 parameters can be derived (for example, see the study of Clegg and Brimblecombe<sup>22</sup> of the solubility  
37 of NH<sub>3</sub> in aqueous salt solutions).  
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## 49 **5. MODELLING AND COMPARISONS WITH OTHER DATA**

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51 In this section we use the Pitzer model to compare the results of the solubility experiments with data  
52 for the stoichiometric dissociation constant of TrisH<sup>+</sup> in aqueous NaCl, and EMF measurements of  
53 solutions containing dissolved Tris, TrisHCl and NaCl. These comparisons are made at 25 °C because  
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it is at this temperature that water activities of aqueous Tris and TrisHCl solutions have been determined<sup>11</sup> and Pitzer interaction parameters – necessary for the analysis – are known.

**5.1 Tris – TrisHCl – NaCl Solutions.** The parameters in eq 8 and 9 that describe the salting out behaviour that is observed in aqueous Tris – NaCl mixtures (Figures 6 and 7) are  $\lambda_{\text{Tris,Na}}$ ,  $\zeta_{\text{Tris,Na,Cl}}$ , and possibly  $\mu_{\text{Tris,Tris,Na}}$ . Of these, the first parameter is likely to be the most important. There are two other types of measurement that are relevant, and for which the activity coefficient equations contain the same parameters: titrations yielding values of the stoichiometric dissociation constant of TrisH<sup>+</sup> in aqueous NaCl,<sup>13</sup> and measurements of EMFs of cells containing dissolved NaCl, TrisHCl, and Tris.<sup>28</sup> These measurements, and the parameter values that can be obtained from them, are considered below.

**5.1.1 Dissociation Constants of TrisH<sup>+</sup> in Aqueous NaCl.** The stoichiometric dissociation constant ( $K^*(\text{TrisH}^+)$ ) is defined by:

$$K^*(\text{TrisH}^+) = m_{\text{H}^+} \cdot m_{\text{Tris}} / m_{\text{TrisH}^+} \quad (12a)$$

$$= K(\text{TrisH}^+) \cdot \gamma_{\text{TrisH}} / (\gamma_{\text{H}} \cdot \gamma_{\text{Tris}}) \quad (12b)$$

The value of  $K(\text{TrisH}^+)$  is  $8.47504 \times 10^{-9} \text{ mol kg}^{-1}$  at 25 °C,<sup>2</sup> and the activity coefficients are for trace quantities of the three species in the aqueous NaCl medium. The Pitzer model expressions for these activity coefficients involve parameters for TrisH<sup>+</sup>-Cl<sup>-</sup> and H<sup>+</sup>-Cl<sup>-</sup> interactions, which are known from thermodynamic data for TrisHCl<sub>(aq)</sub> and HCl<sub>(aq)</sub>, and the following mixture parameters:  $\theta_{\text{TrisH,Na}}$ ,  $\psi_{\text{TrisH,Na,Cl}}$ ,  $\lambda_{\text{Tris,Na}}$ , and  $\zeta_{\text{Tris,Na,Cl}}$ . Expressions for the contributions of all the ion interaction parameters to the activity coefficients of TrisH<sup>+</sup> and H<sup>+</sup> can be found in the generalised equations given by Pitzer<sup>7</sup> and by Clegg et al.<sup>27</sup> Combining these expressions, and the relevant parts of eq 8 for  $\ln(\gamma_{\text{Tris}})$ , we obtain:

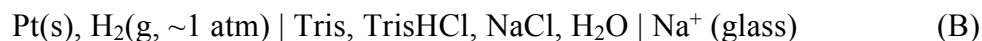
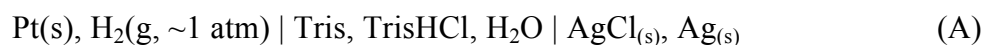
$$\begin{aligned} \ln(K^*(\text{TrisH}^+)) &= \ln(K(\text{TrisH}^+)) + \{\text{TrisH}^+\text{-Cl}^- \text{ terms}\} - \{\text{H}^+\text{-Cl}^- \text{ terms}\} \\ &+ 2m_{\text{NaCl}} \cdot (\theta_{\text{TrisH,Na}} - \theta_{\text{H,Na}} - \lambda_{\text{Tris,Na}}) \end{aligned}$$

$$+ m\text{NaCl}^2 \cdot (\psi_{\text{TrisH,Na,Cl}} - \psi_{\text{H,Na,Cl}} - \zeta_{\text{Tris,Na,Cl}}) \quad (13)$$

The two terms for  $\text{H}^+\text{-Cl}^-$  and  $\text{TrisH}^+\text{-Cl}^-$  interactions in the equation are those that involve parameters  $\beta_{\text{ca}}^{(0)}$ ,  $\beta_{\text{ca}}^{(1)}$ , and  $C_{\text{ca}}^{(0)}$  for cations  $\text{TrisH}^+$  and  $\text{H}^+$ , and anion  $\text{Cl}^-$ . Their values, and those of the two known mixture parameters  $\theta_{\text{H,Na}}$  and  $\psi_{\text{H,Na,Cl}}$ , are given in Table 8. See the Supporting Information for details of the determination of the  $\text{TrisH}^+\text{-Cl}^-$  parameters.

The values of  $K^*(\text{TrisH}^+)$  measured by Millero et al.<sup>13</sup> in 0.5 to 6.0 mol  $\text{kg}^{-1}$  aqueous NaCl are listed in their Table 1. These data show a close to linear relationship of  $\text{p}K^*(\text{TrisH}^+)$  with  $m\text{NaCl}$ . Taking the known values of  $\theta_{\text{H,Na}}$  and  $\psi_{\text{H,Na,Cl}}$  from Table 8, and fitting the measured  $\text{p}K^*(\text{TrisH}^+)$ , yields  $(\theta_{\text{TrisH,Na}} - \lambda_{\text{Tris,Na}}) = -0.02632 \pm 0.0015$  and  $(\psi_{\text{TrisH,Na,Cl}} - \zeta_{\text{Tris,Na,Cl}}) = 0.0$ . The results are shown in Figure 8. Note that the quoted uncertainty does not take into account those inherent in the cation-anion interaction parameters in Table 8, or those of the mixture parameters  $\theta_{\text{H,Na}}$  and  $\psi_{\text{H,Na,Cl}}$ .

**5.1.2 Electromotive Forces of Cells Containing Aqueous Tris, TrisHCl and NaCl.** Tishchenko<sup>28</sup> has measured EMFs of the following cells from 0 °C to 40 °C:



In the experiments in Cell A, the molalities of Tris ranged from 0.01 to 0.1 mol  $\text{kg}^{-1}$  and those of TrisHCl from 0.0075 to 4.0 mol  $\text{kg}^{-1}$ . In Cell B the EMFs of equimolal 0.04 mol  $\text{kg}^{-1}$  Tris/TrisH<sup>+</sup> in 0.05 to 4.0 mol  $\text{kg}^{-1}$  NaCl were measured, and also solutions of equimolal TrisHCl/NaCl (0.1 to 4.0 mol  $\text{kg}^{-1}$  total Cl<sup>-</sup>) containing 0.025 to 3.79 mol  $\text{kg}^{-1}$  Tris. In the definitions of the cells above, the partial pressure of H<sub>2</sub> is equal to the atmospheric pressure at the time of measurement (which was not recorded) minus the partial pressure of water in the saturated stream of H<sub>2</sub> gas. This partial pressure is equal to  $a_{\text{H}_2\text{O}} \cdot p_{\text{H}_2\text{O}}^0$  where  $a_{\text{H}_2\text{O}}$  is the water activity of the test solution and  $p_{\text{H}_2\text{O}}^0$  is the vapour pressure of pure water<sup>29</sup> at the experimental temperature. Tishchenko<sup>28</sup> used his data, with the Pitzer



equations, to develop a thermodynamic model of TrisHCl-NaCl-Tris aqueous solutions. The parameters that were obtained at 25 °C are listed in Table 9. Note that the standard EMFs of the two cells were not determined directly, but were fitted as constants (at each temperature) as a part of the model development process.

The equation relating the measured EMFs to the activities of H<sup>+</sup> and Cl<sup>-</sup> (Cell A) is given below.

$$E_{(\text{meas})} = E^0 + (RT/2F) \cdot \ln(P - p_{\text{H}_2\text{O}} - \text{Jet corr.}) - (RT/F) \cdot \ln(a_{\text{H}^+} \cdot a_{\text{Cl}^-}) \quad (14)$$

In this expression,  $E_{(\text{meas})}$  (V) is the measured EMF at the partial pressure of H<sub>2</sub> in the gas stream,  $E^0$  (V) is the standard EMF of the cell,  $R$  (8.31446 J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant,  $F$  (96485.33 C mol<sup>-1</sup>) is Faraday's constant,  $P$  (atm) is the atmospheric pressure, and  $p_{\text{H}_2\text{O}}$  (atm) is the equilibrium vapour pressure of water above the aqueous test solution. The quantity *Jet corr.* is a small pressure correction related to the depth of the H<sub>2</sub> bubbler below the solution surface in the half cell containing the Pt H<sub>2</sub> electrode.<sup>30</sup> It was assumed to be negligible in these experiments. The activity of H<sup>+</sup> in eq 14 above can be replaced by an expression involving the dissociation of TrisH<sup>+</sup>, and simplified:

$$E_{(\text{meas})} = E^0 + (RT/2F) \cdot \ln(P - p_{\text{H}_2\text{O}}) - (RT/F) \cdot \ln[K(\text{TrisH}^+) \cdot a_{\text{TrisH}^+} \cdot a_{\text{Cl}^-} / a_{\text{Tris}}] \quad (15a)$$

$$= E^0 - (RT/F) \cdot \ln[K(\text{TrisH}^+)] + (RT/2F) \cdot \ln(P - a_{\text{H}_2\text{O}} \cdot p_{\text{H}_2\text{O}}^0) - (RT/F) \cdot \ln(m_{\text{TrisH}^+} \cdot m_{\text{Cl}^-} / m_{\text{Tris}}) - (RT/F) \cdot \ln(\gamma_{\text{TrisH}} \gamma_{\text{Cl}^-} / \gamma_{\text{Tris}}) \quad (15b)$$

In this equation, which is equivalent to eq 1 of Tishchenko,<sup>28</sup> the only unknowns are  $E^0$ ,  $a_{\text{H}_2\text{O}}$ , and the final activity coefficient term. For a solution containing only TrisHCl and Tris, the Pitzer activity coefficient model expression can be written:

$$\ln(\gamma_{\text{TrisH}} \gamma_{\text{Cl}^-} / \gamma_{\text{Tris}}) = \ln(K(\text{TrisH}^+)) + \{\text{TrisH}^+, \text{Cl}^- \text{ terms}\} - \{\text{Tris terms}\} + 2(m_{\text{Tris}} - m_{\text{TrisHCl}}) \cdot \lambda_{\text{Tris}, \text{TrisH}}$$

$$\begin{aligned}
 & + m_{\text{Tris}} \cdot m_{\text{TrisHCl}} \cdot (2\zeta_{\text{Tris,TrisH,Cl}} - 6\mu_{\text{Tris,Tris,TrisH}}) \\
 & + 3m_{\text{Tris}}^2 \cdot \mu_{\text{Tris,Tris,TrisH}} - m_{\text{TrisHCl}}^2 \cdot \zeta_{\text{Tris,TrisH,Cl}} \quad (16)
 \end{aligned}$$

where the quantity {TrisH<sup>+</sup>, Cl<sup>-</sup> terms} is the sum of the Pitzer model terms for the logarithm of the activity coefficient product of TrisH<sup>+</sup> and Cl<sup>-</sup> in a pure aqueous solution of TrisHCl at its molality in the mixture. It can be calculated at 25 °C using the parameters for TrisH<sup>+</sup>-Cl<sup>-</sup> interactions listed in Table 8. Similarly, the quantity {Tris terms} is the contribution to ln( $\gamma_{\text{Tris}}$ ) of the model terms that arise in a pure aqueous solution of Tris at its molality in the mixture ( $2m_{\text{Tris}} \cdot \lambda_{\text{Tris,Tris}} + 3m_{\text{Tris}}^2 \cdot \mu_{\text{Tris,Tris,Tris}}$ , see eq 8 above). The unknowns in the equation are the mixture parameters  $\lambda_{\text{Tris,TrisH}}$ ,  $\zeta_{\text{Tris,TrisH,Cl}}$ , and  $\mu_{\text{Tris,Tris,TrisH}}$ . An analogous expression, containing the same parameters, can be written for the osmotic coefficient of the solution, and hence the water activity  $a_{\text{H}_2\text{O}}$ , in eq 15. These parameters appear both in the Pitzer expression for the activity coefficient of Tris in TrisHCl and (TrisH)<sub>2</sub>SO<sub>4</sub> solutions (from eq 8), and in those for the activity coefficients that can be determined from the measurements by Tishchenko<sup>28</sup> using Cell B.

The following expression relates the measured EMF in Cell B to the activities of H<sup>+</sup> and Na<sup>+</sup> in the test solutions:

$$E_{(\text{meas})} = E^0 + (RT/2F) \cdot \ln(P - p_{\text{H}_2\text{O}} - \text{Jet corr.}) - (RT/F) \cdot \ln(a_{\text{H}^+}/a_{\text{Na}^+}) \quad (17)$$

A similar analysis to that carried out for Cell A yields:

$$\begin{aligned}
 E_{(\text{meas})} = E^0 + (RT/2F) \cdot \ln(P - p_{\text{H}_2\text{O}}) \\
 - (RT/F) \cdot \ln[K(\text{TrisH}^+) \cdot a_{\text{TrisH}^+}/(a_{\text{Tris}} \cdot a_{\text{Na}^+})] \quad (18a)
 \end{aligned}$$

$$\begin{aligned}
 = E^0 - (RT/F) \cdot \ln[K(\text{TrisH}^+)] + (RT/2F) \cdot \ln(P - a_{\text{H}_2\text{O}} \cdot p_{\text{H}_2\text{O}}^0) \\
 - (RT/F) \cdot \ln(m_{\text{TrisH}^+}/(m_{\text{Tris}} \cdot m_{\text{Na}^+})) - (RT/F) \cdot \ln(\gamma_{\text{TrisH}}/(\gamma_{\text{Tris}} \cdot \gamma_{\text{Na}})) \quad (18b)
 \end{aligned}$$

In this equation the unknowns are again  $E^0$ ,  $a_{\text{H}_2\text{O}}$ , and the final activity coefficient term. For a solution containing NaCl, TrisHCl and Tris, the Pitzer activity coefficient model expression is more complex than eq 16 and contains several additional mixture parameters:

$$\begin{aligned} \ln(\gamma_{\text{TrisH}}/\gamma_{\text{Tris}}\gamma_{\text{Na}}) = & \ln(K(\text{TrisH}^+)) + \{\text{TrisH}^+\text{-Cl}^- \text{ terms}\} - \{\text{Na}^+\text{-Cl}^- \text{ terms}\} - \{\text{Tris terms}\} \\ & + 2m\text{Tris}\cdot(\lambda_{\text{Tris,TrisH}} - \lambda_{\text{Tris,Na}}) + 2m\text{Na}^+\cdot(\theta_{\text{Na,TrisH}} - \lambda_{\text{Tris,Na}}) \\ & - 2m\text{TrisH}^+\cdot(\theta_{\text{Na,TrisH}} + \lambda_{\text{Tris,TrisH}}) + m\text{Tris}\cdot m\text{Cl}^-\cdot(\zeta_{\text{Tris,TrisH,Cl}} - \zeta_{\text{Tris,Na,Cl}}) \\ & + m\text{Na}^+\cdot m\text{Cl}^-\cdot(\psi_{\text{Na,TrisH,Cl}} - \zeta_{\text{Tris,Na,Cl}}) - m\text{TrisH}^+\cdot m\text{Cl}^-\cdot(\psi_{\text{Na,TrisH,Cl}} + \zeta_{\text{Tris,TrisH,Cl}}) \\ & + m\text{Tris}\cdot m\text{Na}^+\cdot(\eta_{\text{Tris,Na,TrisH}} - 6\mu_{\text{Tris,Tris,Na}}) - m\text{Tris}\cdot m\text{TrisH}^+\cdot(\eta_{\text{Tris,Na,TrisH}} + \mu_{\text{Tris,Tris,TrisH}}) \\ & - m\text{Na}^+\cdot m\text{TrisH}^+\cdot\eta_{\text{Tris,Na,TrisH}} + 3m\text{Tris}^2\cdot(\mu_{\text{Tris,Tris,TrisH}} - \mu_{\text{Tris,Tris,Na}}) \end{aligned} \quad (19)$$

In the above expression  $\{\text{TrisH}^+\text{-Cl}^- \text{ terms}\}$  is the sum of the Pitzer model contributions to  $\ln(\gamma_{\text{TrisH}})$  that arise from the interactions of  $\text{TrisH}^+$  with  $\text{Cl}^-$  only, and the meaning of  $\{\text{Na}^+\text{-Cl}^- \text{ terms}\}$  is analogous. The quantity  $\{\text{Tris terms}\}$  is the same as for eq 16. All three terms can be calculated using the parameters in Table 8. The contributions of the mixture terms have been written out in full, even though only a subset of these are likely to be significant. See Pitzer<sup>7</sup> for the general expressions for ion and neutral species activity coefficients, and the osmotic coefficient of the solution, that include these types of parameters. The mixture parameters that are common to both the Cell A and Cell B expressions are  $\lambda_{\text{Tris,TrisH}}$ ,  $\zeta_{\text{Tris,TrisH,Cl}}$  and  $\mu_{\text{Tris,Tris,TrisH}}$ .

The Pitzer model parameters obtained by Tishchenko,<sup>28</sup> and listed in Table 9, include values for both  $\text{TrisH}^+\text{-Cl}^-$  interactions ( $\beta_{\text{TrisH,Cl}}^{(0)}$ ,  $\beta_{\text{TrisH,Cl}}^{(1)}$  and  $C_{\text{TrisH,Cl}}^{(0)}$ ), and Tris self-interactions ( $\lambda_{\text{Tris,Tris}}$  and  $\mu_{\text{Tris,Tris,Tris}}$ ). In addition to fitting the data from Cells A and B, Tishchenko also used isopiestic measurements of the water activities of aqueous TrisHCl and Tris solutions at 25 °C.<sup>11</sup> However, the values of  $\lambda_{\text{Tris,Tris}}$  and  $\mu_{\text{Tris,Tris,Tris}}$  that were obtained are not consistent with the results of Robinson and Bower,<sup>11</sup> which show close to ideal behaviour. For our own analysis of the EMF results we first

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3 fitted the two Pitzer model coefficients to the isopiestic data, recalculated using values for the NaCl  
4 reference solutions from the study of Archer<sup>21</sup> (see Table 8, and the Appendix).

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7 Tishchenko<sup>28</sup> carried out two sets of experiments using Cell B. In the first of these, the solution  
8 compositions were chosen so that the only unknown mixture parameters (in addition to  $\lambda_{\text{Tris,TrisH}}$  and  
9  $\zeta_{\text{Tris,TrisH,Cl}}$  whose values can be determined from data from Cell A) are  $\lambda_{\text{Tris,Na}}$  and  $\zeta_{\text{Tris,Na,Cl}}$  (we  
10 neglect, for now, the other ternary parameters  $\eta_{\text{Tris,Na,TrisH}}$ ,  $\mu_{\text{Tris,Tris,TrisH}}$ , and  $\psi_{\text{Tris,Tris,Na}}$ ). In the second  
11 set of experiments the additional unknowns are  $\theta_{\text{Na,TrisH}}$  and  $\phi_{\text{Na,TrisH,Cl}}$ . We have fitted the data for  
12 Cells A and B, while applying the constraints  $\psi_{\text{Na,TrisH,Cl}} = \zeta_{\text{Tris,Na,Cl}}$  and  $(\theta_{\text{Na,TrisH}} - \lambda_{\text{Tris,Na}}) = -0.02632$   
13 determined in section 5.1.1 above from the titration measurements. The results are listed in Table 10,  
14 and plotted in Figure 9. This figure shows the fitted activity coefficient products, and the values  
15 derived from the EMF measurements. For Cell A, and for the experiments in Cell B in which the  
16 solutions contain equimolal 0.04 m Tris and TrisH<sup>+</sup>, the results are satisfactory over the entire chloride  
17 molality range, with no systematic deviations apparent in the residuals. In the case of the Cell B  
18 solutions containing high molalities of Tris (Figure 9c) there is a clear trend in the residuals with Tris  
19 molality, with the most positive values at about 1.0 mol kg<sup>-1</sup> Tris. Removal of data for these higher  
20 Tris molalities allows  $\zeta_{\text{Tris,TrisH,Cl}}$  to be omitted from the fit, and yields a value of  $\lambda_{\text{Tris,TrisH}}$  close to that  
21 obtained by Tishchenko.  
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42 **5.1.3 Solubilities of Tris in Aqueous TrisHCl.** We have fitted the measured solubilities at 25 °C to  
43 obtain  $\lambda_{\text{Tris,TrisH}} = -0.01241 \pm 0.00098$ , see Figure 10. The salting-in behaviour observed in these  
44 mixtures is also implied by the negative value obtained by Tishchenko for the same parameter (Table  
45 9). However, his value of  $\lambda_{\text{Tris,TrisH}}$  (-0.02445) is of greater magnitude. In our fit of the data for Cells A  
46 and B, see Table 10, the parameter  $\zeta_{\text{Tris,TrisH,Cl}}$  was found to be significant, and in this result the value  
47 of  $\lambda_{\text{Tris,TrisH}}$  (-0.0197) is also more negative than for the solubility data.  
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3 As a further test, we fitted the data for Cell A only and obtained  $\lambda_{\text{Tris,TrisH}}$  equal to -0.0228, which is  
4 quite close to Tischenko's result. It therefore appears that the measured Tris solubilities in these  
5 solutions and the EMF data for Cell A are not fully thermodynamically consistent: the EMF  
6 measurements imply a greater degree of salting-in (i.e., corresponding to a more negative value of  
7  $\lambda_{\text{Tris,TrisH}}$ ) than is observed. Finally, it is also possible that the interaction parameter  $\mu_{\text{Tris,Tris,TrisH}}$  has a  
8 non-zero value. It could significantly influence the description of the solubilities by eq 6 and 8, a  
9 positive value of  $\mu_{\text{Tris,Tris,TrisH}}$  implying a more negative  $\lambda_{\text{Tris,TrisH}}$ . It would have a negligible effect for  
10 the solutions measured in Cell A, in which the Tris molalities were all 0.1 mol kg<sup>-1</sup> or lower. We note  
11 that this type of parameter was found, in an earlier study, to be needed to describe solubilities of  
12 several electrolytes in aqueous NH<sub>3</sub>. However, this was for molalities of NH<sub>3</sub> of 20 mol kg<sup>-1</sup> or more,  
13 which are far greater than the Tris molalities in our experiments.  
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28 **5.1.4 Solubilities of Tris in Aqueous NaCl.** The salting out of Tris by dissolved NaCl decreases  
29 with NaCl molality, see Figure 6. We first fitted eq 6 and eq 8 to solubilities of Tris at 25 °C from 0 to  
30 4.0 mol kg<sup>-1</sup> NaCl – ignoring the final data point which appears to be anomalously high – and obtained  
31  $\lambda_{\text{Tris,Na}} = 0.02817 \pm 0.00077$ . Measured and calculated solubilities are shown in Figure 11. This value  
32 of  $\lambda_{\text{Tris,Na}}$  is similar to that obtained by Tishchenko (0.02106, Table 9). However, in our fit of the EMF  
33 data we obtained  $\zeta_{\text{Tris,Na,Cl}}$  equal to -0.00940 (Table 10). Including this parameter, fixed to the same  
34 value, in a fit of the Tris solubilities yields  $\lambda_{\text{Tris,Na}}$  equal to  $0.0420 \pm 0.00090$ , and the dashed line in  
35 Figure 11. This is similar to the value we obtained from the EMFs (Table 10). However, this pair of  
36 parameter values implies an *increase* in solubility of NaCl in aqueous Tris solutions, which is not  
37 what is observed.  
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51 **5.1.5 Solubilities of NaCl in Aqueous Tris.** The solubility of NaCl in water is only slightly reduced  
52 by the presence of Tris, from about 6.15 mol kg<sup>-1</sup> in pure water to just below 6.0 mol kg<sup>-1</sup> in 4 to 5 mol  
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kg<sup>-1</sup> Tris solutions. A fit of the data to 3.5 mol kg<sup>-1</sup> Tris, using eq 7 and 9, yielded  $\lambda_{\text{Tris,Na}}$  equation to  $0.0163 \pm 0.0023$  (with  $\zeta_{\text{Tris,Na,Cl}}$  set to zero). This result is very dependent upon the maximum Tris molality of the fit though, and reductions to 2.0 and then 1.0 mol kg<sup>-1</sup> Tris yield  $\lambda_{\text{Tris,Na}}$  equal to  $0.01815 \pm 0.0029$  and  $0.02740 \pm 0.0037$ , respectively.

Fixing  $\zeta_{\text{Tris,Na,Cl}} = -0.00940$  (the value obtained by fitting to the EMF data) and refitting the NaCl solubilities yields  $\lambda_{\text{Tris,Na}}$  equal to  $0.0726 \pm 0.0023$  which is much larger than the 0.0466 obtained from the EMF data. Calculated solubilities for the three cases are shown in Figure 12. The slope of the 0 to 1.0 mol kg<sup>-1</sup> Tris molality range ( $\lambda_{\text{Tris,Na}}$  equal to 0.02740) is consistent with that for Tris solubility in aqueous NaCl ( $\lambda_{\text{Tris,Na}}$  equal to 0.02817).

In order to understand the observed behaviour better, we have used the measured solubilities to calculate the quantity  $\Delta \ln(\gamma_{\text{Na}} \cdot \gamma_{\text{Cl}})$ , given by:

$$\Delta \ln(\gamma_{\text{Na}} \cdot \gamma_{\text{Cl}}) = \ln(K_S(\text{NaCl})) - \ln(m\text{Na}^+) - \ln(m\text{Cl}^-) - \ln(\gamma_{\text{Na}})^P - \ln(\gamma_{\text{Cl}})^P \quad (20)$$

where  $K_S(\text{NaCl})$  (eq 7b) is the thermodynamic solubility product of NaCl at 25 °C (38.30 mol<sup>2</sup> kg<sup>-1</sup>),  $m\text{Na}^+$  and  $m\text{Cl}^-$  are the molalities of the ions in the solution saturated with respect to NaCl(s), and  $(\gamma_{\text{Na}})^P$  and  $(\gamma_{\text{Cl}})^P$  are the model-calculated activity coefficients of the ions in eq 9, but neglecting the mixture terms. Therefore:

$$\begin{aligned} \Delta \ln(\gamma_{\text{Na}} \cdot \gamma_{\text{Cl}}) = & 2 m\text{Tris} \cdot \lambda_{\text{Tris,Na}} + 2 m\text{Tris} \cdot m\text{NaCl} \cdot \zeta_{\text{Tris,Na,Cl}} \\ & + 3 m\text{Tris}^2 \cdot \mu_{\text{Tris,Tris,Na}} \end{aligned} \quad (21)$$

The value of the left hand side of eq 20, determined from the measured solubilities and calculated pure solution contributions to the activity coefficients  $(\gamma_{\text{Na}})^P$  and  $(\gamma_{\text{Cl}})^P$ , is plotted in Figure 13. The relationship with  $m\text{Tris}$  is non-linear. The values of  $\Delta \ln(\gamma_{\text{Na}} \cdot \gamma_{\text{Cl}})$  calculated using the  $\lambda_{\text{Tris,Na}}$  obtained by Tishchenko<sup>28</sup> from the EMF data, and by us from measured Tris solubilities in aqueous NaCl, are

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3 also shown in Figure 13 and are consistent with the data up to 1 mol kg<sup>-1</sup> Tris, but not for higher  
4 molalities. The measurements as a whole – including the solubilities at 3.5 and 4.5 mol kg<sup>-1</sup> Tris –  
5  
6 imply a non-zero value of  $\mu_{\text{Tris,Tris,Na}}$  rather than  $\zeta_{\text{Tris,Na,Cl}}$ . However, this parameter would also  
7  
8 contribute to activity coefficients in the solutions for which EMFs were measured (Cell B), and to the  
9  
10 activity coefficient of Tris in aqueous NaCl. Test calculations that we have carried out for these  
11  
12 solutions do not suggest this. The resolution of this discrepancy will require further measurements.  
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17 **5.2 Tris – (TrisH)<sub>2</sub>SO<sub>4</sub> Solutions.** The only data from which the Tris-SO<sub>4</sub><sup>2-</sup> interaction can be  
18  
19 determined are the solubilities of Tris in aqueous (TrisH)<sub>2</sub>SO<sub>4</sub> measured in this work. We note that  
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21 Millero et al.<sup>13</sup> measured  $\text{p}K^*(\text{TrisH}^+)$  in aqueous solutions containing both NaCl and Na<sub>2</sub>SO<sub>4</sub>, but the  
22  
23 bisulphate formation in these solutions (which was not independently determined) prevents the  
24  
25 quantitative determination of Tris-SO<sub>4</sub><sup>2-</sup> interactions from the data.  
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29 Tris is salted out by (TrisH)<sub>2</sub>SO<sub>4</sub>, see Figure 5b. We have fitted the data at 25 °C, using eq 6 and eq  
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31 8, to yield  $(2\lambda_{\text{Tris,TrisH}} + \lambda_{\text{Tris,SO}_4})$  equal to  $0.05763 \pm 0.0036$ . Measured and calculated solubilities are  
32  
33 shown in Figure 14. Adopting the value of  $\lambda_{\text{Tris,TrisH}}$  determined from the Tris solubilities in TrisHCl (-  
34  
35 0.01241),  $\lambda_{\text{Tris,SO}_4}$  is equal to  $0.08245 \pm 0.0041$ . As an alternative, the value of  $\lambda_{\text{Tris,TrisH}}$  obtained from  
36  
37 the fit to the EMF data (-0.0197) yields  $\lambda_{\text{Tris,SO}_4}$  equal to  $0.0970 \pm 0.0043$ . The strength of the Tris-  
38  
39 SO<sub>4</sub><sup>2-</sup> interaction is thus several times that of Tris-Na<sup>+</sup>. This is qualitatively similar to what has been  
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41 found for the solute NH<sub>3</sub> (see Table VI of Clegg and Brimblecombe<sup>22</sup>), although for that solute the  
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43 difference is larger.  
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## 47 48 **6. SUMMARY AND DISCUSSION**

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50 The purpose of this study is to make thermodynamic measurements that contribute to a Pitzer-based  
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52 speciation model of Tris pH buffers in solutions containing the components of artificial seawater. The  
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54 use of highly concentrated media – well above the 0.72 mol kg<sup>-1</sup> ionic strength of a seawater of  
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3 salinity 35 – increases the strength of the ion-ion and ion-Tris interactions, and in principle allows the  
4 interaction parameters to be more precisely determined. However, it is also the case that some higher  
5 order interactions may be needed in order to fit the experimental data. These parameters, principally  
6  $\mu_{\text{Tris,Tris,Na}}$  and  $\zeta_{\text{Tris,Na,Cl}}$ , have little effect in solutions of seawater ionic strength, but do influence the  
7 values of the important  $\lambda_{\text{Tris,ion}}$  parameters that are determined from the data.  
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12 Our measurements of Tris solubility in pure water (Figure 2) agree well with other data, and extend  
13 the range of measurements from 15 – 40 °C to 5 – 45 °C. The solubility of NaCl in pure water varies  
14 very little with temperature (e.g., from about 6.103 mol kg<sup>-1</sup> at 5 °C to 6.248 mol kg<sup>-1</sup> at 45 °C). Our  
15 results agree well with solubilities from the critical review of Cohen-Adad et al.<sup>19</sup> up to 30 °C, but  
16 appear to be systematically low by up to about 0.04 mol kg<sup>-1</sup> at higher temperatures, see Figure 3.  
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21 The compound Tris is salted out (its solubility reduced) in aqueous NaCl and (TrisH)<sub>2</sub>SO<sub>4</sub>, but  
22 salted in by TrisHCl. This is qualitatively similar behaviour to that of dissolved NH<sub>3</sub> in aqueous salt  
23 solutions. Robinson and Bower<sup>11</sup> have also noted that the measured osmotic coefficients of aqueous  
24 TrisHCl and NH<sub>4</sub>Cl at 25 °C are close in value up to about 1.0 mol kg<sup>-1</sup> concentration. Sodium  
25 chloride is salted out in aqueous Tris solutions.  
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30 Using the Pitzer activity coefficient model we have investigated the consistency of our results with  
31 measurements of the stoichiometric dissociation constant of TrisH<sup>+</sup> in aqueous NaCl at 25 °C, and of  
32 the EMFs of electrochemical cells containing dissolved Tris, TrisH<sup>+</sup>, Na<sup>+</sup> and Cl<sup>-</sup>. Data for osmotic  
33 coefficients of aqueous Tris and TrisHCl solutions were also used in the analyses of these results (and  
34 are described in the Supporting Information). In our treatment of the EMF data we constrained the  
35 fitted interaction parameters to agree with the dissociation constant results.  
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40 Solubilities of Tris in aqueous NaCl at 25 °C are described by a Tris-Na<sup>+</sup> interaction parameter  
41 ( $\lambda_{\text{Tris,Na}}$ ) equal to 0.02817. It is demonstrated in Figure 13 that this is consistent with the measured  
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3 solubilities of NaCl in aqueous Tris up to about 1 mol kg<sup>-1</sup>, and also with the value of  $\lambda_{\text{Tris,Na}}$  obtained  
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5 by Tishchenko<sup>28</sup> in his own fit of the EMF data. However, our own fits of the EMFs suggest that a  
6  
7 ternary interaction, described by the parameter  $\zeta_{\text{Tris,Na,Cl}}$ , is important. This is not consistent with the  
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9 values of  $\lambda_{\text{Tris,Na}}$  noted above nor with the measured solubilities of NaCl at high Tris molalities. It is  
10  
11 possible that either our measured solubilities for *m*Tris above 1 mol kg<sup>-1</sup> are systematically too high by  
12  
13 about 0.1 to 0.2 mol kg<sup>-1</sup> or that there is a higher order interaction (described by parameter  $\mu_{\text{Tris,Tris,Na}}$ )  
14  
15 that needs to be taken into account. It should also be borne in mind that there is no information with  
16  
17 which to evaluate the stability of the glass Na<sup>+</sup> electrode used by Tishchenko<sup>28</sup> for measurements of  
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19 Cell B, in response to the large range of Tris molalities used.  
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24 The measured salting in of Tris in TrisHCl solutions at 25 °C, represented using the interaction  
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26 parameter  $\lambda_{\text{Tris,TrisH}}$  equal to -0.01241, is qualitatively consistent with the EMF data, although the  
27  
28 parameter values determined from these measurements are larger in magnitude (see Tables 9 and 10).  
29  
30 In (TrisH)<sub>2</sub>SO<sub>4</sub> solutions Tris is salted out, and this behaviour is described at 25 °C by the combined  
31  
32 parameter ( $2\lambda_{\text{Tris,TrisH}} + \lambda_{\text{Tris,SO4}}$ ) equal to 0.05763. There are no other data to compare with this result.  
33  
34 The value of the interaction parameter  $\lambda_{\text{Tris,SO4}}$  determined from these measurements is clearly  
35  
36 dependent upon the value of  $\lambda_{\text{Tris,TrisH}}$  adopted.  
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40 Parameters for the fitting equations representing the Tris and NaCl solubilities at all temperatures  
41  
42 are listed in Table 7, and provisional values of the Tris-ion interaction parameters at 25 °C determined  
43  
44 from the solubility data, are given in Table 11. The estimation of interaction parameters at other  
45  
46 temperatures will require information on the variation of the osmotic and activity coefficients of  
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48 aqueous Tris with temperature or, for EMF measurements using Cell A, those of aqueous TrisHCl.  
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51 Gallego-Urrea and Turner<sup>6</sup> have investigated the use of the Pitzer model to calculate the pH of Tris  
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53 buffers in low salinity waters containing the ions Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, and compared  
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3 their results with EMF measurements of DelValls and Dickson<sup>3</sup> and Pratt.<sup>31</sup> Best results were obtained  
4 using a set of interaction parameters optimised by fitting to several datasets (see Figure 1 of Gallego-  
5 Urrea and Turner<sup>6</sup>), which suggested possible inconsistencies between the EMF data and osmotic  
6 coefficients of aqueous TrisHCl. The results presented in this work provide the first direct  
7 determinations of the Tris-SO<sub>4</sub><sup>2-</sup> and Tris-TrisH<sup>+</sup> interaction parameters ( $\lambda_{\text{Tris},\text{SO}_4}$  and  $\lambda_{\text{Tris},\text{TrisH}}$ ), which  
8 may help to resolve these differences. The interactions of the major seawater cations with Tris have  
9 previously been measured by Millero et al.<sup>13</sup> at 25 °C, although the titration approach used yields the  
10 value of  $(\theta_{\text{TrisH},\text{ion}} - \lambda_{\text{Tris},\text{ion}})$  rather than  $\lambda_{\text{Tris},\text{ion}}$ . The solubility results presented here for Tris-NaCl  
11 aqueous solutions enable  $\lambda_{\text{Tris},\text{Na}}$  to be determined independently, although there remain some  
12 unresolved questions regarding the solubility of NaCl at high Tris molalities (section 5.1.5).

13  
14  
15 Overall, it is clear that the thermodynamic information from existing data – solubilities, EMFs,  
16 osmotic coefficients, and potentiometric titrations – cannot yet be completely reconciled within the  
17 Pitzer activity coefficient model. However, some recent comparisons of modelled and measured EMFs  
18 of Tris buffers in artificial seawater (not shown) suggest that small revisions to the interaction  
19 parameters of TrisHCl are likely to result in improvements. Further measurements, especially using  
20 Harned Cells, of aqueous mixtures containing Tris, TrisHCl and the ions of seawater are also  
21 essential. Together they should enable the solubility data to be used to refine the speciation model of  
22 Tris buffer in solutions containing the ions of seawater at all temperatures.

#### 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 **AUTHOR INFORMATION**

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**Notes**

The authors declare no competing financial interest.

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**APPENDIX****OSMOTIC COEFFICIENTS OF AQUEOUS Tris AT VERY HIGH MOLALITIES**

Electrodynamic balances (edbs) have long been used to determine the relationship between water activity and aqueous concentration for

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3 solutions highly supersaturated with respect to dissolved solids.<sup>32</sup> In  
4 a typical edb, a single charged droplet, of about 5  $\mu\text{m}$  in diameter,  
5 is suspended in an atmosphere of controlled relative humidity ( $RH$ )  
6 and temperature, and the relative mass or diameter of the droplet is  
7 recorded as the  $RH$  is changed.<sup>32, 33</sup> Rovelli et al.<sup>24</sup> describe a  
8 refinement of this method, in which  $RH$  is reduced rapidly in the  
9 chamber, and the equilibrium  $p_{\text{H}_2\text{O}}$  (hence water activity) of the  
10 droplet is calculated from its size change relative to a similar  
11 droplet containing a known standard such as NaCl. The droplet is  
12 illuminated by light from a laser (Laser Quantum, Ventus, 532 nm) and  
13 the scattering pattern produced by the droplet in the forward  
14 direction takes the form of interference fringes. The angular  
15 separation between the fringes is used to measure the droplet  
16 diameter during evaporation.

17  
18 We have used this method to determine the water activities of  
19 supersaturated aqueous Tris solutions at 293 K. Densities of the  
20 aqueous particles, which are required for the processing of the  
21 results,<sup>24</sup> were calculated using densities of pure water from Kell<sup>34</sup>  
22 and the following expression for the apparent molar volume of Tris  
23 ( $V^\phi$ ) which was fitted to densities of Taha and Lee<sup>23</sup> (25  $^\circ\text{C}$  to 55  $^\circ\text{C}$ )  
24 and apparent molar volumes determined by Ford et al.<sup>35</sup> (at 0.35 MPa, 5  
25  $^\circ\text{C}$  to 65  $^\circ\text{C}$ ):

$$V^\phi = 72.5935 + 0.0631778 \cdot T + 1.05061 \cdot wtfrac \quad (A1)$$

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2  
3 where  $V^\phi$  ( $\text{cm}^3 \text{mol}^{-1}$ ) is the apparent molar volume of Tris,  $T$  (K) is  
4 temperature, and  $w_{\text{frac}}$  is the weight fraction of Tris in the pure  
5 aqueous solution. The results are shown in Figure A1.  
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10 The refractive index is also required to calculate the diameter from  
11 the elastic light scattering pattern using the geometric optics  
12 approximation.<sup>36</sup> Throughout an evaporation experiment the solution  
13 becomes more concentrated so the refractive index of a droplet is not  
14 constant. We account for this variation by using the following  
15 equation:<sup>37</sup>  
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$$n_e = [(2R_e + M_e/\rho_e)/(M_e/\rho_e - R_e)]^{1/2} \quad (\text{A2})$$

23  
24 where  $n_e$  (unitless) is the refractive index of the Tris solution,  $M_e$   
25 ( $\text{g mol}^{-1}$ ) is the mass of one mole of solution (water plus Tris),  $\rho_e$  ( $\text{g}$   
26  $\text{cm}^{-3}$ ) is its density, and  $R_e$  ( $\text{cm}^3 \text{mol}^{-1}$ ) is the molar refraction of the  
27 solution. The quantity  $R_e$  for an aqueous mixture is estimated using  
28 the following mole-fraction weighted summation of molar volumes and  
29 refractive indices of the pure liquid components:  
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$$R_e = \sum_i x_i V_i (n_i^2 - 1)/(n_i^2 + 2) \quad (\text{A3})$$

39  
40 where  $x_i$  is the mole fraction of component  $i$  in the mixture,  $V_i$  is  
41 its molar volume (equivalent to  $M_i/\rho_i$ ), and  $n_i$  is the refractive index  
42 of pure liquid  $i$ . (The value of the refractive index of water at 293  
43 K is 1.333, and the estimated molar volume of pure liquid Tris is  
44  $95.50 \text{ cm}^3 \text{mol}^{-1}$ .) The refractive indices ( $n_e$ ) of eight bulk aqueous  
45 Tris solutions, of weight fractions ranging from 0.01 to 0.34, were  
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3 measured at 293 K (using a MISCO PA203 refractometer, 589.3 nm).  
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5 These were then fitted using the above equations to obtain the value  
6  
7 of the pure component subcooled-melt refractive index of Tris,  $n_{\text{Tris}}$ ,  
8  
9 in eq A3. Its value was determined to be 1.5365.  
10  
11

12 Initially, the elastic light scattering collected by the edb was converted into a particle diameter using  
13  
14 a fixed refractive index of 1.335. In a post-processing step, the diameter change for each time step  
15  
16 (every  $\sim 0.01$  s) was used to estimate the refractive index, and then correct the diameters retrieved by  
17  
18 the edb. The corrected diameter yields a better estimate of the refractive index, and the estimate of the  
19  
20 diameter for every time step can be corrected again. This process is typically iterated three times to  
21  
22 allow convergence of the droplet diameter and refractive index values. The amount of Tris solute  
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24 present in the droplet during the experiment is known from the initial concentration of the droplet  
25  
26 solution.  
27  
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29

30 The electrodynamic balance and measurement procedure are as  
31  
32 described by Rovelli et al.<sup>24</sup> Probe droplets were used as reference  
33  
34 standards to determine the ambient relative humidity ( $RH$ , equivalent  
35  
36 to water activity) in the edb cell. The probe droplets consisted of  
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38 pure water (for  $RH > 80\%$ ) or aqueous NaCl (for  $RH$  between 45% and  
39  
40 80%). The experimental temperature was 293.5 K (20.4 °C). Four sets of  
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42 measurements were made, evaporating aqueous Tris particles into  
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44 ambient  $RH$  of 83%, 81%, 76%, and 68%, using a different initial  
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46 concentration of Tris in each case. These were highest for  
47  
48 evaporation into the lowest  $RH$  environments in order to reduce the  
49  
50 amount of evaporation experienced by the droplet (too rapid an  
51  
52 evaporation causes a reduction in droplet temperature and leads to  
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3 error). The concentrations of each dataset overlapped with the  
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5 previous one, and each one represents repeated measurements over 10  
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7 to 13 droplets, and the results averaged.  
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10 Bulk aqueous Tris solutions (Sigma Aldrich,  $\geq 99.9\%$ ) and aqueous NaCl solutions (Sigma Aldrich,  
11  
12 BioXtra,  $\geq 99.5\%$ ) were prepared using water (Fisher Scientific, HPLC Gradient Grade) with known  
13  
14 initial mass fraction. A single charged droplet of initial radius  $\sim 25 \mu\text{m}$  was generated from the bulk  
15  
16 solution using a microdispenser (MJ-ABP-01, MicroFab Technologies), outside of the edb chamber  
17  
18 and injected into the centre of the instrument. A sheath gas flow of  $\text{N}_2$  was continuously passed over  
19  
20 the levitated droplet at a velocity of  $3 \text{ cm s}^{-1}$  to keep the environment surrounding the droplet free of  
21  
22  $\text{CO}_2$ . The gas flow was formed by mixing a dry- and a humidified- $\text{N}_2$  gas flow so that the  $RH$  inside  
23  
24 the instrument could be controlled by varying the ratio between the flows with mass flow controllers  
25  
26 (mks).  
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30  
31 The osmotic coefficients determined from the measurements are presented in Table A1, and are  
32  
33 shown in Figure A2 where they are compared with values calculated using the Tris self-interaction  
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35 parameters determined in this work, and those determined by Tishchenko.<sup>28</sup> The extrapolated values  
36  
37 determined in this work by fitting only to the measurements of Robinson and Bower<sup>11</sup> agree more  
38  
39 closely with the measurements, especially in terms of the trend with molality, although there appears  
40  
41 to be an offset of about 0.03 in the osmotic coefficient. The reason for this is not known. The possible  
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43 influence of the  $5 \text{ }^\circ\text{C}$  difference in temperature can be qualitatively assessed by comparison with  $\text{NH}_3$   
44  
45 solutions. In a  $4 \text{ mol kg}^{-1}$   $\text{NH}_3$  solution, the increase in the osmotic coefficient from  $20 \text{ }^\circ\text{C}$  to  $25 \text{ }^\circ\text{C}$  is  
46  
47 about  $+0.003$  (calculated using the Pitzer model parameters given by Clegg and Brimblecombe<sup>22</sup>).  
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49 This is only about 10% of the difference that can be seen in the figure, which suggests that the  
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51 difference in temperature between the two experiments is not the cause of the apparent offset.  
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**Associated Content:**

- Osmotic coefficients of aqueous Tris and TrisHCl.
- Figure S1: Measured and fitted osmotic coefficients ( $\phi$ ) of aqueous TrisHCl at 25 °C, plotted against the square root of TrisHCl molality.
- Figure S2: Measured and fitted osmotic coefficients ( $\phi$ ) of aqueous Tris at 25 °C, plotted against Tris molality.

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31 NH<sub>4</sub>Cl from 0 to 50 °C, including extrapolations to very low  
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## TABLES

**Table 1.** Experimental solubilities  $m\text{Tris}_{(\text{sat.})}$  of Tris in pure water at temperature  $T^a$

$T$ (K)	$m\text{Tris}_{(\text{sat.})}$ ( $\text{mol} \cdot \text{kg}^{-1}$ )	Standard uncertainty $y, u(m)^b$	Source <sup>c</sup>	$T$ (K)	$m\text{Tris}_{(\text{sat.})}$ ( $\text{mol} \cdot \text{kg}^{-1}$ )	Standard uncertainty $y, u(m)^b$	Source <sup>c</sup>
278.2	3.6284	0.0385	1 (i)	298.1 5	5.780	0.008	3
283.2	4.1363	0.0171	1 (i)	298.1 5	5.76	0.02	5
288.2	4.3861	0.0647	1 (i)	303.2	6.1668	0.0593	1 (i)
288.2	4.5231	0.0298	1 (ii)	303.1 5	6.2568	0.0069	4
288.2	4.4917	0.0123	1 (iii)	308.2	7.0257	0.0337	1 (i)
288.1 5	4.564	0.0032	2	308.2	7.0798	0.0686	1 (ii)
288.1 5	4.593	0.001	3	308.2	7.0796	0.0884	1 (iii)
293.2	4.9570	0.0378	1 (i)	308.1 5	7.16	0.0012	2
293.1 5	5.0308	0.02	4	308.1 5	6.8536	0.091	4
298.2	5.6688	0.0190	1 (i)	308.1 5	7.261	0.004	3
298.2	5.8340	0.0461	1 (ii)	313.2	8.0106	0.0966	1 (i)
298.2	5.7421	0.0396	1 (iii)	313.1 5	7.7707	0.0072	4
298.1 5	5.766	0.0057	2	318.2	8.6632	0.0646	1 (i)



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3 298.1 5.6242 0.0068 4  
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6 <sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded  
7 uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol  
8  $\text{kg}^{-1}$  (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of  
9 the measurement of the molality of the Tris solute in the saturated  
10 solution, and is equal to the standard deviation of 6–13 molalities  
11 determined from replicate samples extracted from the flask containing  
12 the solution. <sup>c</sup>The sources of the parameters are as follows: 1 - this  
13 work ((i) from Tris solubility in NaCl experiments, (ii) from Tris  
14 solubility in TrisHCl experiments, and (iii) from Tris solubility in  
15  $(\text{TrisH})_2\text{SO}_4$  experiments); 2 - El-Harakany and Barakat;<sup>38</sup> 3 - Schindler  
16 *et al.*;<sup>39</sup> 4 - Jouyban-Gharamaleki *et al.*;<sup>40</sup> 5 - Taha and Lee.<sup>23</sup>  
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**Table 2.** Experimental solubilities  $m\text{NaCl}_{(\text{sat.})}$  of NaCl in pure water at temperature  $T$ <sup>a</sup>

$T$ (K)	$m\text{NaCl}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty, $u(m)$ <sup>b</sup>	$T$ (K)	$m\text{NaCl}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty, $u(m)$ <sup>b</sup>
278.2	6.0913	0.0075	303.2	6.1660	0.0166
283.2	6.0967	0.0581	308.2	6.1739	0.0067
288.2	6.1034	0.0061	313.2	6.1904	0.0102
293.2	6.1144	0.0366	318.2	6.2060	0.0083
298.2	6.1350	0.0067			

<sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol kg<sup>-1</sup> (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of the measurement of the molality of the NaCl solute in the saturated solution, and is equal to the standard deviation of 4-6 molalities determined from replicate samples extracted from the flask containing the solution.

**Table 3.** Experimental solubilities  $m\text{NaCl}_{(\text{sat.})}$  of NaCl in aqueous Tris of different concentrations at temperature  $T^a$

$T$ (K)	$m\text{Tris}$ (mol · k g <sup>-1</sup> )	$m\text{NaCl}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$	$T$ (K)	$m\text{Tris}$ (mol · k g <sup>-1</sup> )	$m\text{NaCl}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$
278. 2	0.500	6.0266	0.0097	283. 2	2.00	5.9412	0.0141
283. 2	0.500	6.0198	0.0207	288. 2	2.00	5.9549	0.0253
288. 2	0.500	6.0409	0.0526	293. 2	2.00	5.9716	0.0248
293. 2	0.500	6.0659	0.0081	298. 2	2.00	6.0319	0.015
298. 2	0.500	6.0925	0.0123	303. 2	2.00	6.0812	0.0167
303. 2	0.500	6.1366	0.0169	308. 2	2.00	6.1067	0.0094
308. 2	0.500	6.1386	0.0113	313. 2	2.00	6.1359	0.0055
313. 2	0.500	6.1355	0.0109	318. 2	2.00	6.1394	0.0204
318. 2	0.500	6.1628	0.0054	278. 2	2.50	5.9329	0.0189
278. 2	1.00	5.9796	0.0132	283. 2	2.50	5.9224	0.0098
283. 2	1.00	5.9871	0.0053	288. 2	2.50	5.9313	0.0131
288. 2	1.00	6.0013	0.0462	293. 2	2.50	5.9531	0.0317
293. 2	1.00	6.0225	0.0297	298. 2	3.50	5.9832	0.0298

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3	298.	1.00	6.0645	0.0259	303.	3.50	6.038	0.0174
4	2				2			
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6	303.	1.00	6.1102	0.0209	308.	3.50	6.0570	0.0164
7	2				2			
8								
9	308.	1.00	6.1208	0.0108	313.	3.50	6.1067	0.01
10	2				2			
11								
12	313.	1.00	6.1527	0.0097	318.	3.50	6.1003	0.0186
13	2				2			
14								
15	318.	1.00	6.164	0.013	298.	4.50	5.9903	0.033
16	2				2			
17								
18	278.	1.50	5.9545	0.0071	303.	4.50	6.0308	0.0194
19	2				2			
20								
21	283.	1.50	5.96	0.0145	308.	4.50	6.0636	0.0133
22	2				2			
23								
24	288.	1.50	5.979	0.0348	313.	4.50	6.1044	0.0134
25	2				2			
26								
27	293.	1.50	5.997	0.0056	318.	4.50	6.0989	0.0128
28	2				2			
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30								
31	278.	2.00	5.9339	0.0197				
32	2							
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<sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol  $\text{kg}^{-1}$  (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of the measurement of the molality of the NaCl solute in the saturated solution, and is equal to the standard deviation of 6-10 molalities determined from replicate samples extracted from the flask containing the solution. Molality ( $m$ ) is expressed in moles per kilogram of pure water.

**Table 4.** Experimental solubilities  $m\text{Tris}_{(\text{sat.})}$  of Tris in aqueous NaCl of different concentrations at temperature  $T^a$

$T$ (K)	$m\text{NaCl}$ (mol · k g <sup>-1</sup> )	$m\text{Tris}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$	$T$ (K)	$m\text{NaCl}$ (mol · k g <sup>-1</sup> )	$m\text{Tris}_{(\text{sat.})}$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$
278. 2	1.00	3.3863	0.0364	303. 2	3.00	5.4139	0.0258
283. 2	1.00	3.8018	0.0515	308. 2	3.00	6.2513	0.0235
288. 2	1.00	4.2572	0.025	313. 2	3.00	7.2871	0.0397
293. 2	1.00	4.7004	0.0047	318. 2	3.00	7.528	0.0155
298. 2	1.00	5.4387	0.0186	278. 2	4.00	2.9142	0.0557
303. 2	1.00	5.7671	0.0298	283. 2	4.00	3.3086	0.0319
308. 2	1.00	6.7232	0.0654	288. 2	4.00	3.6613	0.1358
313. 2	1.00	7.712	0.0827	293. 2	4.00	4.1425	0.0425
318. 2	1.00	7.9325	0.0296	298. 2	4.00	4.7093	0.0614
278. 2	2.00	3.1821	0.031	303. 2	4.00	5.2694	0.0516
283. 2	2.00	3.6071	0.0364	308. 2	4.00	6.1471	0.0662
288. 2	2.00	3.9981	0.0751	313. 2	4.00	7.1034	0.1037
293. 2	2.00	4.4653	0.0338	318. 2	4.00	7.3671	0.036

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3	298.	2.00	5.026	0.0746	278.	5.00	2.9414	0.0186
4	2				2			
5								
6	303.	2.00	5.4524	0.0223	283.	5.00	3.2258	0.0017
7	2				2			
8								
9	308.	2.00	6.4173	0.0862	288.	5.00	3.6606	0.0158
10	2				2			
11								
12	313.	2.00	7.3919	0.1033	293.	5.00	4.1034	0.0096
13	2				2			
14								
15	318.	2.00	7.5621	0.0635	298.	5.00	4.7952	0.0231
16	2				2			
17								
18	278.	3.00	2.9973	0.0244	303.	5.00	5.2975	0.0444
19	2				2			
20								
21	283.	3.00	3.4354	0.0363	308.	5.00	6.151	0.12
22	2				2			
23								
24	288.	3.00	3.8312	0.0569	313.	5.00	7.1108	0.0301
25	2				2			
26								
27	293.	3.00	4.2379	0.0558	318.	5.00	7.4025	0.1008
28	2				2			
29								
30								
31	298.	3.00	4.9333	0.0123				
32	2							
33								

<sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol  $\text{kg}^{-1}$  (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of the measurement of the molality of the Tris solute in the saturated solution, and is equal to the standard deviation of 4-13 molalities determined from replicate samples extracted from the flask containing the solution. Molality ( $m$ ) is expressed in moles per kilogram of pure water.

**Table 5.** Experimental solubilities  $m_{\text{Tris}}(\text{sat.})$  of Tris in aqueous TrisHCl of different concentrations at temperature  $T^a$

$T$ (K)	$m_{\text{TrisHCl}}$ (mol · kg <sup>-1</sup> )	$m_{\text{Tris}}(\text{sat.})$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$	$T$ (K)	$m_{\text{TrisHCl}}$ (mol · kg <sup>-1</sup> )	$m_{\text{Tris}}(\text{sat.})$ (mol · kg <sup>-1</sup> )	Standard uncertainty $y, u(m)^b$
288. 2	0.500	4.5747	0.0075	308. 2	2.00	7.2927	0.0606
298. 2	0.500	5.898	0.0148	288. 2	3.00	4.8255	0.0119
308. 2	0.500	7.1391	0.0219	298. 2	3.00	6.1444	0.0441
288. 2	1.00	4.6201	0.0594	308. 2	3.00	7.4257	0.0159
298. 2	1.00	5.9224	0.017	288. 2	4.00	4.9977	0.009
308. 2	1.00	7.2018	0.0237	298. 2	4.00	6.3032	0.0325
288. 2	2.00	4.7182	0.0062	308. 2	4.00	7.585	0.0214
298. 2	2.00	6.0346	0.0178				

<sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol kg<sup>-1</sup> (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of the measurement of the molality of the Tris solute in the saturated solution, and is equal to the standard deviation of 4–12 molalities determined from replicate samples extracted from the flask containing the solution. Molality ( $m$ ) is expressed in moles per kilogram of pure water.

**Table 6.** Experimental solubilities  $m\text{Tris}_{(\text{sat.})}$  of Tris in aqueous  $(\text{TrisH})_2\text{SO}_4$  of different concentrations at temperature  $T^a$

$T$ (K)	$m(\text{TrisH})_2$ $\text{SO}_4$ (mol · kg <sup>-1</sup> )	$m\text{Tris}_{(\text{sa})}$ t.) (mol · kg <sup>-1</sup> )	Standard uncertain ty, $u(m)^b$	$T$ (K)	$m(\text{TrisH})_2$ $\text{SO}_4$ (mol · kg <sup>-1</sup> )	$m\text{Tris}_{(\text{sa})}$ t.) (mol · kg <sup>-1</sup> )	Standard uncertain ty, $u(m)^b$
288. 2	0.250	4.2973	0.0254	298. 2	1.50	4.8879	0.0644
298. 2	0.250	5.5779	0.0072	308. 2	1.50	6.0420	0.0293
308. 2	0.250	6.8369	0.0471	288. 2	2.00	3.6225	0.0152
288. 2	1.00	3.9933	0.0183	298. 2	2.00	4.7067	0.0391
298. 2	1.00	5.1115	0.0708	308. 2	2.00	5.7934	0.0873
308. 2	1.00	6.4016	0.0740				

<sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.2$  K. Expanded uncertainty for the stock solution concentrations is  $U(m) = 8 \cdot 10^{-5}$  mol kg<sup>-1</sup> (0.95 level of confidence). <sup>b</sup>This is the standard uncertainty of the measurement of the molality of the Tris solute in the saturated solution, and is equal to the standard deviation of 4-8 molalities determined from replicate samples extracted from the flask containing the solution. Molality ( $m$ ) is expressed in moles per kilogram of pure water.



**Table 7.** Coefficients of the equations used to represent the measured solubilities<sup>a</sup>.

Solutions		RMSE <sup>b</sup>	Coefficients					
			a <sub>0</sub>	a <sub>1</sub>	b <sub>0</sub>	b <sub>1</sub>	b <sub>2</sub>	c
Tris water	in	0.012	1.7397±0.0 019	-1933±15	-	-	-	-
NaCl water	in	0.024	1.8155±0.0 005	- 44.52±3. 57	-	-	-	-
Tris TrisHCl <sub>(aq)</sub>	in	0.069	-	-	0.0226±0.0 005	1587±247	0.0	-
Tris (TrisH) <sub>2</sub> SO <sub>4</sub> (aq)	in	0.068	-	-	- 0.1044±0.0 015	426.0±15 4.6	0.0	-
Tris NaCl <sub>(aq)</sub>	in	0.165	-	-	- 0.0704±0.0 024	643.2±69 .2	0.00707±0.00 058	2. 0
NaCl Tris <sub>(aq)</sub>	in	0.016	-	-	- 0.0171±0.0 006	1035±79	0.00521±0.00 034	1. 5

<sup>a</sup>Coefficients a<sub>0-1</sub> are for eq 4, and b<sub>0-2</sub> and c for eq 5. <sup>b</sup>The column RMSE contains the root mean square deviations of the measured from the fitted solubilities.

**Table 8.** Pitzer model parameters for  $pK^*(\text{TrisH}^+)$  and EMF calculations<sup>a</sup>

Species	Parameter	Value	Source <sup>b</sup>
TrisH <sup>+</sup> Cl <sup>-</sup> <sup>(c)</sup>	$\beta^{(0)}$	0.0426783	1
TrisH <sup>+</sup> Cl <sup>-</sup>	$\beta^{(1)}$	0.196255	1
TrisH <sup>+</sup> Cl <sup>-</sup>	$C^{(0)}$	-0.0014451	1
Na <sup>+</sup> Cl <sup>-</sup>	$\beta^{(0)}$	0.0806342	3
Na <sup>+</sup> Cl <sup>-</sup>	$\beta^{(1)}$	0.263098	3
Na <sup>+</sup> Cl <sup>-</sup>	$C^{(0)}$	0.00026239	3
Na <sup>+</sup> Cl <sup>-</sup>	$C^{(1)}$ <sup>d</sup>	-0.010052	3
H <sup>+</sup> Na <sup>+</sup>	$\theta$	0.036	4
H <sup>+</sup> Na <sup>+</sup> Cl <sup>-</sup>	$\psi$	-0.004	4
H <sup>+</sup> Cl <sup>-</sup>	$\beta^{(0)}$	0.17567	2
H <sup>+</sup> Cl <sup>-</sup>	$\beta^{(1)}$	0.297786	2
H <sup>+</sup> Cl <sup>-</sup>	$C^{(0)}$	0.0006847	2
Tris Tris <sup>e</sup>	$\lambda$	-0.00516	1
Tris Tris Tris	$\mu$	0.000703	1

<sup>a</sup>See section 5.1 for the parameter values that were fitted to the  $pK^*(\text{TrisH}^+)$  measurements of Millero *et al.*<sup>13</sup> in this work. Those listed above, and used in eq 13, were taken from the literature. <sup>b</sup>The sources of the parameters are as follows: 1 - this work (see Supporting Information); 2 - Waters and Millero,<sup>10</sup> taken from Campbell *et al.*;<sup>41</sup> 3 - Archer;<sup>21</sup> 4 - Waters and Millero,<sup>10</sup> taken from Harvie *et al.*<sup>42</sup> <sup>c</sup>The root mean square deviation of measured from fitted osmotic coefficients of aqueous TrisHCl solutions is 0.00093. <sup>d</sup>The parameter  $C^{(1)}$  is only used for Na<sup>+</sup>-Cl<sup>-</sup> interactions. For the other electrolytes it is set to zero. <sup>e</sup>The root mean square deviation of measured from fitted osmotic coefficients of aqueous Tris solutions is 0.0021.

**Table 9.** Pitzer model parameters obtained by Tischenko<sup>28</sup> for Tris-TrisHCl-NaCl solutions at 25 °C<sup>a</sup>

Species	Parameter	Value
TrisH <sup>+</sup> Cl <sup>-</sup>	$\beta^{(0)}$	0.04389
TrisH <sup>+</sup> Cl <sup>-</sup>	$\beta^{(1)}$	0.17395
TrisH <sup>+</sup> Cl <sup>-</sup>	$C^{(0)}$	-0.00150
Tris Na <sup>+</sup>	$\lambda$	0.02106
Tris TrisH <sup>+</sup>	$\lambda$	-0.02445
Tris Tris	$\lambda$	0.02707
Tris Tris Tris	$\mu$	-0.003433
Na <sup>+</sup> TrisH <sup>+</sup>	$\theta$	-0.00017
Na <sup>+</sup> TrisH <sup>+</sup> Cl <sup>-</sup>	$\psi$	-0.001455

<sup>a</sup>These values are from Tishchenko's Table 2. The source of the interaction parameters for Na<sup>+</sup> and Cl<sup>-</sup> that were used in Tishchenko's model are not stated, nor values given, but are likely to come from Pitzer *et al.*<sup>43</sup>

**Table 10.** Fitted Pitzer model parameters for Tris-TrisHCl-NaCl solutions at 25 °C<sup>a</sup>

Species	Parameter	Value	Standard error
Tris Na <sup>+</sup>	$\lambda$	0.04662	0.0011
Tris TrisH <sup>+</sup>	$\lambda$	-0.01970	0.0012
Tris TrisH <sup>+</sup> Cl <sup>-</sup>	$\zeta$	-0.00182	0.00071
Tris Na <sup>+</sup> Cl <sup>-</sup>	$\zeta$	-0.00940	0.00061
Na <sup>+</sup> TrisH <sup>+</sup>	$\theta^b$	-0.0203	0.0019
Na <sup>+</sup> TrisH <sup>+</sup> Cl <sup>-</sup>	$\psi^b$	-0.00940	

<sup>a</sup>The fits of the model to data for Cells A and B used the parameters listed in Table 8 for TrisH<sup>+</sup>-Cl<sup>-</sup>, Na<sup>+</sup>-Cl<sup>-</sup>, and Tris-Tris interactions. The root mean square deviation of the observed from the fitted EMFs was 0.12 mV. <sup>b</sup>These values, which were used in the fitted model, were assigned according to the constraints determined in section 5.1.1 from the measurements of stoichiometric dissociation constants of TrisH<sup>+</sup>.

**Table 11.** Pitzer model parameters determined from solubility measurements at 25 °C<sup>a</sup>

Species	Parameter	Value		Species	Parameter	Value	
Tris Na <sup>+</sup>	$\lambda$	0.02817	$\pm$	Tris	$\lambda$	0.08245	$\pm$
		0.00077 <sup>b</sup>		SO <sub>4</sub> <sup>2-</sup>		0.0041 <sup>c</sup>	
Tris	$\lambda$	-0.0124	$\pm$				
TrisH <sup>+</sup>		0.00098					

<sup>a</sup>Tris-Tris interaction parameters in Table 8 were used in these determinations. <sup>b</sup>From measured Tris solubilities in aqueous NaCl. <sup>c</sup>Obtained from measurements of Tris solubilities in aqueous (TrisH)<sub>2</sub>SO<sub>4</sub>, and using the Tris-TrisH<sup>+</sup> interaction parameter given in this table.

**Table 12.** CAS Registry Number and Mass Fraction Purity of the Chemicals

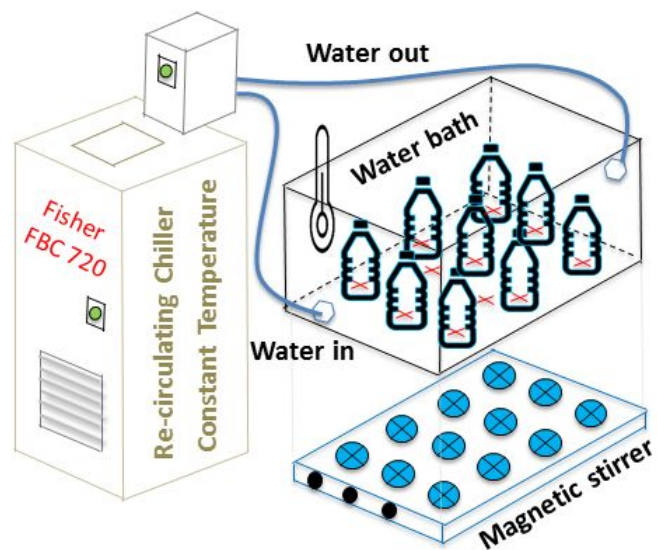
component	CAS No.	Reg. suppliers	mass fraction
Tris <sup>a</sup>	77-86-1	VWR International	≥99.9%
TrisHCl <sup>b</sup>	1185-53-1	VWR International	≥99%
(TrisH) <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	132499-87-7	Sigma-Aldrich	≥99%
Sodium chloride	7647-14-5	VWR International	≥99.9%
Silver nitrate, 0.1N	7761-88-8	Alfa Aesar™	Standardized Solution
Potassium thiocyanate, 0.1N	333-20-0	Alfa Aesar™	Standardized Solution
Hydrochloric acid	7647-01-0	Fisher Scientific	32-35%
Sodium tetraborate decahydrate	1303-96-4	Sigma-Aldrich	≥99.5%
Nitric acid	7697-37-2	Honeywell Fluka™	≥65%
Trichloromethane	67-66-3	Carl Roth	≥99.9%
Ammonium iron(III) sulphate dodecahydrate	7783-83-7	ACROS Organics™	>99%
Nitrogen	7727-37-9	Air Liquid	99.999%

<sup>a</sup>2-amino-2-(hydroxymethyl)propane-1,3-diol.  
 (hydroxymethyl)propane-1,3-diol;  
 (hydroxymethyl)propane-1,3-diol;

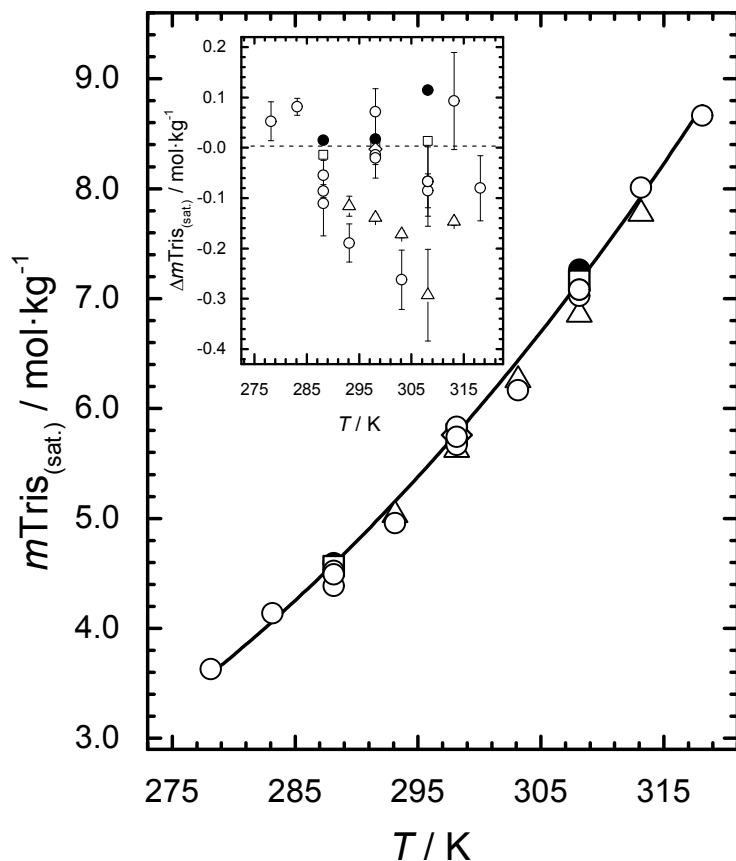
hydrochloride.  
 sulfuric

<sup>b</sup>2-amino-2-  
<sup>c</sup>2-amino-2-  
 acid.

## FIGURES

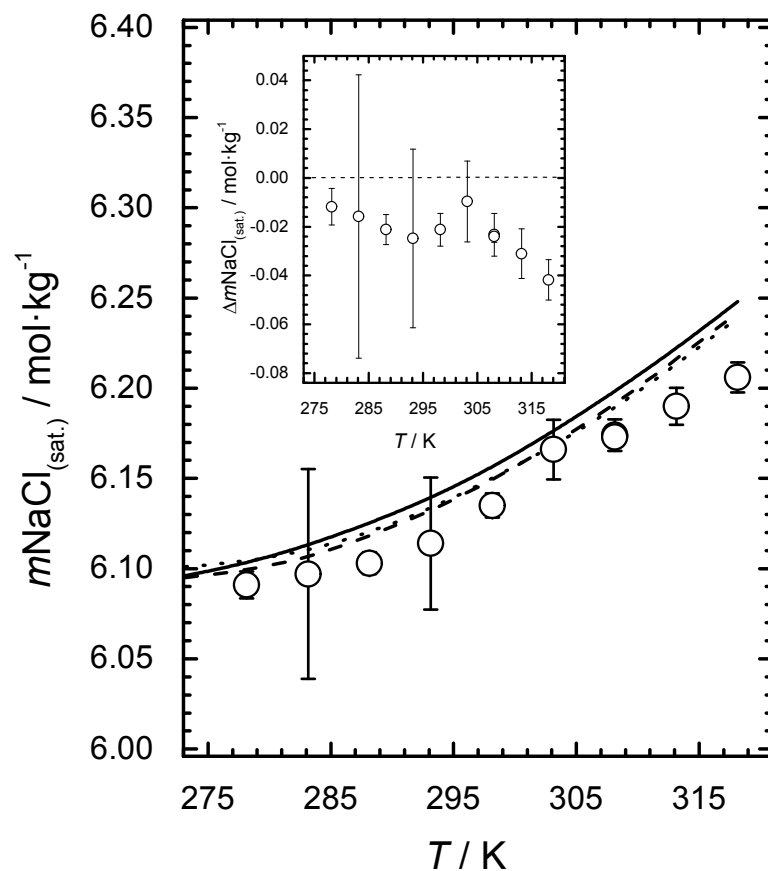


**Figure 1.** Schematic representation of the set-up used for the solubility experiments. A re-circulating chiller was used to feed a steady flow of water to a thermally isolated bath, containing sealed glass bottles with the studied solutions. These solutions were agitated using a magnetic stirrer placed underneath the bath.

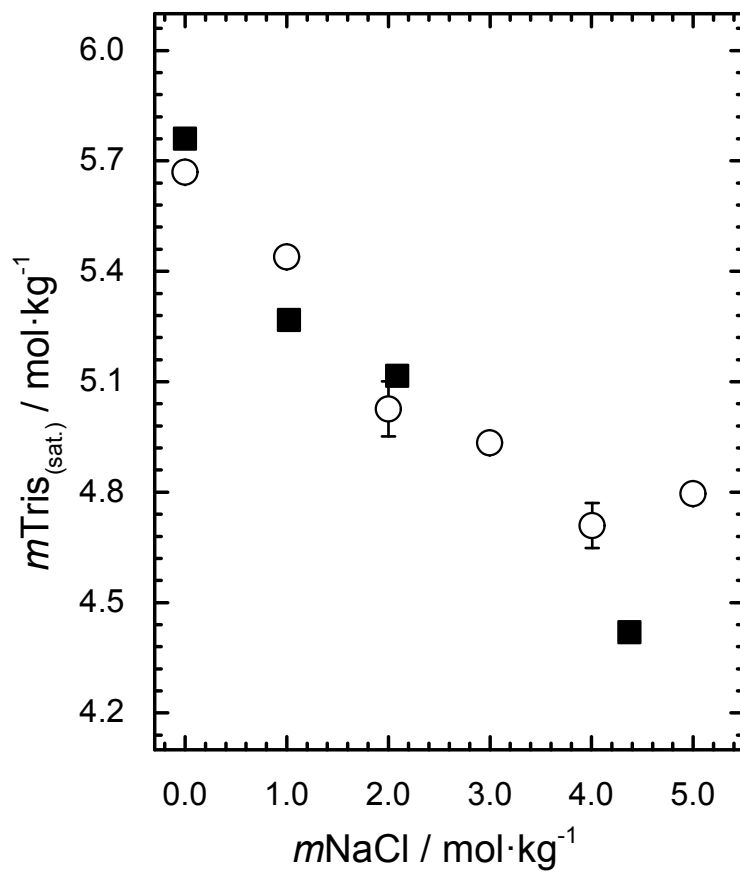


**Figure 2.** Measured solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in pure water as a function of temperature ( $T$ ). Key: circle, mean values (with standard uncertainties) from this study, as listed in Table 1; black dot, Schindler *et al.*;<sup>39</sup> square, El Harakany and Barakat;<sup>38</sup> diamond, Taha and Lee;<sup>23</sup> triangle, Jouyban-Gharamaleki *et al.*;<sup>40</sup> line, eq 1. Inset: deviations (measured - calculated) from the fitted line (eq 1) with standard uncertainties of the measurements.

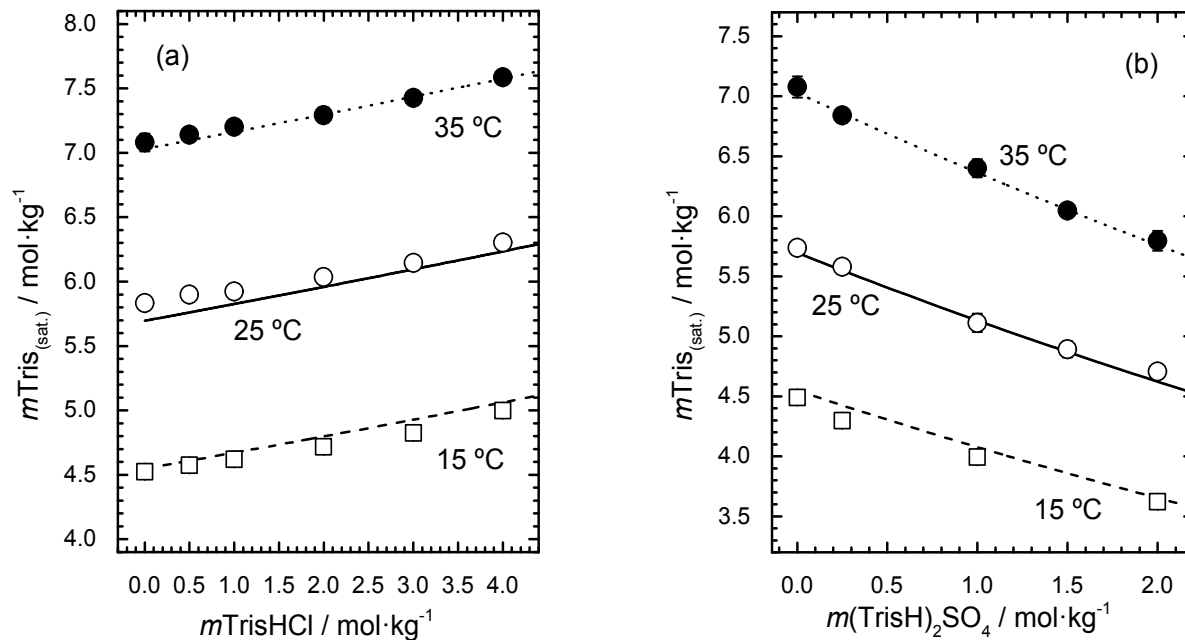




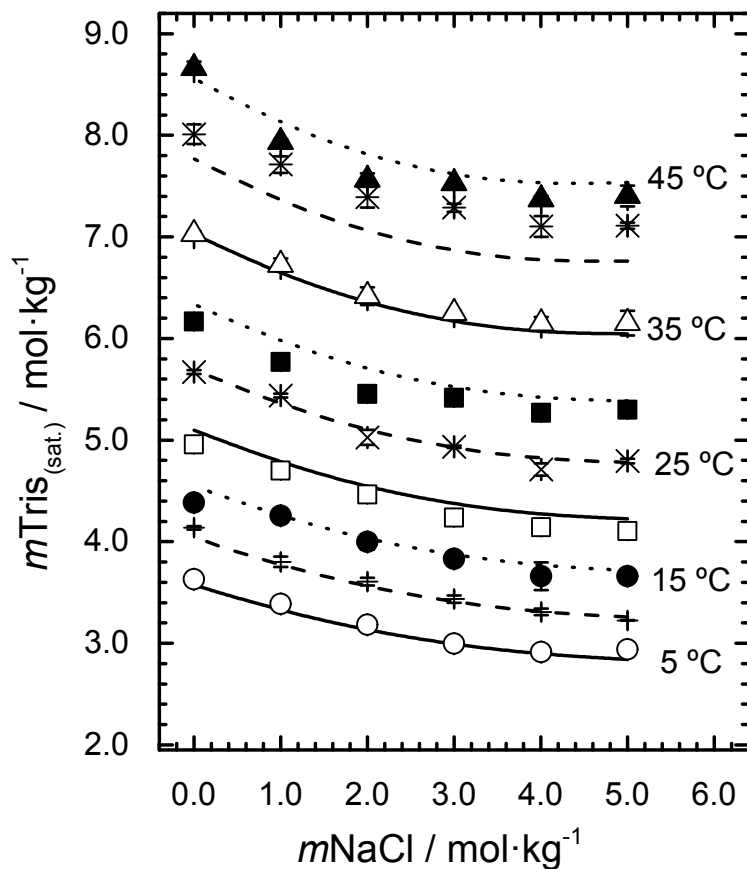
**Figure 3.** Solubilities of NaCl ( $m\text{NaCl}_{(\text{sat.})}$ ) in pure water as a function of temperature ( $T$ ). Key: circle, mean values (with standard uncertainties) from this study, as listed in Table 2; solid line, critical evaluation of Cohen-Adad *et al.*;<sup>19</sup> dashed and dotted lines, calculated from the thermodynamic evaluations of Archer.<sup>20, 21</sup> Inset: deviations (measured - calculated) from the equation of Cohen-Adad *et al.*,<sup>19</sup> with standard uncertainties of the measurements.



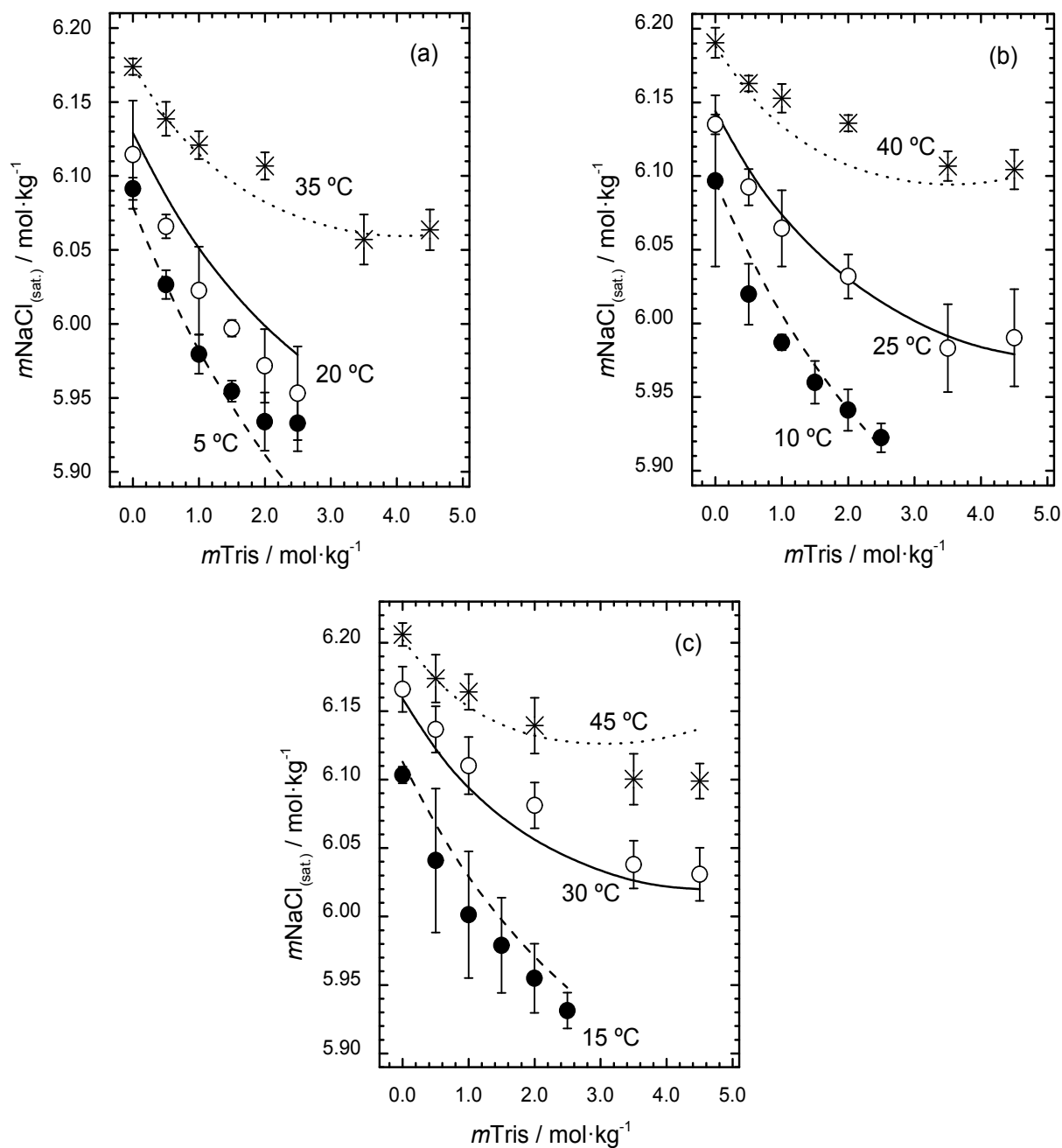
**Figure 4.** Measured solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in aqueous NaCl at 25 °C, as a function of NaCl molality ( $m\text{NaCl}$ ). Key: circle, mean values (with standard uncertainties) from this study, as listed in Table 4; solid square, measurements of Taha and Lee.<sup>23</sup>



**Figure 5.** Measured and fitted solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in: (a) aqueous TrisHCl; and (b) aqueous  $(\text{TrisH})_2\text{SO}_4$ . Key (both plots): square, 15 °C; circle, 25 °C; dot, 35 °C; lines, fitted values (eq 5, with parameters in Table 7).

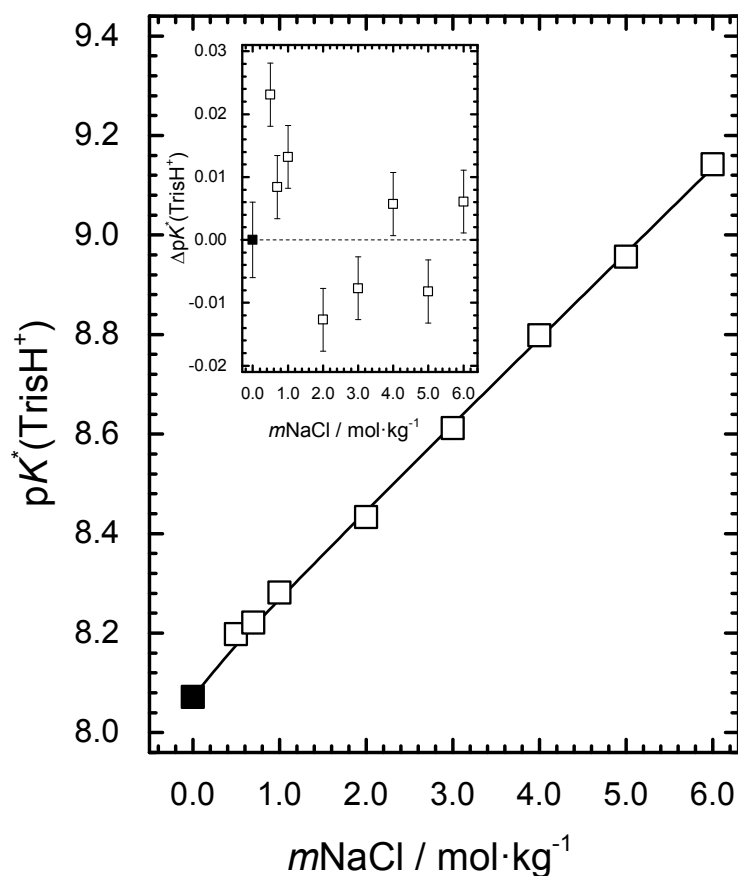


**Figure 6.** Measured and fitted solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in aqueous NaCl at different temperatures. Key: circle, 5 °C; plus, 10 °C; dot, 15 °C; open square, 20 °C; cross, 25 °C; solid square, 30 °C; open triangle, 35 °C; asterisk, 40 °C; solid triangle, 45 °C; lines, fitted values (eq 5, with parameters in Table 7).



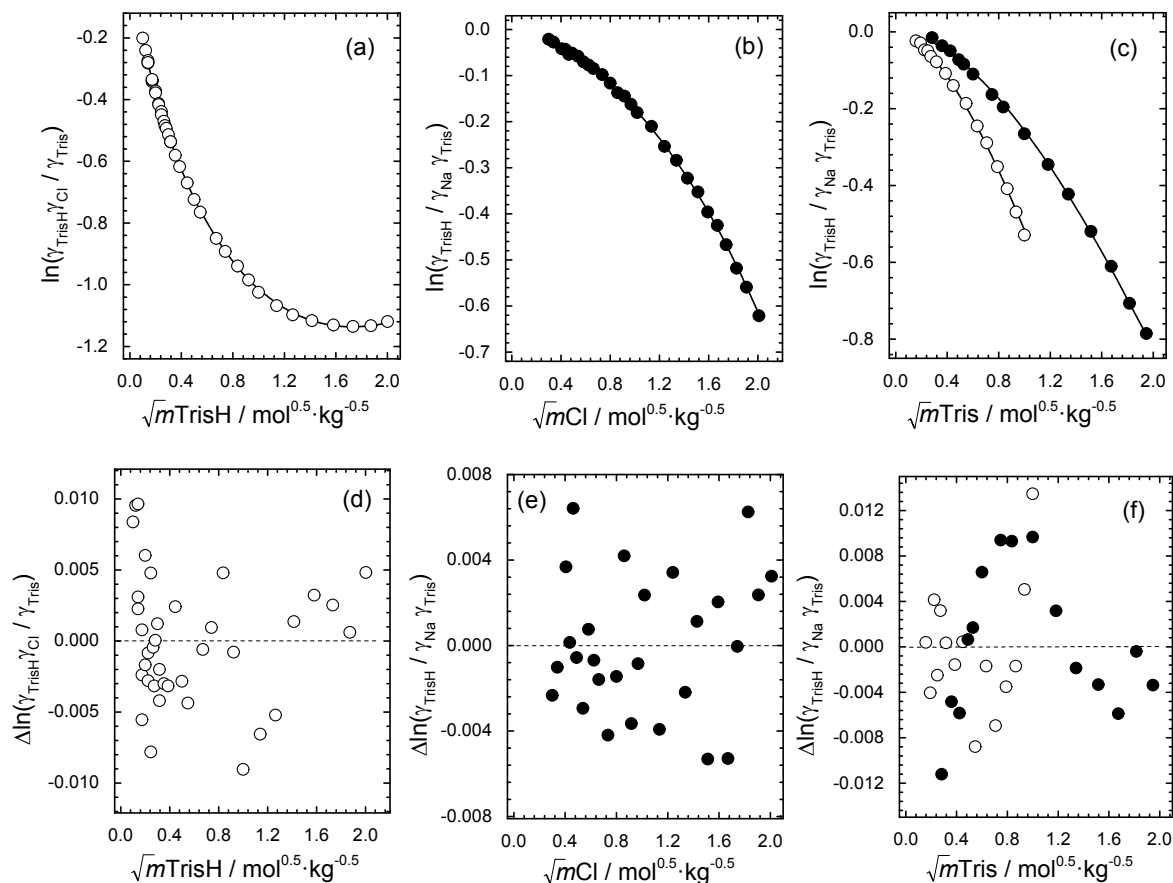
**Figure 7.** Measured and fitted solubilities of NaCl ( $m\text{NaCl}_{(\text{sat.})}$ ) in aqueous Tris at different temperatures. (a) 5 °C to 35 °C. Key: dot, 5 °C; circle, 20 °C; asterisk, 35 °C. (b) 10 °C to 40 °C. Key: dot, 10 °C; circle, 25 °C; asterisk, 40 °C. (c) 15 °C to 45 °C. Key: dot, 15 °C; circle, 25 °C; asterisk, 40 °C.

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3 °C; circle, 30 °C; asterisk, 45 °C. The lines are fitted values (eq 5,  
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6 with parameters in Table 7).



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42 **Figure 8.** Measured and fitted stoichiometric dissociation constants  
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44 of  $\text{TrisH}^+$  ( $pK^*(\text{TrisH}^+)$ , where  $K^*(\text{TrisH}^+)$  is in  $\text{mol kg}^{-1}$ ) in aqueous  
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46  $\text{NaCl}$  at 25 °C, as a function of  $\text{NaCl}$  molality ( $m\text{NaCl}$ ). Key: solid  
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48 black square, value in pure water (fixed), measured by Bates and  
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50 Hetzer;<sup>2</sup> square, Millero et al.;<sup>13</sup> line, fitted values (eq 11). The  
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3 inset shows the difference between the measured and calculated values  
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5 (observed - fitted) with standard uncertainties of the measurements.  
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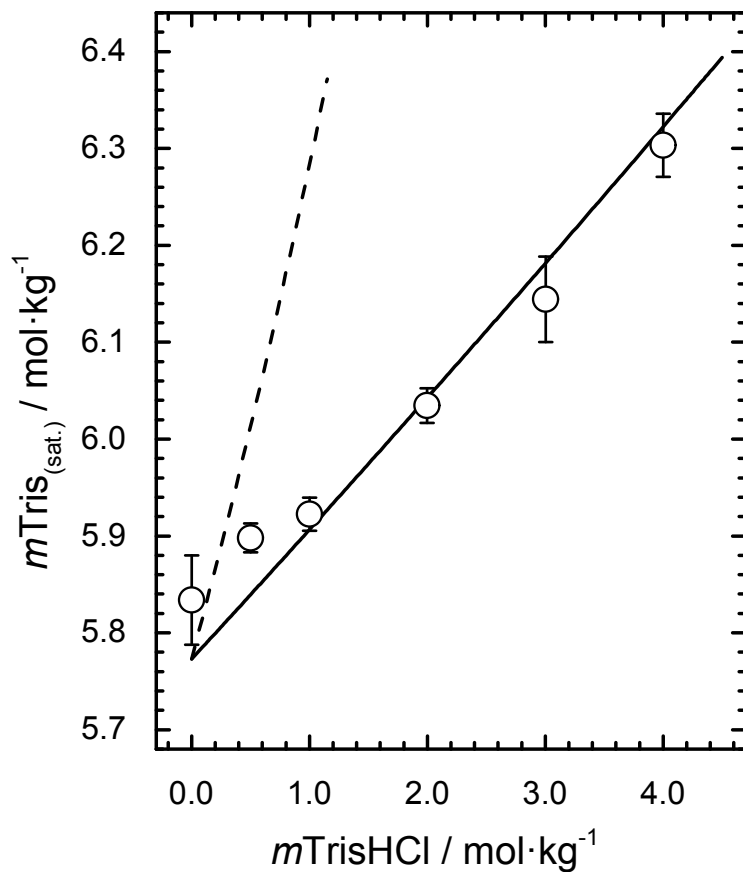


**Figure 9.** Measured and fitted values of the data from Cell A and Cell B at 25 °C,<sup>28</sup> expressed as logarithms of activity coefficient products determined from eq 13 and 16. (a) Cell A, the quantity  $\ln(\gamma_{\text{TrisH}^+}\gamma_{\text{Cl}^-}/\gamma_{\text{Tris}})$  plotted against the square root of TrisH<sup>+</sup> molality ( $m_{\text{TrisH}^+}$ ). Key: circle, measurements; line, the fitted model. (b) Cell B (solutions containing equimolar Tris and TrisH<sup>+</sup>), the quantity  $\ln(\gamma_{\text{TrisH}^+}/\gamma_{\text{Na}^+}\gamma_{\text{Tris}})$  plotted against the square root of Cl<sup>-</sup> molality ( $m_{\text{Cl}^-}$ ). Key: dot, measurements; line, the fitted model. (c) Cell B (solutions containing equimolar Na<sup>+</sup> and TrisH<sup>+</sup>), the quantity

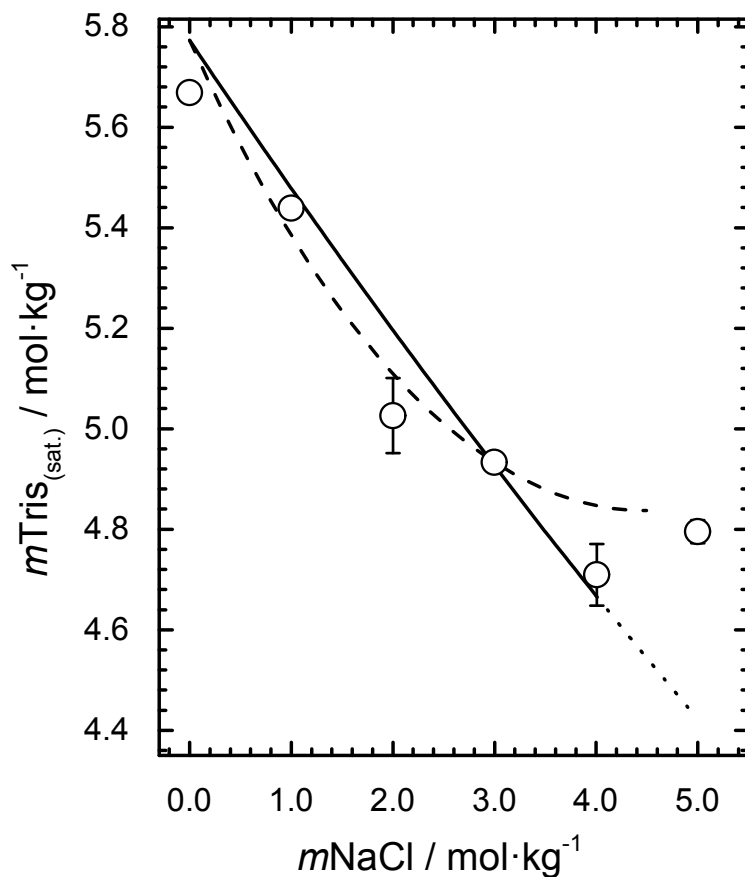


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3  $\ln(\gamma_{\text{TrisH}} / (\gamma_{\text{Na}} \gamma_{\text{Tris}}))$  plotted against the square root of Tris molality  
4 ( $m_{\text{Tris}}$ ). Key: circle, measured values for solutions in which  $m_{\text{Cl}^-}$  is  
5 equal to  $4m_{\text{Tris}}$ ; dot, measured values for solutions in which  $m_{\text{Cl}^-}$  and  
6  $m_{\text{Tris}}$  are equal; lines, the fitted model. Panels (d) to (f) show the  
7 deviations of the model from the measurements (observed - fitted).  
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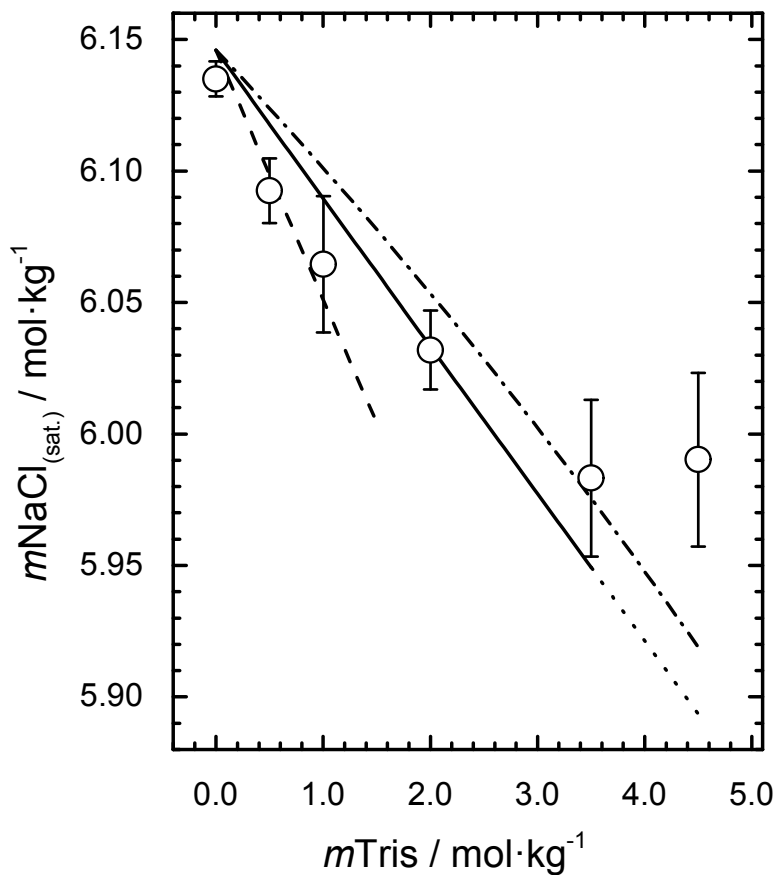
The symbols have the same meanings as for panels (a) to (c).



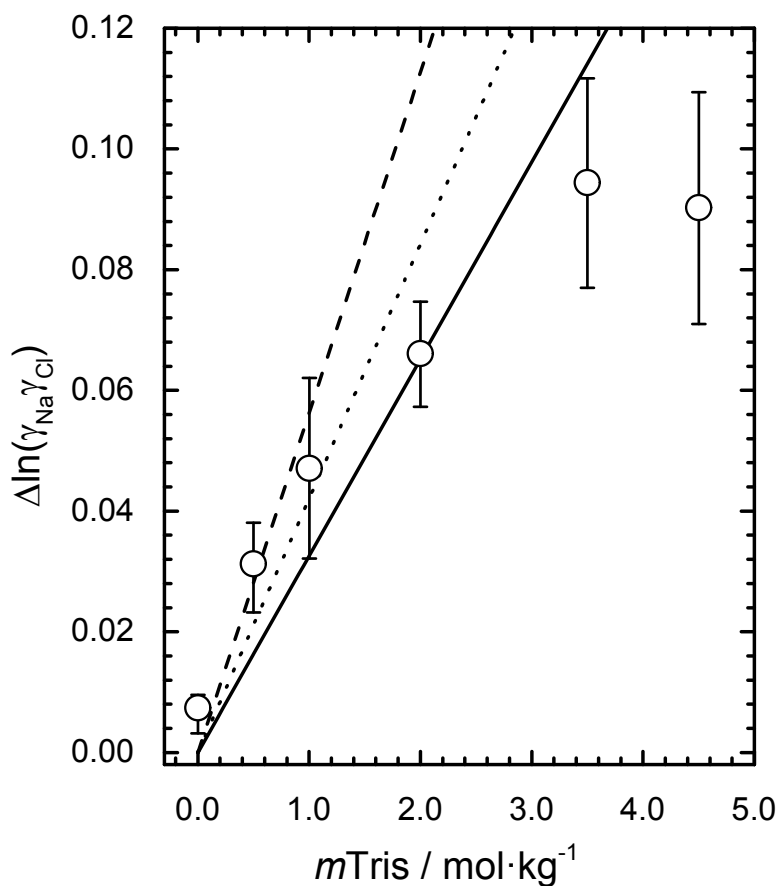
**Figure 10.** Measured and fitted solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in aqueous TrisHCl at 25 °C. Key: circle, measured values (this study); solid line, our fitted model; dashed line, calculated using the interaction parameters of Tishchenko.<sup>28</sup>



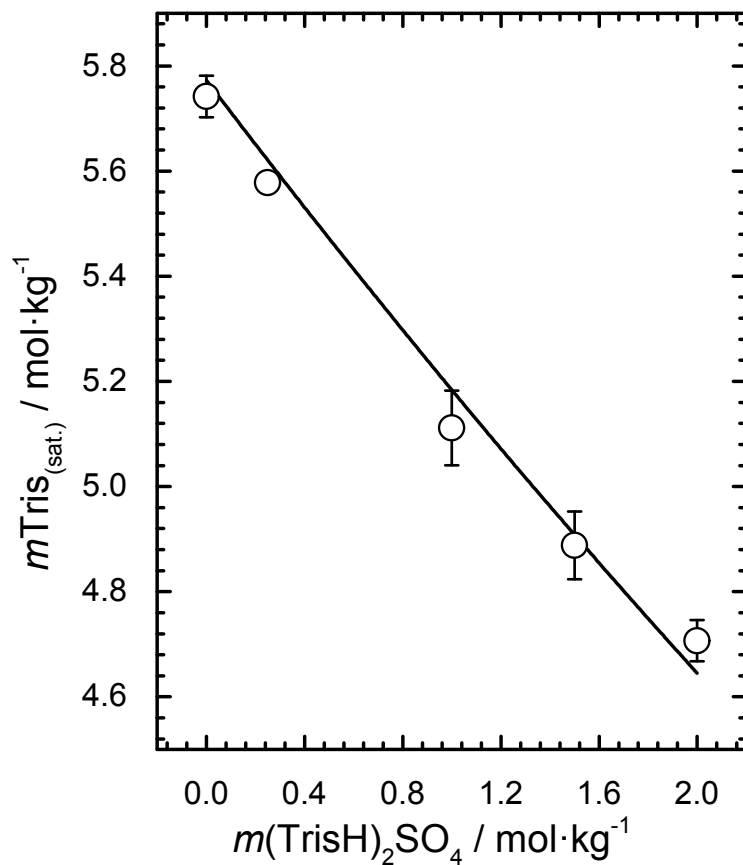
**Figure 11.** Measured and fitted solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in aqueous NaCl at 25 °C. Key: circle, measured values (this study); solid line with dotted extension, the fitted model (to 4.0 mol·kg<sup>-1</sup> NaCl); dashed line, fitted (with non-zero  $\zeta_{\text{Tris,Na,Cl}}$  value as described in the text).



**Figure 12.** Measured and fitted solubilities of NaCl ( $m_{\text{NaCl}_{(\text{sat.})}}$ ) in aqueous Tris at 25 °C. Key: circle, measured values (this study); solid line with dotted extension, fitted (to 3.5 mol·kg<sup>-1</sup> Tris); dashed line, fitted (to 1.0 mol·kg<sup>-1</sup> Tris); dash-dot line, fitted (with non-zero  $\zeta_{\text{Tris,Na,Cl}}$  value as described in the text).



**Figure 13.** The value of  $\Delta \ln(\gamma_{\text{Na}}\gamma_{\text{Cl}})$  determined from eq 18 and the measured solubilities of NaCl in aqueous Tris at 25 °C. Key: circle, from measured values (this study); solid line, calculated using the value of  $\lambda_{\text{Tris,Na}}$  (0.0163) determined from these solubilities; dashed line, calculated using the value of  $\lambda_{\text{Tris,Na}}$  (0.02817) obtained from measured solubilities of Tris in aqueous NaCl; dotted line, calculated using the value of  $\lambda_{\text{Tris,Na}}$  (0.02106) determined by Tishchenko<sup>28</sup> from EMF measurements.



**Figure 14.** Measured and fitted solubilities of Tris ( $m\text{Tris}_{(\text{sat.})}$ ) in aqueous  $(\text{TrisH})_2\text{SO}_4$  at 25 °C. Key: circle, measured values (this study); solid line, our fitted model.

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7 **TABLES APPENDIX**  
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10 **Table A1.** Osmotic coefficients ( $\phi$ ) of aqueous Tris at 20.4 °C,<sup>a</sup> at  
11 different Tris molalities ( $m_{\text{Tris}}$ ), from electrodynamic balance  
12 experiments.  
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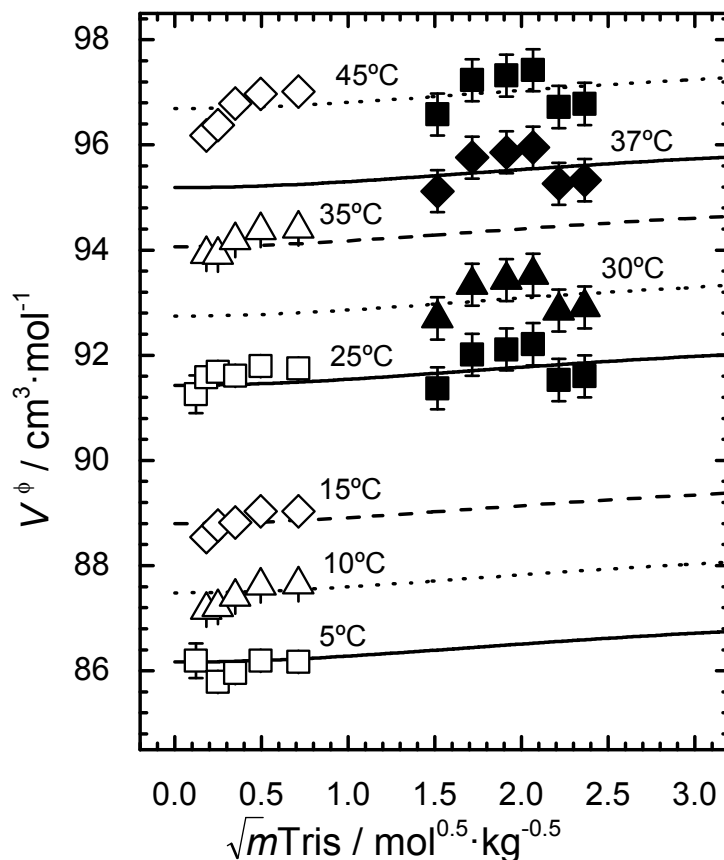
$\sqrt{m_{\text{Tris}}}$ (mol · kg <sup>-1</sup> ) <sup>0.5</sup>	Standard uncertainty, $u(\sqrt{m})^b$	$\phi$	Standard uncertainty, $u(\phi)^b$	$\sqrt{m_{\text{Tris}}}$ (mol · kg <sup>-1</sup> ) <sup>0.5</sup>	Standard uncertainty, $u(\sqrt{m})^b$	$\phi$	Standard uncertainty, $u(\phi)^b$
4.5000	0.0187	1.053 4	0.0103	3.1321	0.0083	1.118 5	0.0129
4.4879	0.0176	1.040 3	0.0097	3.0872	0.0066	1.126 3	0.0102
4.4546	0.0379	1.035 0	0.0213	3.0211	0.0046	1.129 4	0.0073
4.3883	0.0461	1.044 5	0.0274	2.9809	0.0061	1.126 8	0.0102
4.3316	0.0575	1.052 2	0.0359	2.9432	0.0075	1.120 7	0.0134
4.2875	0.0660	1.053 0	0.0426	2.8734	0.0078	1.127 8	0.0153
4.2300	0.0727	1.060 1	0.0495	2.8395	0.0094	1.117 8	0.0194
4.1766	0.0704	1.062 9	0.0502	2.7954	0.0113	1.110 5	0.0261
4.1200	0.0762	1.067 6	0.0570	2.7395	0.0101	1.111 8	0.0248
4.0685	0.0855	1.073 4	0.0670	2.6896	0.0086	1.113 0	0.0222
4.0413	0.0839	1.069 3	0.0675	2.6397	0.0100	1.108 4	0.0283

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2								
3	3.9553	0.0685	1.088	0.0601	2.5907	0.0087	1.105	0.0271
4			0				2	
5								
6	3.8947	0.1375	1.097	0.1279	2.5258	0.0087	1.111	0.0292
7			0				8	
8								
9	3.9005	0.0765	1.078	0.0703	2.4796	0.0088	1.105	0.0289
10			5				6	
11								
12	3.8137	0.0624	1.090	0.0626	2.4282	0.0095	1.099	0.0346
13			3				2	
14								
15	3.6446	0.0349	1.166	0.0358	2.3710	0.0071	1.094	0.0307
16			9				5	
17								
18	3.6497	0.0092	1.138	0.0093	2.3109	0.0087	1.091	0.0339
19			4				9	
20								
21	3.6069	0.0111	1.138	0.0117	2.2391	0.0104	1.099	0.0379
22			9				5	
23								
24	3.6063	0.0115	1.114	0.0121	2.1852	0.0096	1.097	0.0409
25			1				2	
26								
27	3.5462	0.0173	1.123	0.0193	2.1270	0.0087	1.086	0.0431
28			3				7	
29								
30	3.4974	0.0184	1.124	0.0220	2.0593	0.0101	1.083	0.0446
31			3				4	
32								
33	3.4525	0.0255	1.122	0.0318	2.0000	0.0099	1.075	0.0460
34			7				7	
35								
36	3.3992	0.0226	1.129	0.0308	1.9449	0.0074	1.063	0.0469
37			2				9	
38								
39	3.3560	0.0225	1.125	0.0312	1.8815	0.0090	1.057	0.0624
40			9				2	
41								
42	3.3062	0.0230	1.131	0.0344	1.7959	0.0094	1.060	0.0586
43			1				7	
44								
45	3.2732	0.0246	1.118	0.0382	1.7268	0.0081	1.054	0.0730
46			9				6	
47								
48	3.2066	0.0264	1.133	0.0434	1.6789	0.0074	1.032	0.1106
49			7				4	
50								
51	3.1637	0.0285	1.126	0.0488				
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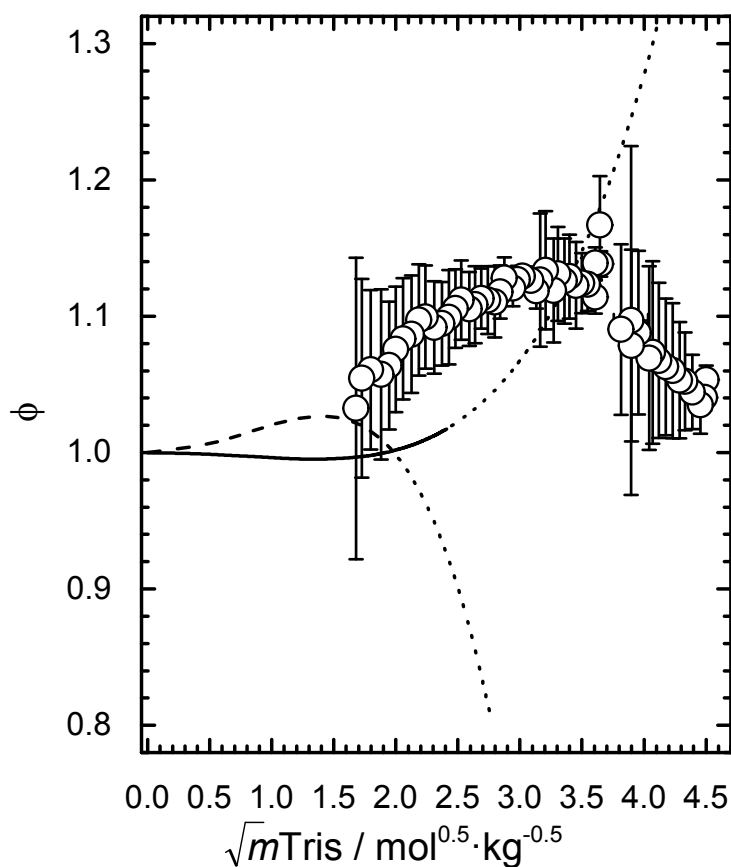
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3     <sup>a</sup>Standard uncertainty for temperature is  $u(T) = 0.5$  K. <sup>b</sup>The standard  
4 uncertainty for the osmotic coefficients arises from experimental  
5 uncertainty in the relative humidity ( $\pm 0.5$  %) and temperature ( $\pm 0.5$   
6 K) of the EDB measurements, which contribute to the derivation of the  
7 droplet water activity. The uncertainty in the molality arises from  
8 the standard deviation of the binning process of averaging across a  
9 minimum of 10 droplets.  
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## FIGURES APPENDIX



**Figure A1.** Measured and fitted apparent molar volumes of Tris ( $V^\phi$ ) in pure aqueous solutions as a function of the square root of Tris molality ( $m\text{Tris}$ ), at selected temperatures from 5 °C to 45 °C. Key: open symbols, measurements of Ford et al.;<sup>35</sup> solid symbols, calculated from densities determined by Taha and Lee;<sup>23</sup> lines, fitted equation (eq A1). The temperatures of the measurements are, starting from the bottom of the plot: 5 °C (square, and solid line); 10 °C (triangle, and dotted line); 15 °C (diamond, and dashed line); 25 °C (square,

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3 solid square, and solid line); 30 °C (solid triangle, and dotted  
4 line); 35 °C (triangle, and dashed line); 37 °C (solid diamond, and  
5 solid line); 45 °C (diamond, solid square, and dotted line). The  
6 values of the measured and fitted  $V^\phi$  were spaced out vertically by  
7 adding a constant value of  $V^\phi$  at each temperature: 5 °C (-4); 10 °C (-  
8 3); 15 °C (-2); 25 °C (unchanged); 30 °C (+1); 35 °C (+2); 37 °C (+3);  
9 45 °C (+4).  
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**Figure A2.** Osmotic coefficients ( $\phi$ ) of aqueous Tris at 20.4 °C, determined using an electrodynamic balance, and plotted against the square root of Tris molality ( $m\text{Tris}$ ). Key: circles, mean values (with standard uncertainties) from this study, as listed in Table A1; solid line, calculated using the Pitzer model parameters from Table 7 (for 25 °C) and with extrapolation beyond the maximum molality of fit (dotted line); dashed line, same as for solid line except that the parameters determined by Tishchenko<sup>28</sup> (Table 8) were used.

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