

Solid–Liquid Equilibria in Aqueous Solutions of Tris, Tris-NaCl, Tris-TrisHCl, and Tris-(TrisH)₂SO₄ at Temperatures from 5 to 45 °C

Pablo Lodeiro,* David R. Turner, Eric P. Achterberg, Florence K. A. Gregson, Jonathan P. Reid, and Simon L. Clegg*



Cite This: *J. Chem. Eng. Data* 2021, 66, 437–455



Read Online

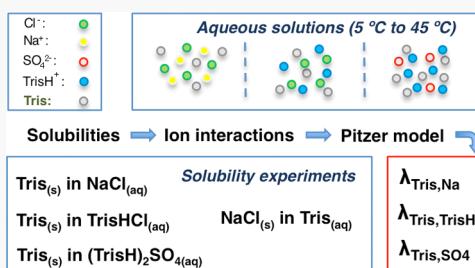
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

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, Tris^+ , 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 $\text{Tris}_{(s)}$ in water and aqueous solutions of NaCl, TrisHCl, and $(\text{TrisH})_2\text{SO}_4$ and the solubility of $\text{NaCl}_{(s)}$ in aqueous $\text{Tris}_{(aq)}$ from 5 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 Tris^+ in aqueous NaCl, and to electromotive forces of cells containing dissolved Tris, TrisHCl, and NaCl. Values of parameters for the interactions of Tris with the ions Tris^+ , Na^+ , and SO_4^{2-} at 25 °C are determined.



1. INTRODUCTION

The compound Tris, together with its conjugate acid Tris^+ , is used in aqueous buffer solutions for the calibration of pH measurements in natural waters, including seawater.¹ The thermodynamic $\text{p}K_a$ for the acid dissociation $\text{TrisH}_{(aq)}^+ \leftrightarrow \text{H}_{(aq)}^+ + \text{Tris}_{(aq)}$ has been determined experimentally by Bates and Hetzer² for temperatures in the range of 0–50 °C, and the values (e.g., 8.07 at 25 °C) make it suitable for buffering of solutions in the pH range of 7–9. Solutions of equimolar Tris and Tris^+ in artificial seawater, which contains the ions Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , and SO_4^{2-} , are used to define the pH scale used for measuring the acidity of seawater over the range of salinities 5–40 and for temperatures from 0 to 45 °C.^{3,4} This concentration-based “total” pH scale ($\text{pH} = -\log_{10}([\text{H}^+] + [\text{HSO}_4^-])$) is applicable only to saline waters containing the major ions of seawater in the ratios found in the open ocean, and it is desirable for several reasons to develop a chemical speciation model of Tris^+ dissociation in salt solutions: (1) to more accurately extend the pH scale to low-salinity waters; (2) to be able to calculate the pH of buffers for saline waters whose stoichiometry differs from that of open ocean seawater; and (3) to address metrological concerns regarding the link between the total pH scale and SI base units.⁵

Gallego-Urrea and Turner⁶ have summarized the application of a Pitzer-based⁷ speciation model to describe solute and solvent activities in solutions containing Tris buffer and artificial seawater at 25 °C.

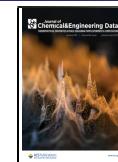
There are also several models for acid–base equilibria in artificial seawater based on the Pitzer formalism.^{8–10} In these models, the variations in solute and solvent activity coefficients and other thermodynamic properties are described in terms of interactions between pairs and triplets of solute species.⁷ The values of the interaction parameters, which are functions of both temperature and pressure, are determined from thermodynamic measurements that yield (directly or indirectly) values of activities or their differentials with respect to T or P . Examples of such data, from which activities can be determined, include isopiestic measurements of water activity, electromotive forces (EMFs) of electrochemical cells, solute or solvent vapor pressures, and solubilities of solids.

Osmotic coefficients have been measured at 25 °C for solutions of Tris,¹¹ TrisHCl,¹¹ and $(\text{TrisH})_2\text{SO}_4$ ¹² and stoichiometric values of the K_a of Tris^+ ($K_a^* = m\text{H}^+ \cdot m\text{Tris} / m\text{Tris}^+$, where m denotes molality) have been measured in various chloride solutions by Millero et al.¹³ Gallego-Urrea and Turner⁶ have used these and other data to derive Pitzer parameters for the interaction of Tris and Tris^+ with seawater

Received: August 14, 2020

Accepted: November 11, 2020

Published: December 14, 2020



ions. The resulting Pitzer thermodynamic model for equimolar Tris buffers in artificial seawater showed significant offsets from the experimental EMFs reported by DelValls and Dickson³ for these solutions.

With the aim of developing a speciation model of pH of Tris buffers in saline waters, we have measured solubilities of $\text{Tris}_{(s)}$ in water and aqueous solutions of NaCl , TrisHCl , and $(\text{TrisH})_2\text{SO}_4$ and the solubility of $\text{NaCl}_{(s)}$ in $\text{Tris}_{(aq)}$ at temperatures from 5 to 45 °C. We also report new measurements of the water activities of aqueous Tris solutions at 293.5 K to high supersaturation with respect to the solid phase.

The results at 25 °C are compared with EMF and other literature data that yield activities of Tris and TrisH^+ , and we have obtained preliminary values of Pitzer model parameters for the interaction of Tris with the ions Na^+ , TrisH^+ , and SO_4^{2-} from the solubility measurements.

2. EXPERIMENTAL METHODS

In all the experiments, ultrapure water obtained from a Milli-Q water purification system (Merck group), with a resistivity of 18.2 MΩ·cm and total organic carbon of <5 ppb, was used. Ultrapure (≥99.9%) NaCl and Tris, Tris hydrochloride (TrisHCl), and Tris hemisulfate ($(\text{TrisH})_2\text{SO}_4$) were purchased from VWR International and dried at 110 °C for 48 h before use (Table 12). All the samples were prepared gravimetrically using a 1 mg precision balance (Sartorius, model AS). The linearity of the balance from a calibration certificate (3 mg) allowed us to obtain the uncertainty of the weights using the formula: $3/(3)^{0.5} = \pm 1.73$ mg. This contribution has been counted twice (tare and gross weight), giving an uncertainty of ± 2.45 mg. Using a coverage factor (k) of 2, an uncertainty of ± 4.9 mg is obtained, which applying error propagation results in an expanded uncertainty ($U(m)$, 0.95 level of confidence) for the stock solution concentrations of $\pm 8 \cdot 10^{-5}$ mol kg⁻¹.

2.1. Tris Solubility in Aqueous NaCl , TrisHCl , and $(\text{TrisH})_2\text{SO}_4$. Stock solutions of NaCl (~5 mol kg⁻¹), TrisHCl (~4 mol kg⁻¹), and $(\text{TrisH})_2\text{SO}_4$ (~2 mol kg⁻¹) were prepared by accurate weighing of the respective salts. Buoyancy corrections were made to all weighings, including those made in order to determine solubilities, using the equations presented in Dickson et al.¹⁴

In each experiment, 8–9 glass flasks containing about 200–300 cm³ of the background electrolyte and excess solid Tris were introduced into a water bath with constant temperature control (± 0.2 °C) and were magnetically stirred at the selected temperature (in the range of 5–45 °C). The water bath consisted of 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 recirculating 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⁻¹; (b) TrisHCl —0, 0.5, 1, 2, 3, and 4 mol kg⁻¹; and (c) $(\text{TrisH})_2\text{SO}_4$ —0, 0.25, 1, 1.5, and 2 mol kg⁻¹. Flasks containing 4 mol kg⁻¹ aqueous NaCl and 1 and 3 mol kg⁻¹ aqueous TrisHCl were prepared in duplicate. In addition, a flask containing pure water with no added salts was used as a 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⁻¹ NaCl , in which aliquots were withdrawn every 24 h and measured to check for variations in Tris concentrations over time. In this case, 48 h was enough to attain equilibrium;

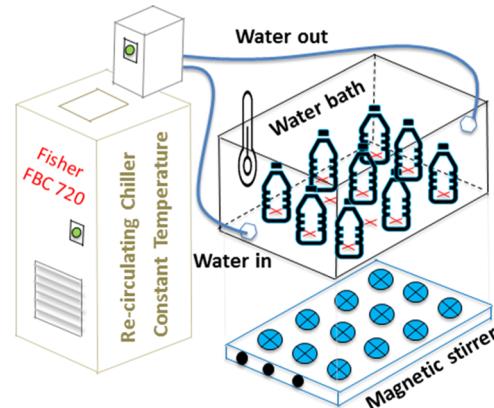


Figure 1. Schematic representation of the setup used for the solubility experiments. A recirculating chiller was used to feed a steady flow of water to a thermally isolated bath, containing sealed glass bottles with the studied solutions. These solutions were agitated using a magnetic stirrer placed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

however, because longer times can be expected for lower temperatures, we decided to wait for at least 12 days to ensure equilibrium between solid and liquid phases at all temperatures and solution compositions studied.

Typically, the experiments were started at 25 °C, and once finished, the temperature was increased in 5 °C intervals. Afterward, the temperature was set to 20 °C, and subsequent experiments followed a decreasing trend until the lowest temperature was achieved. No significant differences were observed between measured Tris solubilities for which the experimental temperatures had been approached from either higher or lower temperatures.

In the experiments containing TrisHCl and $(\text{TrisH})_2\text{SO}_4$, the same flasks were used for the whole range of temperatures. For the experiments containing NaCl in the range of 5–20 °C, a different set of flasks were used to ensure proper agitation; these flasks contained identical background electrolyte molalities but lower amounts of solid Tris than were used for the experiments in the range of 25–45 °C.

Once equilibrium was reached, samples were withdrawn from each flask in triplicate or duplicate (for the flasks containing the same background electrolyte concentration) using a preheated glass syringe with a 0.2 μm Minisart RC filter (Sartorius Stedim Biotech) attached, to remove any particles of solid Tris suspended in the solution. These samples, generally weighing 5–10 g, were then diluted and the concentration of Tris was quantified by potentiometric titrations. At least two samples, about 35 g each, from each diluted solution were then weighed and placed in a 50 cm³ water-jacketed cell maintained at a constant 25 ± 0.1 °C using a temperature-controlled bath (Julabo Labortechnik F25). These samples were titrated against ~0.5 mol kg⁻¹ HCl (Optima Grade, Fisher Scientific) added from an automatic burette (Metrohm Dosimat 665) and maintained under N_2 bubbling. Densities of the aqueous HCl at the laboratory temperature of 22 °C were taken from the critical evaluation of Clegg and Wexler.¹⁵ EMF measurements were made with a glass pH and reference electrode (Thermo Scientific Orion Ross), both connected to a pH-meter (Thermo Orion 720A+). The burette and pH-meter were computer-controlled using a Matlab script. The HCl solution was previously standardized by titration of known amounts of sodium tetraborate decahydrate (borax) supplied by Sigma-Aldrich. The equivalence points of the titrations of the Tris in

Table 1. Experimental Solubilities $m\text{Tris}_{(\text{sat.})}$ of Tris in Pure Water at Temperature T^a

T (K)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg $^{-1}$)	standard uncertainty, $u(m)^b$	source ^c	T (K)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg $^{-1}$)	standard uncertainty, $u(m)^b$	source ^c
278.2	3.6284	0.0385	1 (i)	298.15	5.780	0.008	3
283.2	4.1363	0.0171	1 (i)	298.15	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)	303.15	6.2568	0.0069	4
288.2	4.4917	0.0123	1 (iii)	308.2	7.0257	0.0337	1 (i)
288.15	4.564	0.0032	2	308.2	7.0798	0.0686	1 (ii)
288.15	4.593	0.001	3	308.2	7.0796	0.0884	1 (iii)
293.2	4.9570	0.0378	1 (i)	308.15	7.16	0.0012	2
293.15	5.0308	0.02	4	308.15	6.8536	0.091	4
298.2	5.6688	0.0190	1 (i)	308.15	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)	313.15	7.7707	0.0072	4
298.15	5.766	0.0057	2	318.2	8.6632	0.0646	1 (i)
298.15	5.6242	0.0068	4				

^aStandard 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 $^{-1}$ (0.95 level of confidence). ^bThis 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 6–13 molalities determined from replicate samples extracted from the flask containing the solution. ^cThe sources of the parameters are as follows: 1—this work [(i) from Tris solubility in NaCl experiments, (ii) from Tris solubility in TrisHCl experiments, and (iii) from Tris solubility in (TrisH) $_2$ SO $_4$ experiments]; 2—El-Harakany and Barakat;³⁸ 3—Schindler et al.;³⁹ 4—Jouyban-Gharamaleki et al.;⁴⁰ and 5—Taha and Lee.²³

the samples from the test solutions were determined using Gran's plot approach,¹⁶ and the molalities of the Tris in the solutions were calculated from these results. Four to six measurements of the Tris molality were made in each flask.

2.2. NaCl Solubility in Aqueous Tris. Two Tris stock solutions of 2.5 and 4.5 mol kg $^{-1}$ concentrations were prepared from weighed amounts of solid Tris and water. Each of these stock solutions was used to prepare flasks containing excess solid NaCl over its expected solubility, and the fixed molalities of Tris are 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mol kg $^{-1}$ (1 and 2 mol kg $^{-1}$ flasks prepared in duplicate) for experiments from 5 to 20 °C and 0, 0.5, 1.0, 2.0, 3.5, and 4.5 mol kg $^{-1}$ for experiments from 25 to 45 °C (1.0 and 3.5 mol kg $^{-1}$ flasks were prepared in duplicate). In the same way as for the other experiments, the flasks were placed in a water bath with constant temperature control (± 0.2 °C) and were magnetically stirred for at least 12 days at each temperature to ensure equilibrium. Samples were withdrawn from each flask in triplicate (where there was only a single flask containing a particular Tris molality) or duplicate (where there were two such flasks) using a preheated glass syringe with a filter attached, as described earlier. Immediately after sampling, the samples (each of 10–18 g of solution) were diluted and the concentration of chloride was determined by titration following a modification of Volhard's method.¹⁷ The procedure was as follows: at least two samples (of 8–9 g) from each of the diluted primary solution samples were weighed and placed in a glass cell together with approximately 3.5 g of HNO $_3$ (purity $\geq 65\%$, Fluka), 38 g of ultrapure water, 2 cm 3 of chloroform (Carl Roth, >99.9%), and 0.4 cm 3 of NH $_4$ Fe(SO $_4$) $_2 \cdot 12$ H $_2$ O (Acros Organics, +99%). An accurately weighed mass of about 10.1 g of AgNO $_3$ (0.1 M volumetric solution, Fisher Scientific) was also added to the glass cell. A density of 1.0119 g·cm $^{-3}$ for 0.1 M AgNO $_3$ at the laboratory temperature (22 °C) was used to determine the amount of silver. This density was calculated from the apparent molar volume of AgNO $_3$ at 25 °C in a 0.1 M solution¹⁸ and the molar volume of water at 22 °C.

These samples were titrated against KSCN (0.1 N standardized solution, Alfa Aesar) added from an automatic burette (Dosimat 665, Metrohm) until a color change was observed,

from pale white yellow to dark red, once all the silver ions added had reacted to form a silver thiocyanate precipitate, and the excess of thiocyanate bound to Fe $^{3+}$ to form a red complex. At least four measurements of the NaCl molality were made in each flask.

2.3. Water Activities of Supersaturated Tris Solutions. A description of the experimental method is presented in the Appendix.

3. RESULTS

The averaged measured solubilities for each solution composition, including those of Tris and NaCl in pure water, are listed in Tables 1–6. The standard uncertainties (u) for our measure-

Table 2. Experimental Solubilities $m\text{NaCl}_{(\text{sat.})}$ of NaCl in Pure Water at Temperature T^a

T (K)	$m\text{NaCl}_{(\text{sat.})}$ (mol·kg $^{-1}$)	standard uncertainty, $u(m)^b$	T (K)	$m\text{NaCl}_{(\text{sat.})}$ (mol·kg $^{-1}$)	standard uncertainty, $u(m)^b$
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			

^aStandard 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 $^{-1}$ (0.95 level of confidence). ^bThis 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.

ments were calculated as $(\sum(x - \bar{x})^2 / (n - 1))^{0.5}$ where x is the measured sample value, \bar{x} is the sample mean, and n is the sample size.

3.1. Solubilities in Pure Water. The solubility of Tris in water (Table 1) has been measured over the temperature range of 15–40 °C by several groups and is compared with our results

Table 3. Experimental Solubilities $m\text{NaCl}_{(\text{sat.})}$ of NaCl in Aqueous Tris of Different Molalities at Temperature T^a

T (K)	$m\text{Tris}$ (mol·kg ⁻¹)	$m\text{NaCl}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$	T (K)	$m\text{Tris}$ (mol·kg ⁻¹)	$m\text{NaCl}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$
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
298.2	1.00	6.0645	0.0259	303.2	3.50	6.038	0.0174
303.2	1.00	6.1102	0.0209	308.2	3.50	6.0570	0.0164
308.2	1.00	6.1208	0.0108	313.2	3.50	6.1067	0.01
313.2	1.00	6.1527	0.0097	318.2	3.50	6.1003	0.0186
318.2	1.00	6.164	0.013	298.2	4.50	5.9903	0.033
278.2	1.50	5.9545	0.0071	303.2	4.50	6.0308	0.0194
283.2	1.50	5.96	0.0145	308.2	4.50	6.0636	0.0133
288.2	1.50	5.979	0.0348	313.2	4.50	6.1044	0.0134
293.2	1.50	5.997	0.0056	318.2	4.50	6.0989	0.0128
278.2	2.00	5.9339	0.0197				

^aStandard uncertainty for temperature is $u(T) = 0.2$ K. Expanded uncertainty for the stock solution concentrations is $U(m) = 8 \times 10^{-5}$ mol kg⁻¹ (0.95 level of confidence). ^bThis 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 Molalities at Temperature T^a

T (K)	$m\text{NaCl}$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$	T (K)	$m\text{NaCl}$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$
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
298.2	2.00	5.026	0.0746	278.2	5.00	2.9414	0.0186
303.2	2.00	5.4524	0.0223	283.2	5.00	3.2258	0.0017
308.2	2.00	6.4173	0.0862	288.2	5.00	3.6606	0.0158
313.2	2.00	7.3919	0.1033	293.2	5.00	4.1034	0.0096
318.2	2.00	7.5621	0.0635	298.2	5.00	4.7952	0.0231
278.2	3.00	2.9973	0.0244	303.2	5.00	5.2975	0.0444
283.2	3.00	3.4354	0.0363	308.2	5.00	6.151	0.12
288.2	3.00	3.8312	0.0569	313.2	5.00	7.1108	0.0301
293.2	3.00	4.2379	0.0558	318.2	5.00	7.4025	0.1008
298.2	3.00	4.9333	0.0123				

^aStandard uncertainty for temperature is $u(T) = 0.2$ K. Expanded uncertainty for the stock solution concentrations is $U(m) = 8 \times 10^{-5}$ mol kg⁻¹ (0.95 level of confidence). ^bThis 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 Molalities at Temperature T^a

T (K)	$m\text{TrisHCl}$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$	T (K)	$m\text{TrisHCl}$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$
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				

^aStandard uncertainty for temperature is $u(T) = 0.2$ K. Expanded uncertainty for the stock solution concentrations is $U(m) = 8 \times 10^{-5}$ mol kg⁻¹ (0.95 level of confidence). ^bThis 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 Molalities at Temperature T^a

T (K)	$m(\text{TrisH})_2\text{SO}_4$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$	T (K)	$m(\text{TrisH})_2\text{SO}_4$ (mol·kg ⁻¹)	$m\text{Tris}_{(\text{sat.})}$ (mol·kg ⁻¹)	standard uncertainty, $u(m)^b$
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				

^aStandard uncertainty for temperature is $u(T) = 0.2$ K. Expanded uncertainty for the stock solution concentrations is $U(m) = 8 \times 10^{-5}$ mol kg⁻¹ (0.95 level of confidence). ^bThis 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.

in Figure 2. The combined data can be represented by the following equation, obtained by a weighted fit

$$\ln(m\text{Tris}_{(\text{sat.})}) = (1.75317 \pm 0.0013) - (1974.42 \pm 12.0) \times (1/T - 1/T_r) \quad (1)$$

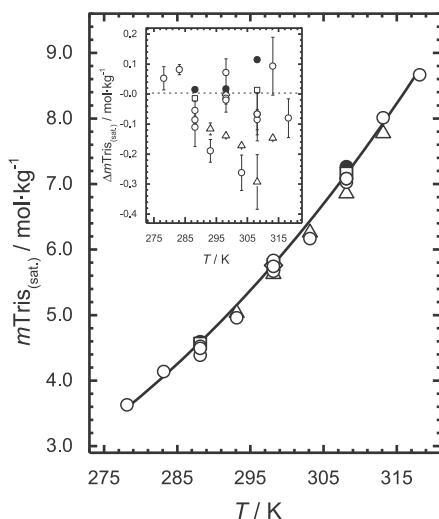


Figure 2. Measured solubilities of Tris ($m\text{Tris}_{(\text{sat.})}$) in pure water as a function of temperature (T). Key: circle, mean values from this study, as listed in Table 1; dot, Schindler et al.,³⁹ square, El Harakany and Barakat,³⁸ diamond, Taha and Lee,²³ triangle, Jouyban-Gharamaleki et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

where $m\text{Tris}_{(\text{sat.})}$ (mol kg⁻¹) is the molality of Tris in the saturated solution, T (K) is the temperature, and T_r is the reference temperature of 298.15 K. The plot of deviations from eq 1 is shown in the inset of Figure 2. The mean absolute deviation of all measurements from the fitted line is 0.099 mol kg⁻¹.

The solubilities of NaCl in pure water determined in this work are listed in Table 2. Measurements in the literature up to 1983 have been critically evaluated by Cohen-Adad et al.¹⁹ and represented by the following function Y

$$Y(x) = 2 \ln(x/(1+x)) \quad (2)$$

where x is the mole fraction of NaCl in the saturated solution, calculated as $m\text{NaCl}/(m\text{NaCl} + 1000/M_w)$, where the prefix m denotes molality and M_w is the molar mass of water (18.0153 g mol⁻¹). The dependence of Y on temperature, from 273 to 1073 K, is given by

$$Y(x) = Y(x_0) + A \cdot (1/T - 1/T_0) + B \cdot \ln(T/T_0) + C \cdot (T - T_0) \quad (3)$$

where T_0 is 273.15 K, the mole fraction x_0 at the same temperature is 0.09896, A is equal to 99.14456, B is equal to -1.53935, and C equals 0.00724959. Solubilities of NaCl in water can also be calculated from the thermodynamic evaluations by Archer of $\text{NaCl}_{(s)}$ ²⁰ and $\text{NaCl}-\text{H}_2\text{O}$ solutions,²¹ which are particularly relevant to this study because the Pitzer activity coefficient equations⁷ were used to represent solvent and solute activities in the aqueous solutions.

Solubilities of NaCl in pure water measured in this study are shown in Figure 3 together with values calculated using eq 3

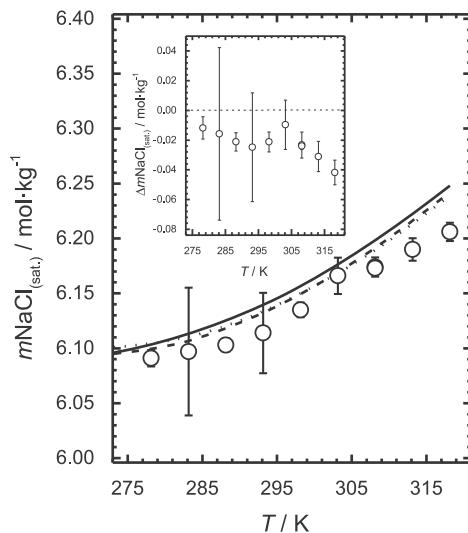


Figure 3. Solubilities of NaCl ($m\text{NaCl}_{(\text{sat.})}$) in pure water as a function of temperature (T). Key: circle, mean values (with standard uncertainties) from this study, as listed in Table 2; solid line, critical evaluation of Cohen-Adad et al.;¹⁹ and dashed and dotted lines, calculated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

mentioned above and from the work of Archer.^{20,21} It is clear that the variation in solubility with temperature is slight—only a 2.5% increase from 0 to 45 °C. Our results agree quite well with the critical evaluation of Cohen-Adad et al.¹⁹ up to about 30 °C. At 25 °C, their equation yields a solubility of 6.156 mol kg⁻¹, and the 39 measurements that Cohen-Adad et al. fitted at this temperature have a mean value of 6.1536 ± 0.024 mol kg⁻¹. Our own value is 6.135 ± 0.0067 mol kg⁻¹, which agrees satisfactorily. However, at higher temperatures, our measured solubilities are lower: by -0.37% at 35 °C and -0.67% at 45 °C. Insufficient equilibration time in the experiments does not appear to be the reason for this because solubilities at 35 °C were measured twice, in one case the previous equilibration having been at a lower temperature and in the other case at a higher temperature. The two results are 6.1742 ± 0.0067 and 6.1734 ± 0.0023 mol kg⁻¹, which agree well.

3.2. Solubilities in Mixtures. Measured solubilities of NaCl in aqueous Tris are listed in Table 3 and those of Tris in aqueous solutions of NaCl, TrisHCl, and $(\text{TrisH})_2\text{SO}_4$ are listed in Tables 4–6, respectively. The overall behavior observed is that the solubility of Tris is reduced, relative to that in pure water at the same temperature, in aqueous NaCl and aqueous $(\text{TrisH})_2\text{SO}_4$ (salting out) but increased slightly in aqueous TrisHCl (salting in). We note that this is qualitatively the same as is observed for NH_3 solubilities in NaCl, $(\text{NH}_4)_2\text{SO}_4$, and NH_4Cl solutions.²² Sodium chloride is salted out in aqueous Tris solutions (Table 3), as would be expected from the corresponding results for Tris solubilities in $\text{NaCl}_{(\text{aq})}$.

The only data with which these results can be compared directly are solubilities of Tris in aqueous NaCl at 25 °C inferred from density measurements (see Figure 1 and Table 4 of Taha and Lee²³). The data of Taha and Lee are compared with our own in Figure 4. There is generally good agreement, except at the highest NaCl molalities for which our measurements suggest that there might be a slight increase in Tris solubility (this tendency is also shown at other temperatures; see Section 5.1.4). The uncertainties in the data of Taha and Lee²³ for Tris

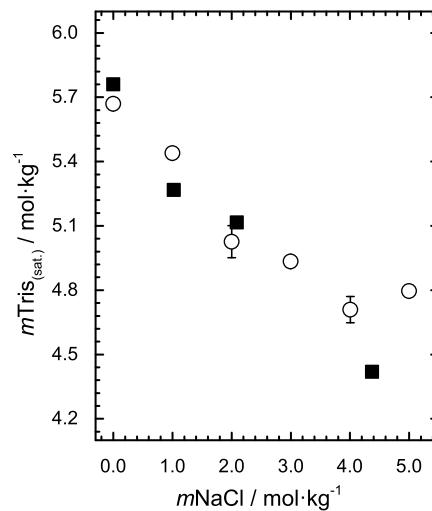


Figure 4. Measured solubilities of Tris ($m\text{Tris}_{(\text{sat.})}$) in aqueous NaCl at 25 °C, as a function of NaCl molality ($m\text{NaCl}$). Key: circle, mean values (with standard uncertainties) from this study, as listed in Table 4; and solid square, measurements of Taha and Lee.²³

solubility are not stated but seem likely to be greater than for our measurements because of the indirect way in which they are obtained.

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 (excluding other data) in pure water were described by an equation of the same form as eq 1

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

where $mS_{(\text{sat.})}^o$ (mol kg⁻¹) 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, $(\text{TrisH})_2\text{SO}_4$, and NaCl, and of NaCl in aqueous Tris solutions

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

where $\ln(mS_{(\text{sat.})}^o)$ is given by eq 4 above, m (mol kg⁻¹) is the molality of the solute 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 $(\text{TrisH})_2\text{SO}_4$. 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 nonlinear, and an extra coefficient (b_2) is required in eq 5. The results at all molalities of NaCl, at 40 and 45 °C, do not appear to be fully consistent with the data for lower temperatures and are poorly represented. We note that it is difficult to keep the glass-sampling syringe at temperatures

Table 7. Coefficients of the Equations Used to Represent the Measured Solubilities^a

solutions	RMSE ^b	coefficients					
		a_0	a_1	b_0	b_1	b_2	c
Tris in water	0.012	1.7397 ± 0.0019	-1933 ± 15				
NaCl in water	0.024	1.8155 ± 0.0005	-44.52 ± 3.57				
Tris in $\text{TrisHCl}_{(\text{aq})}$	0.069			0.0226 ± 0.0005	1587 ± 247	0.0	
Tris in $(\text{TrisH})_2\text{SO}_4_{(\text{aq})}$	0.068			-0.1044 ± 0.0015	426.0 ± 154.6	0.0	
Tris in $\text{NaCl}_{(\text{aq})}$	0.165			-0.0704 ± 0.0024	643.2 ± 69.2	0.00707 ± 0.00058	2.0
NaCl in $\text{Tris}_{(\text{aq})}$	0.016			-0.0171 ± 0.0006	1035 ± 79	0.00521 ± 0.00034	1.5

^aCoefficients a_{0-1} are for eq 4 and b_{0-2} and c are for eq 5. ^bThe column RMSE contains the root mean square deviations of the measured values from the fitted solubilities.

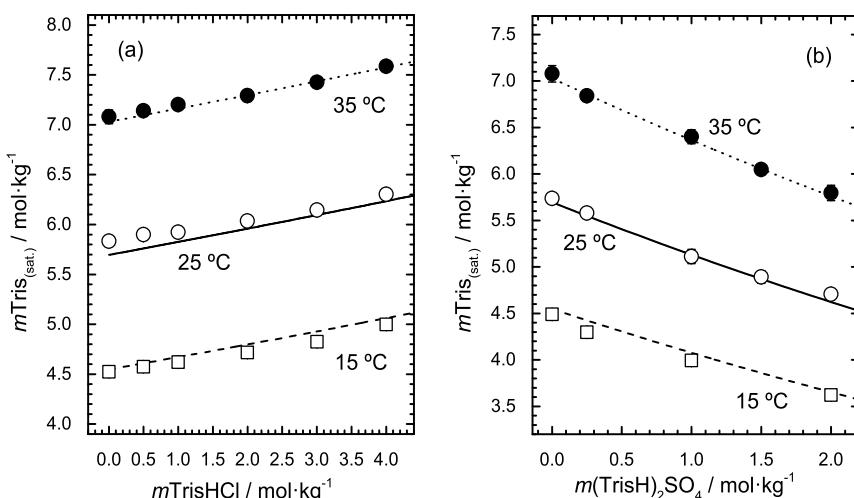


Figure 5. Measured and fitted solubilities of Tris ($m\text{Tris}_{(\text{sat})}$) in (a) aqueous TrisHCl , and (b) aqueous $(\text{TrisH})_2\text{SO}_4$. Key (both plots): square, 15 °C; circle, 25 °C; dot, 35 °C; and lines, fitted values (eq 5, with parameters in Table 7).

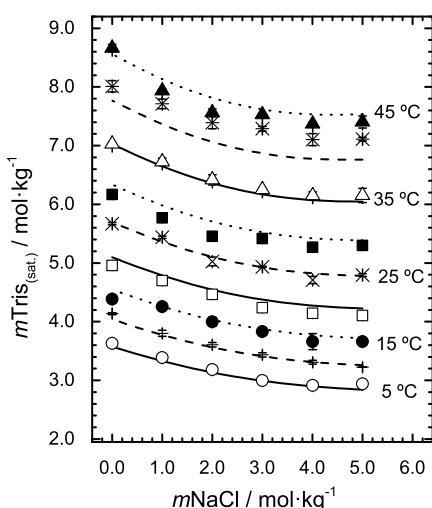


Figure 6. Measured and fitted solubilities of Tris ($m\text{Tris}_{(\text{sat})}$) in aqueous NaCl at different temperatures. Key: circle, 5 °C; plus, 10 °C; dot, 15 °C; open square, 20 °C; cross, 25 °C; solid square, 30 °C; open triangle, 35 °C; asterisk, 40 °C; solid triangle, 45 °C; and lines, fitted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

higher than 40 °C for the long period of time sometimes required for sampling (ca. 1–2 min), which could affect the solubility measurements at the highest temperatures as described above.

Solubilities of NaCl in aqueous Tris are shown in Figure 7. They vary only slightly with Tris molality and are relatively more

scattered than the other results. There is a clear dependence of the slope of the relationship between solubility and Tris molality with temperature, and the data for 25–40 °C suggest that there is a salting-in effect at the highest Tris molalities. However, the results for 45 °C are not fully consistent with this (the measured solubilities decrease almost linearly with Tris molality).

3.3. Water Activities of Supersaturated Tris Solutions.

We have also measured water activities of Tris solutions, to extremely high concentrations, using a kinetic technique in which micron-sized droplets are evaporated in an environment of controlled relative humidity.²⁴ These new experimental data are relevant to the analysis of Tris solubilities at temperatures above 25 °C because the values of the water activities of aqueous Tris are currently known only at 25 °C up to saturation at that temperature (about 5.7 mol kg^{-1}). The results of these experiments are presented in the Appendix.

4. THEORY

The equilibrium between the pure solid-phase Tris and its saturated solution is given by



where $m\text{Tris}$ is the molality of Tris, γ_{Tris} is its molality-based activity coefficient, and K_s (mol kg^{-1}) is the equilibrium constant, which is a function of temperature and pressure. The corresponding equilibrium for NaCl is

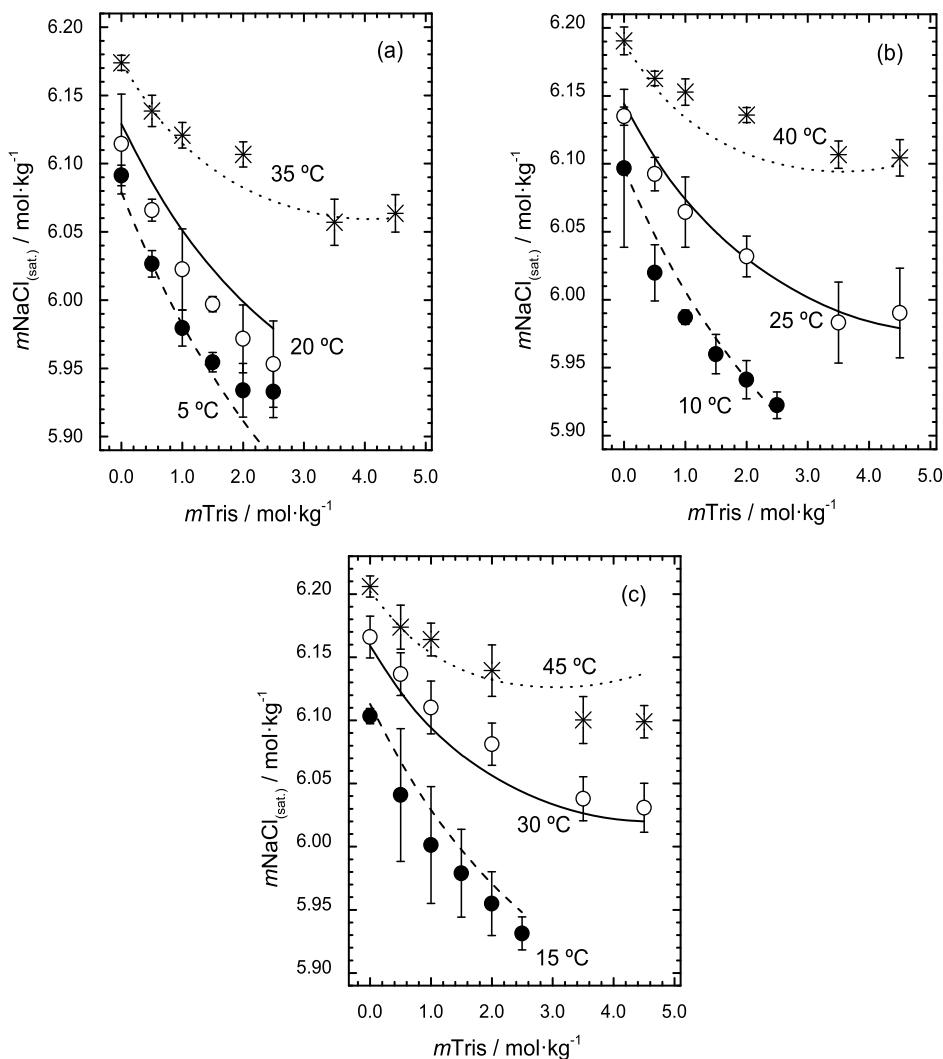


Figure 7. Measured and fitted solubilities of NaCl ($m\text{NaCl}_{(\text{sat})}$) in aqueous Tris at different temperatures. (a) 5–35 °C. Key: dot, 5 °C; circle, 20 °C; and asterisk, 35 °C. (b) 10–40 °C. Key: dot, 10 °C; circle, 25 °C; and asterisk, 40 °C. (c) 15–45 °C. Key: dot, 15 °C; circle, 30 °C; and asterisk, 45 °C. The lines are fitted values (eq 5, with parameters in Table 7).



$$K_{\text{S}}(\text{NaCl}) = m\text{Na}^+ \cdot m\text{Cl}^- \cdot \gamma_{\text{Na}} \cdot \gamma_{\text{Cl}} \quad (7\text{b})$$

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

The variation in the Tris and NaCl solubilities with the composition of the solution medium reflects changes in the activity coefficients in the equations above. These can be expressed using the Pitzer equations⁷ 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 $\text{M}_\nu^+ \text{X}_\nu^-$ is

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

where parameters $\lambda_{\text{N},\text{N}}$ and $\mu_{\text{N},\text{N},\text{N}}$ describe the self-interactions of the solute N and $\lambda_{\text{N},\text{M}}$ and $\lambda_{\text{N},\text{X}}$ describe the interactions with the cation M^{z+} and anion X^{z-} , respectively. In addition, there are parameters for higher order interactions of the solute N with the cation and anion together ($\zeta_{\text{N},\text{M},\text{X}}$) and two molecules of the solute N with the cation ($\mu_{\text{N},\text{N},\text{M}}$) and with the anion ($\mu_{\text{N},\text{N},\text{X}}$). 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,^{22,25} and we do this here for 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 (γ_{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 as

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

where A^φ is the Debye Hückel constant²⁶ (0.391475 at 25 °C and 1 atm pressure), I (mol kg⁻¹) is the ionic strength of the solution, the prefix m denotes molality, and quantities $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, and $C^{(1)}$ are parameters for the interaction of Na^+ with Cl^- ions (determined from measurements of the solute and solute activities in pure aqueous NaCl solutions). The quantities α (2.0) and ω (2.5) are constants, and the functions $g(x)$ and $h(x)$ are given by

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \quad (10)$$

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

The elements of eq 9 for the $\text{Na}^+ - \text{Cl}^-$ interactions can be derived from the equations in the Appendix I of Clegg et al.²⁷ for the general case of a mixture of electrolytes containing an arbitrary number of ions. Generalized expressions for the activity coefficients of neutral (i.e., uncharged) solutes and for the contributions of ion-neutral interactions to the activity coefficients of ions are given by Pitzer.⁷

The existence of three common parameters in eq 9 and in eq 8 for the interaction of the uncharged solute N and Na^+ and Cl^- ions implies that the effect of dissolved NaCl on Tris solubility and vice versa can be determined from measurements of the solubility of either component in a solution of the other. It also means that where both have been measured, as in the present study, the results can be tested for mutual consistency. More broadly, it is possible to compare the results with any thermodynamic measurement yielding solute or solvent activities from which values of the same parameters can be derived (e.g., see the study of Clegg and Brimblecombe²² on the solubility of NH_3 in aqueous salt solutions).

5. MODELLING AND COMPARISONS WITH OTHER DATA

In this section, we use the Pitzer model to compare the results of the solubility experiments with data for the stoichiometric dissociation constant of TrisH^+ in aqueous NaCl and EMF measurements of solutions containing dissolved Tris, TrisHCl, and NaCl. These comparisons are made at 25 °C because it is at this temperature that water activities of aqueous Tris and TrisHCl solutions have been determined¹¹ and Pitzer interaction parameters—necessary for the analysis—are known.

5.1. Tris–TrisHCl–NaCl Solutions. The parameters in eqs 8 and 9 that describe the salting-out behavior that is observed in aqueous Tris–NaCl mixtures (Figures 6 and 7) are $\lambda_{\text{Tris},\text{Na}}$, $\zeta_{\text{Tris},\text{Na},\text{Cl}}$, and possibly $\mu_{\text{Tris},\text{Tris},\text{Na}}$. Of these, the first parameter is likely to be the most important. There are two other types of measurements that are relevant and for which the activity coefficient equations contain the same parameters: titrations yielding values of the stoichiometric dissociation constant of TrisH^+ in aqueous NaCl¹³ and measurements of EMFs of cells containing dissolved NaCl, TrisHCl, and Tris.²⁸ These

measurements and the parameter values that can be obtained from them are considered below.

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

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

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

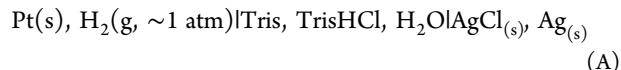
The value of $K(\text{TrisH}^+)$ is 8.47504×10^{-9} mol kg⁻¹ at 25 °C² and the activity coefficients are for trace quantities of the three species in the aqueous NaCl medium. The Pitzer model expressions for these activity coefficients involve parameters for $\text{TrisH}^+ - \text{Cl}^-$ and $\text{H}^+ - \text{Cl}^-$ interactions, which are known from thermodynamic data for $\text{TrisHCl}_{(\text{aq})}$ and $\text{HCl}_{(\text{aq})}$, and the following mixture parameters: $\theta_{\text{Tris},\text{Na}}$, $\psi_{\text{TrisH},\text{Na},\text{Cl}}$, $\lambda_{\text{Tris},\text{Na}}$, and $\zeta_{\text{Tris},\text{Na},\text{Cl}}$. Expressions for the contributions of all the ion interaction parameters to the activity coefficients of TrisH^+ and H^+ can be found in the generalized equations given by Pitzer⁷ and by Clegg et al.²⁷ Combining these expressions and the relevant parts of eq 8 for $\ln(\gamma_{\text{Tris}})$ we obtain

$$\begin{aligned} \ln(K^*(\text{TrisH}^+)) = & \ln(K(\text{TrisH}^+)) \\ & + \{\text{TrisH}^+ - \text{Cl}^- \text{ terms}\} \\ & - \{\text{H}^+ - \text{Cl}^- \text{ terms}\} \\ & + 2m\text{NaCl} \cdot (\theta_{\text{Tris},\text{Na}} - \theta_{\text{H},\text{Na}} - \lambda_{\text{Tris},\text{Na}}) \\ & + m\text{NaCl}^2 \cdot (\psi_{\text{TrisH},\text{Na},\text{Cl}} - \psi_{\text{H},\text{Na},\text{Cl}} - \zeta_{\text{Tris},\text{Na},\text{Cl}}) \end{aligned} \quad (13)$$

The two terms for $\text{H}^+ - \text{Cl}^-$ and $\text{TrisH}^+ - \text{Cl}^-$ interactions in the equation are those that involve the parameters $\beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$, and $C_{\text{ca}}^{(0)}$ for the cations TrisH^+ and H^+ and the anion Cl^- . Their values and those of the two known mixture parameters $\theta_{\text{H},\text{Na}}$ and $\psi_{\text{H},\text{Na},\text{Cl}}$ 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.¹³ in 0.5–6.0 mol 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 $\theta_{\text{H},\text{Na}}$ and $\psi_{\text{H},\text{Na},\text{Cl}}$ from Table 8 and fitting the measured $\text{p}K^*(\text{TrisH}^+)$ yields $(\theta_{\text{Tris},\text{Na}} - \lambda_{\text{Tris},\text{Na}}) = -0.02632 \pm 0.0015$ and $(\psi_{\text{TrisH},\text{Na},\text{Cl}} - \zeta_{\text{Tris},\text{Na},\text{Cl}}) = 0.0$. 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 $\theta_{\text{H},\text{Na}}$ and $\psi_{\text{H},\text{Na},\text{Cl}}$.

5.1.2. Electromotive Forces of Cells Containing Aqueous Tris, TrisHCl, and NaCl. Tishchenko²⁸ has measured EMFs of the following cells from 0 to 40 °C



In the experiments in cell A, the molalities of Tris ranged from 0.01 to 0.1 mol kg⁻¹ and those of TrisHCl ranged from 0.0075 to 4.0 mol kg⁻¹. In cell B, the EMFs of equimolar 0.04 mol kg⁻¹ Tris/TrisH⁺ in 0.05–4.0 mol kg⁻¹ NaCl were measured, and those of solutions of equimolar TrisHCl/NaCl (0.1–4.0 mol kg⁻¹ total Cl^-) containing 0.025–3.79 mol kg⁻¹ Tris were also measured. In the definitions of the cells mentioned above, the partial pressure of H_2 is equal to the atmospheric pressure at the

Table 8. Pitzer Model Parameters for $pK^*(\text{TrisH}^+)$ and EMF Calculations^a

species	parameter	value	source ^b
TrisH ⁺ Cl ⁻ ^c	$\beta^{(0)}$	0.0426783	1
TrisH ⁺ Cl ⁻	$\beta^{(1)}$	0.196255	1
TrisH ⁺ Cl ⁻	$C^{(0)}$	-0.0014451	1
Na ⁺ Cl ⁻	$\beta^{(0)}$	0.0806342	3
Na ⁺ Cl ⁻	$\beta^{(1)}$	0.263098	3
Na ⁺ Cl ⁻	$C^{(0)}$	0.00026239	3
Na ⁺ Cl ⁻	$C^{(1)}$ ^d	-0.010052	3
H ⁺ Na ⁺	θ	0.036	4
H ⁺ Na ⁺ Cl ⁻	ψ	-0.004	4
H ⁺ Cl ⁻	$\beta^{(0)}$	0.17567	2
H ⁺ Cl ⁻	$\beta^{(1)}$	0.297786	2
H ⁺ Cl ⁻	C	0.0006847	2
Tris Tris ^e	λ	-0.00516	1
Tris	μ	0.000703	1

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

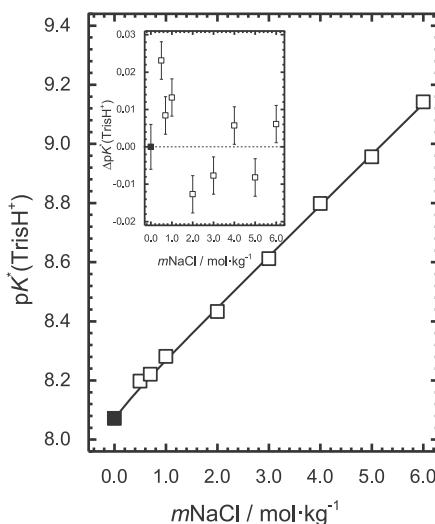


Figure 8. Measured and fitted stoichiometric dissociation constants of TrisH⁺ ($pK^*(\text{TrisH}^+)$, where $K^*(\text{TrisH}^+)$ is in mol kg⁻¹) in aqueous NaCl at 25 °C, as a function of NaCl molality ($m\text{NaCl}$). Key: solid square, value in pure water (fixed), measured by Bates and Hetzer;²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

time of measurement (which was not recorded) minus the partial pressure of water in the saturated stream of H₂ 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 vapor pressure of pure water²⁹ at the experimental temperature. Tishchenko²⁸ 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.

Table 9. Pitzer Model Parameters Obtained by Tishchenko²⁸ for Tris—TrisHCl—NaCl Solutions at 25 °C^a

species	parameter	value
TrisH ⁺ Cl ⁻	$\beta^{(0)}$	0.04389
TrisH ⁺ Cl ⁻	$\beta^{(1)}$	0.17395
TrisH ⁺ Cl ⁻	$C^{(0)}$	-0.00150
Tris Na ⁺	λ	0.02106
Tris TrisH ⁺	λ	-0.02445
Tris	λ	0.02707
Tris	μ	-0.003433
Na ⁺ TrisH ⁺	θ	-0.00017
Na ⁺ TrisH ⁺ Cl ⁻	ψ	-0.001455

^aThese values are from Tishchenko's Table 2. The source of the interaction parameters for Na⁺ and Cl⁻ that were used in Tishchenko's model is not stated, or values given, but they are likely to come from Pitzer et al.⁴³

The equation relating the measured EMFs to the activities of H⁺ and Cl⁻ (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 H₂ in the gas stream, E^0 (V) is the standard EMF of the cell, R (8.31446 J mol⁻¹ K⁻¹) is the gas constant, F (96485.33 C mol⁻¹) is Faraday's constant, P (atm) is the atmospheric pressure, and $p\text{H}_2\text{O}$ (atm) is the equilibrium vapor pressure of water above the aqueous test solution. The quantity "Jet corr." is a small pressure correction related to the depth of the H₂ bubbler below the solution surface in the half cell containing the Pt H₂ electrode.³⁰ It was assumed to be negligible in these experiments. The activity of H⁺ in eq 14 above can be replaced by an expression involving the dissociation of TrisH⁺ and simplified to

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

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

In this equation, which is equivalent to eq 1 of Tishchenko,²⁸ 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 as

$$\begin{aligned}
 \ln(\gamma_{\text{TrisH}}\gamma_{\text{Cl}}/\gamma_{\text{Tris}}) &= \ln(K(\text{TrisH}^+)) + \{\text{TrisH}^+, \text{Cl}^- \text{ terms}\} \\
 &\quad - \{\text{Tris terms}\} \\
 &+ 2(m\text{Tris} - m\text{TrisHCl}) \cdot \lambda_{\text{Tris}, \text{TrisH}} \\
 &+ m\text{Tris} \cdot m\text{TrisHCl} \cdot (2\zeta_{\text{Tris}, \text{TrisH}, \text{Cl}} - 6\mu_{\text{Tris}, \text{Tris}, \text{TrisH}}) \\
 &+ 3m\text{Tris}^2 \cdot \mu_{\text{Tris}, \text{Tris}, \text{TrisH}} - m\text{TrisHCl}^2 \cdot \zeta_{\text{Tris}, \text{TrisH}, \text{Cl}} \\
 \end{aligned} \tag{16}$$

where the quantity $\{\text{TrisH}^+, \text{Cl}^- \text{ terms}\}$ is the sum of the Pitzer model terms for the logarithm of the activity coefficient product of TrisH^+ and Cl^- in a pure aqueous solution of TrisHCl at its molality in the mixture. It can be calculated at 25 °C using the parameters for $\text{TrisH}^+ \cdot \text{Cl}^-$ interactions listed in Table 8. Similarly, the quantity $\{\text{Tris terms}\}$ 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 ($2m\text{Tris} \cdot \lambda_{\text{Tris}, \text{Tris}} + 3m\text{Tris}^2 \cdot \mu_{\text{Tris}, \text{Tris}, \text{Tris}}$; see eq 8 above). The unknowns in the equation are the mixture parameters $\lambda_{\text{Tris}, \text{TrisH}}$, $\zeta_{\text{Tris}, \text{TrisH}, \text{Cl}}$, and $\mu_{\text{Tris}, \text{Tris}, \text{TrisH}}$. 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 15b. These parameters appear both in the Pitzer expression for the activity coefficient of Tris in TrisHCl and $(\text{TrisH})_2\text{SO}_4$ solutions (from eq 8) and in those for the activity coefficients that can be determined from the measurements by Tishchenko²⁸ using cell B.

The following expression relates the measured EMF in cell B to the activities of H^+ and Na^+ in the test solutions

$$\begin{aligned}
 E_{(\text{meas})} &= E^0 + (RT/2F) \cdot \ln(P - p\text{H}_2\text{O} - \text{Jet corr.}) \\
 &\quad - (RT/F) \cdot \ln(a\text{H}^+ / a\text{Na}^+) \\
 \end{aligned} \tag{17}$$

A similar analysis to that carried out for cell A yields

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

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

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:

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

In the above expression, $\{\text{TrisH}^+ \cdot \text{Cl}^- \text{ terms}\}$ is the sum of the Pitzer model contributions to $\ln(\gamma_{\text{TrisH}})$ that arise from the interactions of TrisH^+ with Cl^- only, and the meaning of $\{\text{Na}^+ \cdot \text{Cl}^- \text{ terms}\}$ 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 Pitzer⁷ 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 $\lambda_{\text{Tris}, \text{TrisH}}$, $\zeta_{\text{Tris}, \text{TrisH}, \text{Cl}}$, and $\mu_{\text{Tris}, \text{Tris}, \text{TrisH}}$.

The Pitzer model parameters obtained by Tishchenko²⁸ and listed in Table 9 include values for both $\text{TrisH}^+ \cdot \text{Cl}^-$ interactions ($\beta_{\text{TrisH}, \text{Cl}}^{(0)}$, $\beta_{\text{TrisH}, \text{Cl}}^{(1)}$, and $C_{\text{TrisH}, \text{Cl}}^{(0)}$) and Tris self-interactions ($\lambda_{\text{Tris}, \text{Tris}}$ and $\mu_{\text{Tris}, \text{Tris}, \text{Tris}}$). 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.¹¹ However, the values of $\lambda_{\text{Tris}, \text{Tris}}$ and $\mu_{\text{Tris}, \text{Tris}, \text{Tris}}$ that were obtained are not consistent with the results of Robinson and Bower,¹¹ which show a close to ideal behavior. For our own analysis of the EMF results, we first fitted the two Pitzer model coefficients to the isopiestic data, recalculated using values for the NaCl reference solutions from the study of Archer²¹ (see Table 8 and the Supporting Information).

Tishchenko²⁸ carried out two sets of experiments using cell B. In the first of those, the solution compositions were chosen so that the only unknown mixture parameters (in addition to $\lambda_{\text{Tris}, \text{TrisH}}$ and $\zeta_{\text{Tris}, \text{TrisH}, \text{Cl}}$ whose values can be determined from data from cell A) are $\lambda_{\text{Tris}, \text{Na}}$ and $\zeta_{\text{Tris}, \text{Na}, \text{Cl}}$ (we neglect, for now, the other ternary parameters $\eta_{\text{Tris}, \text{Na}, \text{TrisH}}$, $\mu_{\text{Tris}, \text{Tris}, \text{TrisH}}$, and $\mu_{\text{Tris}, \text{Tris}, \text{Na}}$). In the second set of experiments, the additional unknowns are $\theta_{\text{Na}, \text{TrisH}}$ and $\psi_{\text{Na}, \text{TrisH}, \text{Cl}}$. We have fitted the data for cells A and B while applying the constraints $\psi_{\text{Na}, \text{TrisH}, \text{Cl}} = \zeta_{\text{Tris}, \text{Na}, \text{Cl}}$ and $(\theta_{\text{Na}, \text{TrisH}} - \lambda_{\text{Tris}, \text{Na}}) = -0.02632$ determined in Section 5.1.1 above from the titration measurements. The results are listed in Table 10 and plotted in Figure 9. This figure shows the fitted activity coefficient products and the values derived from the EMF measurements. For cell A and for the experiments in cell B in which the solutions contain equimolar 0.04 m Tris and TrisH^+ , the results are satisfactory over the entire chloride molality range, with no systematic deviations apparent in the

Table 10. Fitted Pitzer Model Parameters for Tris–TrisHCl–NaCl Solutions at 25 °C^a

species	parameter	value	standard error
Tris Na ⁺	λ	0.04662	0.0011
Tris TrisH ⁺	λ	-0.01970	0.0012
Tris TrisH ⁺ Cl ⁻	ζ	-0.00182	0.00071
Tris Na ⁺ Cl ⁻	ζ	-0.00940	0.00061
Na ⁺ TrisH ⁺	θ^b	-0.0203	0.0019
Na ⁺ TrisH ⁺ Cl ⁻	ψ^b	-0.00940	

^aThe fits of the model to data for cells A and B used the parameters listed in Table 8 for TrisH⁺–Cl⁻, Na⁺–Cl⁻, and Tris–Tris interactions. The root mean square deviation of the observed from the fitted EMFs was 0.12 mV. ^bThese 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⁺.

residuals. In the case of the cell B solutions containing high molalities of Tris (Figure 9c), there is a clear trend in the residuals with Tris molality, with the most positive values at about 1.0 mol kg⁻¹ Tris. Removal of data for these higher 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 obtained by Tishchenko.

5.1.3. Solubilities of Tris in Aqueous TrisHCl. We have fitted the measured solubilities at 25 °C to obtain $\lambda_{\text{Tris,TrisH}}$ equal to -0.01241 ± 0.00098 ; see Figure 10. The salting-in behavior observed in these mixtures is also implied by the negative value obtained by Tishchenko for the same parameter (Table 9). However, his value of $\lambda_{\text{Tris,TrisH}}$ (-0.02445) is of greater magnitude. In our fit of the data for cells A and B, see Table 10, the parameter $\zeta_{\text{Tris,TrisH,Cl}}$ was found to be significant, and in this result the value of $\lambda_{\text{Tris,TrisH}}$ (-0.0197) is also more negative than for the solubility data.

As a further test, we fitted the data for cell A only and obtained $\lambda_{\text{Tris,TrisH}}$ equal to -0.0228 , which is quite close to Tishchenko's result. It therefore appears that the measured Tris solubilities in these solutions and the EMF data for cell A are not fully thermodynamically consistent: the EMF measurements imply a greater degree of salting in (i.e., corresponding to a more negative value of $\lambda_{\text{Tris,TrisH}}$) than is observed. Finally, it is also possible that the interaction parameter $\mu_{\text{Tris,Tris,TrisH}}$ has a non-zero value. It could significantly influence the description of the solubilities by eqs 6a and 8, a positive value of $\mu_{\text{Tris,Tris,TrisH}}$ implying a more negative $\lambda_{\text{Tris,TrisH}}$. It would have a negligible effect for the solutions measured in cell A, in which the Tris molalities were all 0.1 mol kg⁻¹ or lower. We note that this type

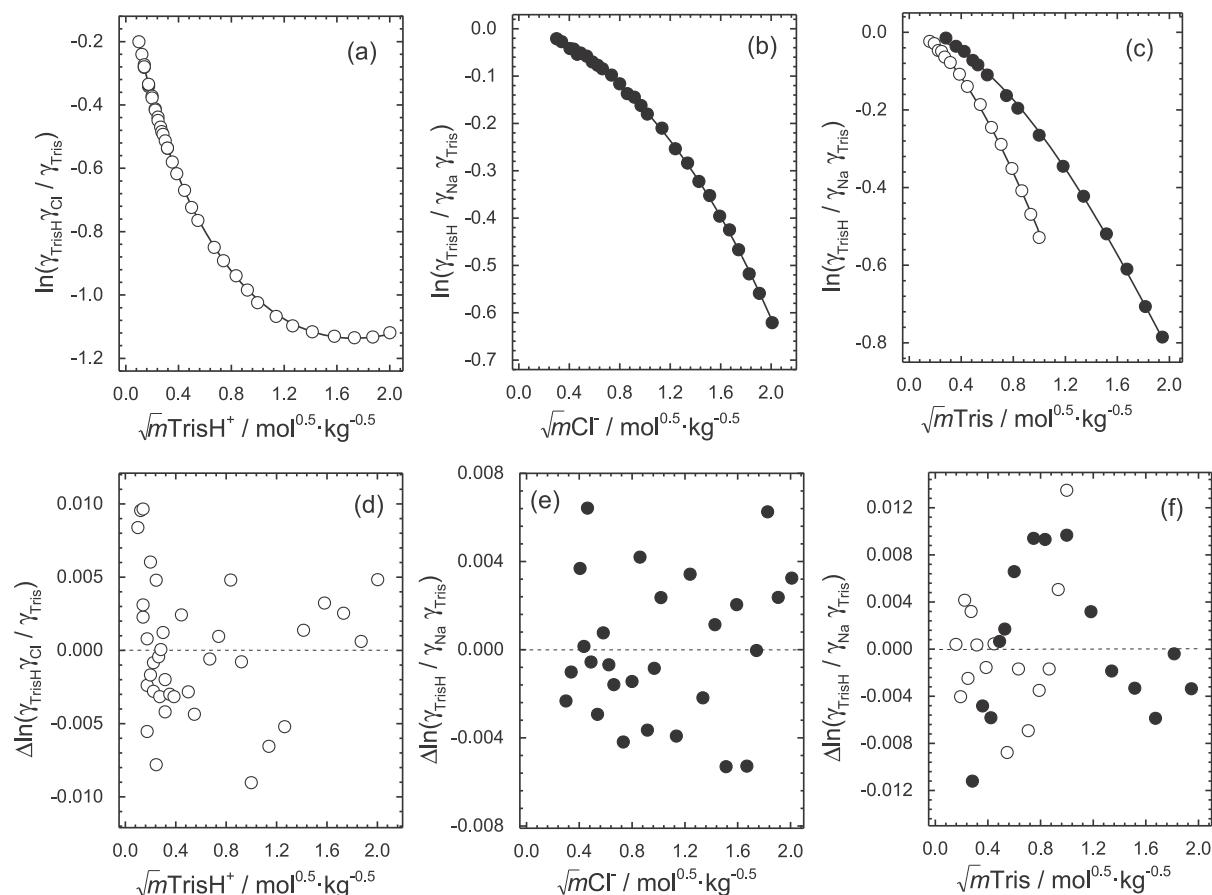


Figure 9. Measured and fitted values of the data from cell A and cell B at 25 °C,²⁸ expressed as logarithms of activity coefficient products determined from eq 15 and eq 18. (a) Cell A, the quantity $\ln(\gamma_{\text{TrisH}} \gamma_{\text{Cl}} / \gamma_{\text{Tris}})$ plotted against the square root of TrisH⁺ molality ($\sqrt{m\text{TrisH}^+}$). Key: circle, measurements; and line, the fitted model. (b) Cell B (solutions containing equimolar Tris and TrisH⁺), the quantity $\ln(\gamma_{\text{TrisH}} / (\gamma_{\text{Na}} \gamma_{\text{Tris}}))$ plotted against the square root of Cl⁻ molality ($\sqrt{m\text{Cl}^-}$). Key: dot, measurements; and line, the fitted model. (c) Cell B (solutions containing equimolar Na⁺ and TrisH⁺), the quantity $\ln(\gamma_{\text{TrisH}} / (\gamma_{\text{Na}} \gamma_{\text{Tris}}))$ plotted against the square root of Tris molality ($\sqrt{m\text{Tris}}$). Key: circle, measured values for solutions in which $m\text{Cl}^-$ is equal to $4m\text{Tris}$; dot, measured values for solutions in which $m\text{Cl}^-$ and $m\text{Tris}$ are equal; and lines, the fitted model. Panels (d–f) show the deviations of the model from the measurements (observed–fitted). The symbols have the same meanings as panels (a–c).

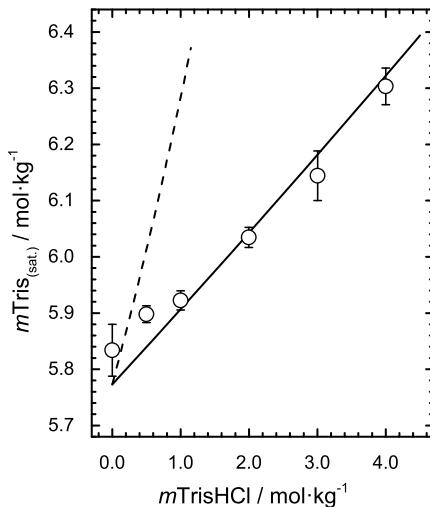


Figure 10. Measured and fitted solubilities of Tris ($m\text{Tris}_{(\text{sat})}$) in aqueous TrisHCl at 25 °C. Key: circle, measured values (this study); solid line, our fitted model; and dashed line, calculated using the interaction parameters of Tishchenko.²⁸

of parameter was found, in an earlier study,²² to be needed to describe solubilities of several electrolytes in aqueous NH_3 . However, this was for molalities of NH_3 of 20 mol kg^{-1} or more, which are far greater than the Tris molalities in our experiments.

5.1.4. Solubilities of Tris in Aqueous NaCl. The salting out of Tris by dissolved NaCl decreases with NaCl molality; see Figure 6. We first fitted eqs 6a and 8 to solubilities of Tris at 25 °C from 0 to 4.0 mol kg^{-1} NaCl—ignoring the final data point, which appears to be anomalously high—and obtained $\lambda_{\text{Tris},\text{Na}} = 0.02817 \pm 0.00077$. Measured and calculated solubilities are shown in Figure 11. This value of $\lambda_{\text{Tris},\text{Na}}$ is similar to that obtained by Tishchenko (0.02106, Table 9). However, in our fit of the EMF data, we obtained $\zeta_{\text{Tris},\text{Na},\text{Cl}}$ equal to −0.00940 (Table 10). Including this parameter, fixed to the same value, in a fit of the Tris solubilities yields $\lambda_{\text{Tris},\text{Na}}$ equal to 0.0420 ± 0.00090 and the dashed line in Figure 11. This is similar to the

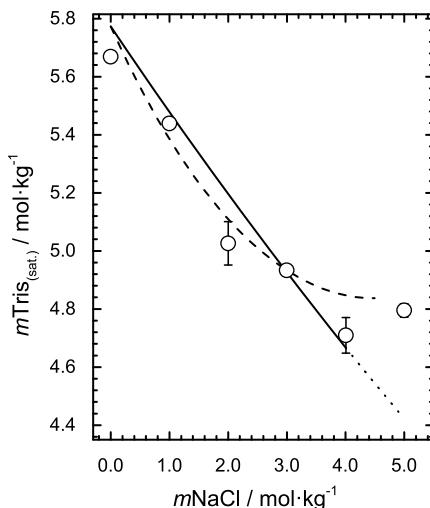


Figure 11. Measured and fitted solubilities of Tris ($m\text{Tris}_{(\text{sat})}$) in aqueous NaCl at 25 °C. Key: circle, measured values (this study); solid line with dotted extension, the fitted model (to 4.0 mol·kg⁻¹ NaCl); and dashed line, fitted (with a non-zero $\zeta_{\text{Tris},\text{Na},\text{Cl}}$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

value we obtained from the EMFs (Table 10). However, this pair of parameter values implies an *increase* in solubility of NaCl in aqueous Tris solutions, which is not what is observed.

5.1.5. Solubilities of NaCl in Aqueous Tris. The solubility of NaCl in water is only slightly reduced by the presence of Tris, from about 6.15 mol kg^{-1} in pure water to just below 6.0 mol kg^{-1} in 4–5 mol kg^{-1} Tris solutions. A fit of the data to 3.5 mol kg^{-1} Tris, using eqs 7a and 9, yielded $\lambda_{\text{Tris},\text{Na}}$ equal to 0.0163 ± 0.0023 (with $\zeta_{\text{Tris},\text{Na},\text{Cl}}$ 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^{-1} Tris yield $\lambda_{\text{Tris},\text{Na}}$ equal to 0.01815 ± 0.0029 and 0.02740 ± 0.0037 , respectively.

Fixing $\zeta_{\text{Tris},\text{Na},\text{Cl}}$ equal to −0.00940 (the value obtained by fitting to the EMF data) and refitting the NaCl solubilities yields $\lambda_{\text{Tris},\text{Na}}$ equal to 0.0726 ± 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 0–1.0 mol kg^{-1} Tris molality range ($\lambda_{\text{Tris},\text{Na}}$ equal to 0.02740) is consistent with that for Tris solubility in aqueous NaCl ($\lambda_{\text{Tris},\text{Na}}$ equal to 0.02817).

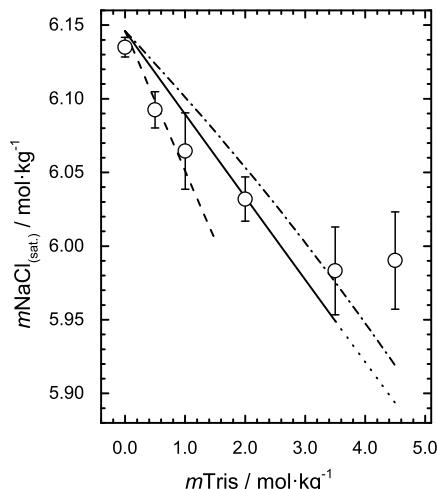


Figure 12. Measured and fitted solubilities of NaCl ($m\text{NaCl}_{(\text{sat})}$) in aqueous Tris at 25 °C. Key: circle, measured values (this study); solid line with dotted extension, fitted (to 3.5 mol·kg⁻¹ Tris); dashed line, fitted (to 1.0 mol·kg⁻¹ Tris); and dash-dot line, fitted (with a non-zero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

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

$$\begin{aligned} \Delta\ln(\gamma_{\text{Na}} \cdot \gamma_{\text{Cl}}) = & \ln(K_{\text{S}}(\text{NaCl})) - \ln(m\text{Na}^+) - \ln(m\text{Cl}^-) \\ & - \ln(\gamma_{\text{Na}})^{\text{P}} - \ln(\gamma_{\text{Cl}})^{\text{P}} \end{aligned} \quad (20)$$

where $K_{\text{S}}(\text{NaCl})$ (eq 7b) is the thermodynamic solubility product of NaCl at 25 °C (38.30 mol² kg^{-2}), $m\text{Na}^+$ and $m\text{Cl}^-$ are the molalities of the ions in the solution saturated with respect to NaCl(s), and $(\gamma_{\text{Na}})^{\text{P}}$ and $(\gamma_{\text{Cl}})^{\text{P}}$ are the model-calculated activity coefficients of the ions in eq 9 but neglecting the mixture terms. Therefore

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

The value of the left-hand side of eq 20, determined from the measured solubilities and calculated pure solution contributions to the activity coefficients $(\gamma_{\text{Na}})^{\text{P}}$ and $(\gamma_{\text{Cl}})^{\text{P}}$, is plotted in Figure 13. The relationship with m_{Tris} is nonlinear. The values of

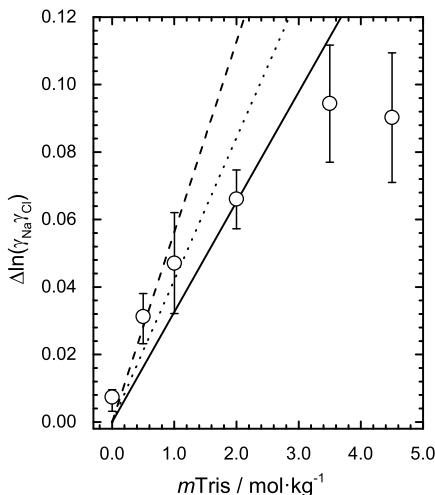


Figure 13. Value of $\Delta \ln(\gamma_{\text{Na}} \gamma_{\text{Cl}})$ determined from eq 18a and the measured solubilities of NaCl in aqueous Tris at 25 °C. Key: circle, from measured values (this study); solid line, calculated using the value of $\lambda_{\text{Tris},\text{Na}}$ (0.0163) determined from these solubilities; dashed line, calculated using the value of $\lambda_{\text{Tris},\text{Na}}$ (0.02817) obtained from measured solubilities of Tris in aqueous NaCl; and dotted line, calculated using the value of $\lambda_{\text{Tris},\text{Na}}$ (0.02106) determined by Tishchenko²⁸ from EMF measurements.

$\Delta \ln(\gamma_{\text{Na}} \gamma_{\text{Cl}})$ calculated using the $\lambda_{\text{Tris},\text{Na}}$ obtained by Tishchenko²⁸ from the EMF data and by us from measured Tris solubilities in aqueous NaCl are also shown in Figure 13 and are consistent with the data up to 1 mol·kg⁻¹ Tris but not for higher molalities. The measurements as a whole—including the solubilities at 3.5 and 4.5 mol·kg⁻¹ Tris—imply a non-zero value of $\mu_{\text{Tris},\text{Tris},\text{Na}}$ rather than $\zeta_{\text{Tris},\text{Na},\text{Cl}}$. However, this parameter would also contribute to activity coefficients in the solutions for which EMFs were measured (cell B), and to the activity coefficient of Tris in aqueous NaCl. Test calculations that we have carried out for these solutions do not suggest this. The resolution of this discrepancy will require further measurements.

5.2. Tris-(TrisH)₂SO₄ Solutions. The only data from which the Tris-SO₄²⁻ interaction can be determined are the solubilities of Tris in aqueous (TrisH)₂SO₄ measured in this work. We note that Millero et al.¹³ measured pK*(TrisH⁺) in aqueous solutions containing both NaCl and Na₂SO₄, but the bisulphate formation in these solutions (which was not independently determined) prevents the quantitative determination of Tris-SO₄²⁻ interactions from the data.

Tris is salted out by (TrisH)₂SO₄; see Figure 5b. We have fitted the data at 25 °C, using eqs 6a and 8, to yield $(2\lambda_{\text{Tris},\text{TrisH}} + \lambda_{\text{Tris},\text{SO}_4})$ equal to 0.05763 ± 0.0036 . Measured and calculated solubilities are shown in Figure 14. Adopting the value of $\lambda_{\text{Tris},\text{TrisH}}$ determined from the Tris solubilities in TrisHCl (-0.01241), $\lambda_{\text{Tris},\text{SO}_4}$ is equal to 0.08245 ± 0.0041 . As an alternative, the value of $\lambda_{\text{Tris},\text{TrisH}}$ obtained from the fit to the EMF data (-0.0197) yields $\lambda_{\text{Tris},\text{SO}_4}$ equal to 0.0970 ± 0.0043 . The strength of the Tris-SO₄²⁻ interaction is thus several times that of Tris-Na⁺. This is qualitatively similar to what has been found for the solute NH₃ (see Table VI of Clegg and

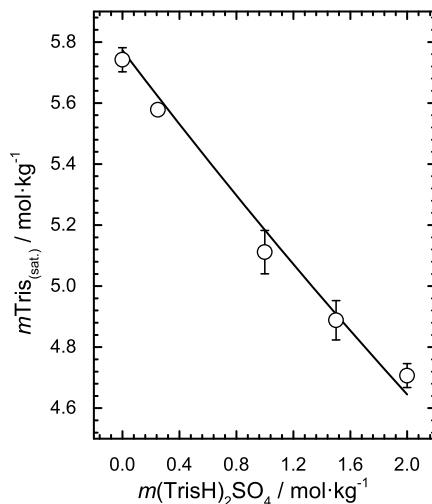


Figure 14. Measured and fitted solubilities of Tris ($m_{\text{Tris}_{(\text{sat.})}}$) in aqueous (TrisH)₂SO₄ at 25 °C. Key: circle, measured values (this study); and solid line, our fitted model.

Brimblecombe²²), although for this solute, the difference is larger.

6. SUMMARY AND DISCUSSION

The purpose of this study is to make thermodynamic measurements that contribute to a Pitzer-based speciation model of Tris pH buffers in solutions containing the components of artificial seawater. The use of highly concentrated media—well above the 0.72 mol·kg⁻¹ ionic strength of seawater of salinity 35—increases the strength of the ion–ion and ion–Tris interactions and in principle allows the interaction parameters to be more precisely determined. However, it is also the case that some higher order interactions may be needed in order to fit the experimental data. These parameters, principally $\mu_{\text{Tris},\text{Tris},\text{Na}}$ and $\zeta_{\text{Tris},\text{Na},\text{Cl}}$, have little effect in solutions of seawater ionic strength but do influence the values of the important $\lambda_{\text{Tris},\text{ion}}$ parameters that are determined from the data.

Our measurements of Tris solubility in pure water (Figure 2) agree well with other data and extend the range of measurements from 15–40 to 5–45 °C. The solubility of NaCl in pure water varies very little with temperature (e.g., from about 6.103 mol·kg⁻¹ at 5 °C to 6.248 mol·kg⁻¹ at 45 °C). Our results agree well with solubilities from the critical review of Cohen-Adad et al.¹⁹ up to 30 °C but appear to be systematically low by up to about 0.04 mol·kg⁻¹ at higher temperatures; see Figure 3.

The compound Tris is salted out (its solubility reduced) in aqueous NaCl and (TrisH)₂SO₄ but salted in by TrisHCl. This is qualitatively similar behavior to that of dissolved NH₃ in aqueous salt solutions. Robinson and Bower¹¹ have also noted that the measured osmotic coefficients of aqueous TrisHCl and NH₄Cl at 25 °C are close in value up to about 1.0 mol·kg⁻¹ concentration. Sodium chloride is salted out in aqueous Tris solutions.

Using the Pitzer activity coefficient model, we have investigated the consistency of our results with measurements of the stoichiometric dissociation constant of TrisH⁺ in aqueous NaCl at 25 °C and of the EMFs of electrochemical cells containing dissolved Tris, TrisH⁺, Na⁺, and Cl⁻. Data for osmotic coefficients of aqueous Tris and TrisHCl solutions were also used in the analyses of these results and are described in the Supporting Information. In our treatment of the EMF data, we

Table 11. Pitzer Model Parameters Determined from Solubility Measurements at 25 °C^a

species	parameter	value	species	parameter	value
Tris Na ⁺	λ	0.02817 ± 0.00077 ^b	Tris SO ₄ ²⁻	λ	0.08245 ± 0.0041 ^c
Tris TrisH ⁺	λ	-0.0124 ± 0.00098			

^aTris–Tris interaction parameters in Table 8 were used in these determinations. ^bFrom measured Tris solubilities in aqueous NaCl. ^cObtained from measurements of Tris solubilities in aqueous (TrisH)₂SO₄ and using the Tris–TrisH⁺ interaction parameter given in this table.

constrained the fitted interaction parameters to agree with the dissociation constant results.

Solubilities of Tris in aqueous NaCl at 25 °C are described using a Tris–Na⁺ interaction parameter ($\lambda_{\text{Tris,Na}}$) equal to 0.02817. It is demonstrated in Figure 13 that this is consistent with the measured solubilities of NaCl in aqueous Tris up to about 1 mol kg⁻¹ and also with the value of $\lambda_{\text{Tris,Na}}$ obtained by Tishchenko²⁸ in his own fit of the EMF data. However, our own fits of the EMFs suggest that a ternary interaction, described by the parameter $\zeta_{\text{Tris,Na,Cl}}$, is important. This is not consistent with the values of $\lambda_{\text{Tris,Na}}$ noted above or with the measured solubilities of NaCl at high Tris molalities. It is possible that either our measured solubilities for mTris above 1 mol kg⁻¹ are systematically too high by about 0.1 to 0.2 mol kg⁻¹ or that there is a higher order interaction (described by the parameter $\mu_{\text{Tris,Tris,Na}}$) that needs to be taken into account. It should also be borne in mind that there is no information to evaluate the stability of the glass Na⁺ electrode used by Tishchenko²⁸ for measurements of cell B in response to the large range of Tris molalities used.

The measured salting in of Tris in TrisHCl solutions at 25 °C, represented using the interaction parameter $\lambda_{\text{Tris,TrisH}}$ equal to -0.01241, is qualitatively consistent with the EMF data, although the parameter values determined from these measurements are larger in magnitude (see Tables 9 and 10). In (TrisH)₂SO₄ solutions, Tris is salted out, and this behavior is described at 25 °C by the combined parameter ($2\lambda_{\text{Tris,TrisH}} + \lambda_{\text{Tris,SO}_4}$) equal to 0.05763. There are no other data to compare with this result. The value of the interaction parameter $\lambda_{\text{Tris,SO}_4}$ determined from these measurements is dependent upon the value of $\lambda_{\text{Tris,TrisH}}$ adopted.

Parameters for the fitting equations representing the Tris and NaCl solubilities at all temperatures are listed in Table 7, and provisional values of the Tris–ion interaction parameters at 25 °C determined from the solubility data are given in Table 11. The estimation of interaction parameters at other temperatures will require information on the variation in the osmotic and activity coefficients of aqueous Tris with temperature or, for EMF measurements using cell A, those of aqueous TrisHCl.

Gallego-Urrea and Turner⁶ have investigated the use of the Pitzer model to calculate the pH of Tris buffers in low-salinity waters containing the ions Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻, and SO₄²⁻ and compared their results with EMF measurements of DeValls and Dickson³ and Pratt.³¹ Best results were obtained using a set of interaction parameters optimized by fitting to several datasets (see Figure 1 of Gallego-Urrea and Turner⁶), which suggested possible inconsistencies between the EMF data and osmotic coefficients of aqueous TrisHCl. The results presented in this work provide the first direct determinations of the Tris–SO₄²⁻ and Tris–TrisH⁺ interaction parameters ($\lambda_{\text{Tris,SO}_4}$ and $\lambda_{\text{Tris,TrisH}}$), which may help in resolving these differences. The interactions of the major seawater cations with Tris have previously been measured by Millero et al.¹³ at 25 °C, although the titration approach used yields the value of ($\theta_{\text{TrisH,ion}} - \lambda_{\text{Tris,ion}}$) rather than

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

component	CAS Reg. no.	suppliers	mass fraction
Tris ^a	77-86-1	VWR International	≥99.9%
TrisHCl ^b	1185-53-1	VWR International	≥99%
(TrisH) ₂ SO ₄ ^c	132499-87-7	Sigma-Aldrich	≥99%
sodium chloride	7647-14-5	VWR International	≥99.9%
silver nitrate, 0.1 N	7761-88-8	Alfa Aesar	Standardized Solution
potassium thiocyanate, 0.1 N	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%

^a2-amino-2-(hydroxymethyl)propane-1,3-diol. ^b2-amino-2-(hydroxymethyl)propane-1,3-diol; hydrochloride. ^c2-amino-2-(hydroxymethyl)propane-1,3-diol; sulfuric acid.

that of $\lambda_{\text{Tris,ion}}$. The solubility results presented here for Tris–NaCl aqueous solutions enable $\lambda_{\text{Tris,Na}}$ to be determined independently, although there remain some unresolved questions regarding the solubility of NaCl at high Tris molalities (Section 5.1.5).

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

APPENDIX

Osmotic Coefficients of Aqueous Tris at Very High Molalities

Electrodynamic balances have long been used to determine the relationship between water activity and aqueous concentration for solutions highly supersaturated with respect to dissolved solids.³² In a typical electrodynamic balance, a single charged droplet, of about 25 μm in diameter, is suspended in an atmosphere of controlled relative humidity (RH) and temperature, and the relative mass or diameter of the droplet is

recorded as the RH is changed.^{32,33} Rovelli et al.²⁴ describe a refinement of this method, in which RH is reduced rapidly in the chamber and the equilibrium $p\text{H}_2\text{O}$ (hence water activity) of the droplet is calculated from its size change relative to a similar droplet containing a known standard such as NaCl. The droplet is illuminated with light from a laser (Laser Quantum, Ventus, 532 nm), and the scattering pattern produced by the droplet in the forward direction takes the form of interference fringes. The angular separation between the fringes is used to measure the droplet diameter during evaporation.

We have used this method to determine the water activities of supersaturated aqueous Tris solutions at 293 K. Densities of the aqueous particles, which are required for the processing of the results,²⁴ were calculated using densities of pure water from Kell³⁴ and the following expression for the apparent molar volume of Tris (V^ϕ), which was fitted to densities of Taha and Lee²³ (25–55 °C) and apparent molar volumes determined by Ford et al.³⁵ (at 0.35 MPa, 5–65 °C)

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

where V^ϕ (cm³ mol⁻¹) is the apparent molar volume of Tris, T (K) is temperature, and wtfrac is the weight fraction of Tris in the pure aqueous solution. The results are shown in Figure A1.

The refractive index is also required to calculate the diameter from the elastic light scattering pattern using the geometric optics approximation.³⁶ Throughout an evaporation experiment, the solution becomes more concentrated, so the refractive index of a droplet is not constant. We account for this variation using the following equation³⁷

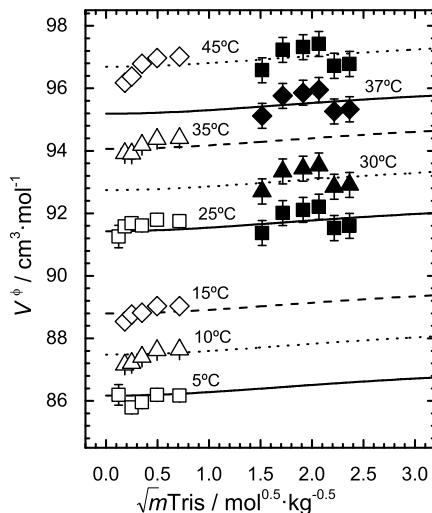


Figure A1. Measured and fitted apparent molar volumes of Tris (V^ϕ) in pure aqueous solutions as a function of the square root of Tris molality ($\sqrt{m\text{Tris}}$), at selected temperatures from 5 to 45 °C. Key: open symbols, measurements of Ford et al.;³⁵ solid symbols, calculated from densities determined by Taha and Lee;²³ and 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 and solid square and solid line); 30 °C (solid triangle and dotted line); 35 °C (triangle and dashed line); 37 °C (solid diamond and solid line); and 45 °C (diamond and solid square and dotted line). The values of the measured and fitted V^ϕ were spaced out vertically by adding a constant value of V^ϕ at each temperature: 5 °C (−4); 10 °C (−3); 15 °C (−2); 25 °C (unchanged); 30 °C (+1); 35 °C (+2); 37 °C (+3); and 45 °C (+4).

$$n_e = [(2R_e + M_e/\rho_e)/(M_e/\rho_e - R_e)]^{1/2} \quad (\text{A2})$$

where n_e (unitless) is the refractive index of the Tris solution, M_e (g mol⁻¹) is the mass of 1 mol solution (water plus Tris), ρ_e (g cm⁻³) is its density, and R_e (cm³ mol⁻¹) is the molar refraction of the solution. The quantity R_e for an aqueous mixture is estimated using the following mole fraction weighted summation of molar volumes and refractive indices of the pure liquid components

$$R_e = \sum_i x_i V_i (n_i^2 - 1)/(n_i^2 + 2) \quad (\text{A3})$$

where x_i is the mole fraction of component i in the mixture, V_i is its molar volume (equivalent to M_i/ρ_i), and n_i is the refractive index of the pure liquid i . (The value of the refractive index of water at 293 K is 1.333, and the estimated molar volume of pure liquid Tris is 95.50 cm³ mol⁻¹.) The refractive indices (n_e) of eight bulk aqueous Tris solutions, with weight fractions ranging from 0.01 to 0.34, were measured at 293 K (using a MISCO PA203 refractometer, 589.3 nm). These were then fitted using the above equations to obtain the value of the pure component subcooled-melt refractive index of Tris, n_{Tris} , in eq A3. Its value was determined to be 1.5365.

Initially, the elastic light scattering collected using the electrodynamic balance was converted into a particle diameter using a fixed refractive index of 1.335. In a postprocessing step, the diameter change for each time step (every ~0.01 s) was used to estimate the refractive index and then correct the diameters retrieved using the electrodynamic balance. The corrected diameter yields a better estimate of the refractive index, and the estimate of the diameter for every time step can be corrected again. This process is typically iterated three times to allow convergence of the droplet diameter and refractive index values. The amount of the Tris solute present in the droplet during the experiment is known from the initial concentration of the droplet solution.

The electrodynamic balance and measurement procedure are as described by Rovelli et al.²⁴ Probe droplets were used as reference standards to determine the ambient relative humidity (RH, equivalent to water activity) in the electrodynamic balance cell. The probe droplets consisted of pure water (for RH > 80%) or aqueous NaCl (for RH between 45 and 80%). The experimental temperature was 293.5 K (20.4 °C). Four sets of measurements were made, evaporating aqueous Tris particles into an ambient RH of 83, 81, 76, and 68%, using a different initial concentration of Tris in each case. These were highest for evaporation into the lowest RH environments in order to reduce the amount of evaporation experienced by the droplet (too rapid an evaporation causes a reduction in droplet temperature and leads to error). The concentrations of each dataset overlapped with the previous one, and each tabulated data set represents repeated measurements over 10–13 droplets, with the results averaged.

Bulk aqueous Tris solutions (Sigma-Aldrich, ≥ 99.9%) and aqueous NaCl solutions (Sigma-Aldrich, BioXtra, ≥ 99.5%) were prepared using water (Fisher Scientific, HPLC Gradient Grade) with known initial mass fraction. A single charged droplet of an initial radius of ~25 μm was generated from the bulk solution, using a microdispenser (MJ-ABP-01, MicroFab Technologies) outside of the electrodynamic balance chamber, and injected into the center of the instrument. A sheath gas flow of N₂ was continuously passed over the levitated droplet at a velocity of 3 cm s⁻¹ to keep the environment surrounding the droplet free of CO₂. The gas flow was formed by mixing dry and humidified N₂

Table A1. Osmotic Coefficients (ϕ) of Aqueous Tris at 20.4 °C,^a at Different Tris Molalities (m_{Tris}), from Electrodynamic Balance Experiments

$\sqrt{m_{\text{Tris}}}$ (mol·kg ⁻¹) ^{0.5}	standard uncertainty, $u(\sqrt{m})$ ^b	ϕ	standard uncertainty, $u(\phi)$ ^b	$\sqrt{m_{\text{Tris}}}$ (mol·kg ⁻¹) ^{0.5}	standard uncertainty, $u(\sqrt{m})$ ^b	ϕ	standard uncertainty, $u(\phi)$ ^b
4.5000	0.0187	1.0534	0.0103	3.1321	0.0083	1.1185	0.0129
4.4879	0.0176	1.0403	0.0097	3.0872	0.0066	1.1263	0.0102
4.4546	0.0379	1.0350	0.0213	3.0211	0.0046	1.1294	0.0073
4.3883	0.0461	1.0445	0.0274	2.9809	0.0061	1.1268	0.0102
4.3316	0.0575	1.0522	0.0359	2.9432	0.0075	1.1207	0.0134
4.2875	0.0660	1.0530	0.0426	2.8734	0.0078	1.1278	0.0153
4.2300	0.0727	1.0601	0.0495	2.8395	0.0094	1.1178	0.0194
4.1766	0.0704	1.0629	0.0502	2.7954	0.0113	1.1105	0.0261
4.1200	0.0762	1.0676	0.0570	2.7395	0.0101	1.1118	0.0248
4.0685	0.0855	1.0734	0.0670	2.6896	0.0086	1.1130	0.0222
4.0413	0.0839	1.0693	0.0675	2.6397	0.0100	1.1084	0.0283
3.9553	0.0685	1.0880	0.0601	2.5907	0.0087	1.1052	0.0271
3.8947	0.1375	1.0970	0.1279	2.5258	0.0087	1.1118	0.0292
3.9005	0.0765	1.0785	0.0703	2.4796	0.0088	1.1056	0.0289
3.8137	0.0624	1.0903	0.0626	2.4282	0.0095	1.0992	0.0346
3.6446	0.0349	1.1669	0.0358	2.3710	0.0071	1.0945	0.0307
3.6497	0.0092	1.1384	0.0093	2.3109	0.0087	1.0919	0.0339
3.6069	0.0111	1.1389	0.0117	2.2391	0.0104	1.0995	0.0379
3.6063	0.0115	1.1141	0.0121	2.1852	0.0096	1.0972	0.0409
3.5462	0.0173	1.1233	0.0193	2.1270	0.0087	1.0867	0.0431
3.4974	0.0184	1.1243	0.0220	2.0593	0.0101	1.0834	0.0446
3.4525	0.0255	1.1227	0.0318	2.0000	0.0099	1.0757	0.0460
3.3992	0.0226	1.1292	0.0308	1.9449	0.0074	1.0639	0.0469
3.3560	0.0225	1.1259	0.0312	1.8815	0.0090	1.0572	0.0624
3.3062	0.0230	1.1311	0.0344	1.7959	0.0094	1.0607	0.0586
3.2732	0.0246	1.1189	0.0382	1.7268	0.0081	1.0546	0.0730
3.2066	0.0264	1.1337	0.0434	1.6789	0.0074	1.0324	0.1106
3.1637	0.0285	1.1265	0.0488				

^aStandard uncertainty for temperature is $u(T) = 0.5$ K. ^bThe standard uncertainty for the osmotic coefficients arises from the experimental uncertainty in the relative humidity ($\pm 0.5\%$) and temperature (± 0.5 K) of the electrodynamic balance measurements, which contribute to the derivation of the droplet water activity. The uncertainty in the molality arises from the standard deviation of the binning process of averaging across a minimum of 10 droplets.

gas flows, so that the RH inside the instrument could be controlled by varying the ratio between the flows with mass flow controllers.

The osmotic coefficients determined from the measurements are presented in Table A1 and are shown in Figure A2, where they are compared with values calculated using the Tris self-interaction parameters determined in this work and those determined by Tishchenko.²⁸ The extrapolated values determined in this work by fitting only to the measurements of Robinson and Bower¹¹ agree more closely with the measurements, especially in terms of the trend with molality, although there appears to be an offset of about 0.03 in the osmotic coefficient. The reason for this is not known. The possible influence of the 5 °C difference in temperature can be qualitatively assessed by comparison with NH₃ solutions. In a 4 mol kg⁻¹ NH₃ solution, the increase in the osmotic coefficient from 20 to 25 °C is about +0.003 (calculated using the Pitzer model parameters of Clegg and Brimblecombe²²). This is only about 10% of the difference that can be seen in the figure, which suggests that the difference in temperature between the two experiments is not the cause of the apparent offset.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.0c00744>.

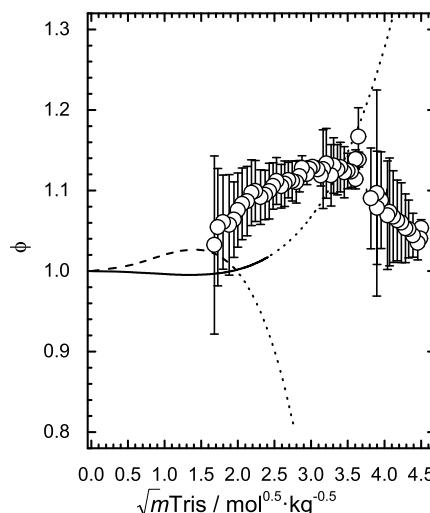


Figure A2. Osmotic coefficients (ϕ) of aqueous Tris at 20.4 °C, determined using an electrodynamic balance and plotted against the square root of Tris molality (m_{Tris}). Key: circles, mean values (with standard uncertainties) from this study, as listed in Table A1; solid line, calculated using the Pitzer model parameters from Table 7 (for 25 °C) and with extrapolation beyond the maximum molality of fit (dotted line); and dashed line, same as for solid line except that the parameters determined by Tishchenko²⁸ (Table 8) were used.

Osmotic coefficients of aqueous Tris and TrisHCl. Measured and fitted osmotic coefficients (ϕ) of aqueous TrisHCl at 25 °C, plotted against the square root of the TrisHCl molality. Measured and fitted osmotic coefficients (ϕ) of aqueous Tris at 25 °C, plotted against the Tris molality (PDF)

AUTHOR INFORMATION

Corresponding Authors

Pablo Lodeiro – GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany;  orcid.org/0000-0002-2557-5391; Email: pablo.lodeiro@udl.cat

Simon L. Clegg – School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom; Email: s.clegg@uea.ac.uk

Authors

David R. Turner – Department of Marine Sciences, University of Gothenburg, SE-40530 Gothenburg, Sweden

Eric P. Achterberg – GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany;  orcid.org/0000-0002-3061-2767

Florence K. A. Gregson – School of Chemistry, University of Bristol, Bristol BS8 1TS, U. K.;  orcid.org/0000-0002-8516-0796

Jonathan P. Reid – School of Chemistry, University of Bristol, Bristol BS8 1TS, U. K.;  orcid.org/0000-0001-6022-1778

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.jced.0c00744>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work of P.L. and E.P.A. was supported by the Helmholtz Association. The work of S.L.C. was supported by the Natural Environment Council of the UK, award number NE/P012361/1 under the joint NERC/NSF:GEO scheme. Authors F.K.A.G. and J.P.R. were supported by the Engineering and Physical Sciences Research Council under the grant code EP/N025245/1. This publication is a contribution of SCOR Working Group 145 (SCOR is the Scientific Committee on Oceanic Research) and of the Joint Committee on Seawater, which is sponsored by SCOR, the International Association for the Properties of Water and Steam, and the International Association for the Physical Sciences of the Oceans. The work of WG 145 presented in this article results, in part, from funding provided by national committees of SCOR and from a grant to SCOR from the U.S. National Science Foundation (OCE-1840868). We thank Florian Radloff, Lucía González Ruiz, and Lesly Ayala Cabana for their assistance with the solubility experiments.

REFERENCES

- (1) Buck, R. P.; Rondinini, S.; Covington, A. K.; Baucke, F. G. K.; Brett, C. M. A.; Camões, M. F.; Milton, M. J. T.; Mussini, T.; Naumann, R.; Pratt, K. W.; Spitzer, P.; Wilson, G. S. Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations 2002). *Pure Appl. Chem.* **2002**, *74*, 2169–2200.
- (2) Bates, R. G.; Hetzer, H. B. Dissociation constant of the protonated acid form of 2-amino-2-(hydroxymethyl)-1,3-propanediol [tris-hydroxymethyl)-aminomethane] and related thermodynamic quantities from 0 to 50°. *J. Solution Chem.* **1961**, *65*, 667–671.

(3) DelValls, T. A.; Dickson, A. G. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol (“tris”) in synthetic sea water. *Deep Sea Res., Part I* **1998**, *45*, 1541–1554.

(4) Müller, J. D.; Bastkowski, F.; Sander, B.; Seitz, S.; Turner, D. R.; Dickson, A. G.; Rehder, G. Metrology for pH measurements in brackish waters—Part 1: Extending electrochemical pH_T measurements of TRIS buffers to salinities 5–20. *Front. Mar. Sci.* **2018**, *5*, 176.

(5) Dickson, A. G.; Camões, M. F.; Spitzer, P.; Fisicaro, P.; Stoica, D.; Pawlowicz, R.; Feistel, R. Metrological challenges for measurements of key climatological observables. Part 3: Seawater pH. *Metrologia* **2016**, *53*, R26–R39.

(6) Gallego-Urrea, J. A.; Turner, D. R. Determination of pH in estuarine and brackish waters: Pitzer parameters for Tris buffers and dissociation constants for m-cresol purple at 298.15 K. *Mar. Chem.* **2017**, *195*, 84–89.

(7) Pitzer, K. S. Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; pp 75–153.

(8) Clegg, S. L.; Whitfield, M. A chemical model of seawater including dissolved ammonia and the stoichiometric dissociation constant of ammonia in estuarine water and seawater from –2 to 40°C. *Geochim. Cosmochim. Acta* **1995**, *59*, 2403–2421.

(9) Millero, F. J.; Pierrot, D. A chemical equilibrium model for natural waters. *Aquat. Geochem.* **1998**, *4*, 153–199.

(10) Waters, J. F.; Millero, F. J. The free proton concentration scale for seawater pH. *Mar. Chem.* **2013**, *149*, 8–22.

(11) Robinson, R. A.; Bower, V. E. Osmotic and activity coefficients of Tris(hydroxymethyl) aminomethane and its hydrochloride in aqueous solution at 25° C. *J. Chem. Eng. Data* **1965**, *10*, 246–247.

(12) Macaskill, J. B.; Bates, R. G. Osmotic and activity coefficients of tris sulfate from isopiestic vapor pressure measurements at 25 °C. *J. Chem. Eng. Data* **1986**, *31*, 416–418.

(13) Millero, F. J.; Hershey, J. P.; Fernandez, M. The pK* of TRISH⁺ in Na-K-Mg-Ca-Cl-SO₄ brines–pH scales. *Geochim. Cosmochim. Acta* **1987**, *51*, 707–711.

(14) *Guide to Best Practices for Ocean CO₂ Measurements*; Dickson, A. G., Sabine, C. L., Christian, J. R., Eds.; PICES Special Publication 3, IOCOP Report No. 8, 2007; 191 pp.

(15) Clegg, S. L.; Wexler, A. S. Densities and apparent molar volumes of atmospherically important electrolyte solutions. 1. The solutes H₂SO₄, HNO₃, HCl, Na₂SO₄, NaNO₃, NaCl, (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl from 0 to 50 °C, including extrapolations to very low temperature and to the pure liquid state, and NaHSO₄, NaOH, and NH₃ at 25 °C. *J. Phys. Chem. A* **2011**, *115*, 3393–3460.

(16) Gran, G.; Dahlénborg, H.; Laurell, S.; Rottenberg, M. Determination of the equivalent point in potentiometric titrations. *Acta Chem. Scand.* **1950**, *4*, 559–577.

(17) Caldwell, J. R.; Moyer, H. V. Determination of chloride: A modification of the Volhard method. *Ind. Eng. Chem., Anal. Ed.* **1935**, *7*, 38–39.

(18) Jones, G.; Colvin, J. H. The viscosity of solutions of electrolytes as a function of the concentration. VII. Silver nitrate, potassium sulfate and potassium chromate. *J. Am. Chem. Soc.* **1940**, *62*, 338–340.

(19) Cohen-Adad, R.; Vallée, P.; Lorimer, J. W. Sodium chloride. In *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*; Cohen-Adad, R., Lorimer, J. W., Eds.; Pergamon: Amsterdam, 1991; pp 64–209.

(20) Archer, D. G. Thermodynamic properties of the NaCl+H₂O System I. Thermodynamic properties of NaCl(cr). *J. Phys. Chem. Ref. Data* **1992**, *21*, 1–21.

(21) Archer, D. G. Thermodynamic properties of the NaCl+H₂O System. II. Thermodynamic properties of NaCl(aq), NaCl·2H₂O(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793–829.

(22) Clegg, S. L.; Brimblecombe, P. Solubility of ammonia in pure aqueous and multicomponent solutions. *J. Phys. Chem.* **1989**, *93*, 7237–7248.

(23) Taha, M.; Lee, M.-J. Buffers and Ionic Salts: Densities and solubilities of aqueous and electrolyte solutions of tris(hydroxymethyl)-

- aminomethane and N-Tris[hydroxymethyl]-4-amino-butanesulfonic acid. *J. Chem. Eng. Data* **2009**, *54*, 2501–2512.
- (24) Rovelli, G.; Miles, R. E. H.; Reid, J. P.; Clegg, S. L. Accurate measurements of aerosol hygroscopic growth over a wide range in relative humidity. *J. Phys. Chem. A* **2016**, *120*, 4376–4388.
- (25) Pitzer, K. S.; Silvester, L. F. Thermodynamics of electrolytes. VI. Weak electrolytes including H_3PO_4 . *J. Solution Chem.* **1976**, *5*, 269–278.
- (26) Archer, D. G.; Wang, P. The dielectric constant of water and Debye–Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371–411.
- (27) Clegg, S. L.; Rard, J. A.; Pitzer, K. S. Thermodynamic properties of 0.6 mol kg^{-1} aqueous sulfuric acid from 273.15 to 328.15 K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1875–1894.
- (28) Tishchenko, P. Y. Non-ideal properties of the TRIS–TRIS–HCl–NaCl– H_2O buffer system in the 0–40 °C temperature interval. Application of the Pitzer equations. *Russ. Chem. Bull.* **2000**, *49*, 674–679.
- (29) Wagner, W.; Pruss, A. International equations for the saturation properties of ordinary water substance. Revised according to the international temperature scale of 1990. Addendum to *J. Phys. Chem. Ref. Data* **16**, 893 (1987). *J. Phys. Chem. Ref. Data* **1993**, *22*, 783–787.
- (30) Hills, G. J.; Ives, D. J. G. The hydrogen electrode. *Nature* **1949**, *163*, 997.
- (31) Pratt, K. W. Measurement of pH_T values of Tris buffers in artificial seawater at varying mole ratios of Tris:Tris-HCl. *Mar. Chem.* **2014**, *162*, 89–95.
- (32) Tang, I. N.; Munkelwitz, H. R. Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. *J. Geophys. Res. Atmos.* **1994**, *99*, 18801–18808.
- (33) Liang, Z.; Chan, C. K. A fast technique for measuring water activity of atmospheric aerosols. *Aerosol Sci. Technol.* **1997**, *26*, 255–268.
- (34) Kell, G. S. Density, thermal expansivity, and compressibility of liquid water from 0 to 150 °C. Correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
- (35) Ford, T. D.; Call, T. G.; Origlia, M. L.; Stark, M. A.; Woolley, E. M. Apparent molar volumes and apparent molar heat capacities of aqueous 2-amino-2-hydroxymethyl-propan-1,3-diol (Tris or THAM) and THAM plus equimolar HCl. *J. Chem. Thermodyn.* **2000**, *32*, 499–516.
- (36) Glantschnig, W. J.; Chen, S.-H. Light scattering from water droplets in the geometrical optics approximation. *Appl. Opt.* **1981**, *20*, 2499–2509.
- (37) Liu, Y.; Daum, P. H. Relationship of refractive index to mass density and self-consistency of mixing rules for multicomponent mixtures like ambient aerosols. *J. Aerosol Sci.* **2008**, *39*, 974–986.
- (38) El-Harakany, A. A.; Barakat, A. O. Solubility of Tris(hydroxymethyl)-aminomethane in water-2-methoxyethanol solvent mixtures and the solvent effect on the dissociation of the protonated base. *J. Solution Chem.* **1985**, *14*, 263–269.
- (39) Schindler, P.; Robinson, R. A.; Bates, R. G. Solubility of tris(hydroxymethyl)aminomethane in water-methanol solvent mixtures and medium effects in the dissociation of the protonated base. *J. Res. Natl. Bur. Stand. A Phys. Chem.* **1968**, *72A*, 141–148.
- (40) Jouyban-Gharamaleki, V.; Jouyban-Gharamaleki, K.; Soleymani, J.; Kenndler, E.; Acree, W. E.; Jouyban, A. Solubility of Tris(hydroxymethyl)aminomethane in methanol + 1-propanol mixtures at various temperatures. *J. Chem. Eng. Data* **2014**, *59*, 4227–4230.
- (41) Campbell, D. M.; Millero, F. J.; Roy, R.; Roy, L.; Lawson, M.; Vogel, K. M.; Porter Moore, C. The standard potential for the hydrogen-silver, silver chloride electrode in synthetic seawater. *Mar. Chem.* **1993**, *44*, 221–233.
- (42) Harvie, C. E.; Møller, N.; Weare, J. H. The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl- SO_4^- -OH- HCO_3^- - CO_3^{2-} - H_2O system to high ionic strengths at 25 °C. *Geochim. Cosmochim. Acta* **1984**, *48*, 723–751.
- (43) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1–102.