

Activity Coefficients of HCl in Solutions Related to “Tris” Buffers in Artificial Seawater. II. HCl + NaCl + TrisHCl + H₂O, and Tris Buffer + NaCl + H₂O, to High Ionic Strength and from 5 to 40 °C

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Cite This: *J. Chem. Eng. Data* 2025, 70, 3614–3629

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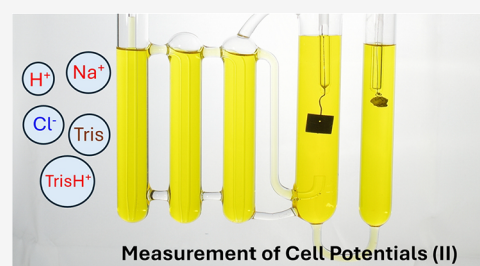


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ABSTRACT: The substance Tris (2-amino-2-hydroxymethyl-1,3-propanediol, CAS 77-86-1), and its protonated form TrisH⁺, are used in the preparation of ‘total’ pH buffers in artificial seawater media. The development of a chemical speciation model of the buffer solutions, using the Pitzer equations to calculate solute activity coefficients, is desirable in order to quantify the effects of composition change, convert the total pH to other scales, and address metrological requirements for traceability to the International System of Units. Here, in the second of a series of studies, we present Harned cell measurements of potentials and mean activity coefficients of HCl in solutions containing HCl, NaCl, and TrisHCl for ionic strengths from 1.0 to 5.5 mol kg^{−1} and from 5 to 40 °C. The results at 25 °C are consistent with those of the literature studies of the two end-member solutions (aqueous HCl + NaCl, and HCl + TrisHCl). We also present results of measurements of buffer solutions containing equimolar Tris and TrisHCl (hence TrisH⁺), and NaCl, at ionic strengths of 0.2, 1.0, and 4.0 mol kg^{−1} at the same temperatures. These are compared with literature data for Tris buffers in an artificial seawater medium. Aspects of the development of a Pitzer model for these solutions are discussed.



1. INTRODUCTION

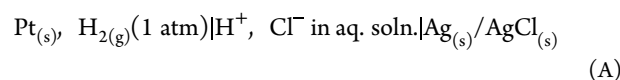
The seawater total hydrogen ion pH scale was established from measurements of cell potentials of solutions of artificial seawater acidified with HCl, and others containing equimolar Tris and its conjugate acid TrisH⁺ as a pH buffer.¹ (The substance Tris is 2-amino-2-hydroxymethyl-1,3-propanediol, and the acidic form TrisH⁺ has a pK_a that is close to the pH of seawater.) Artificial seawaters, and natural seawater, consist of about 90 mol % Na⁺ and Cl[−] ions, plus smaller amounts of Mg²⁺, SO₄^{2−}, Ca²⁺, and K⁺. Other minor species present in natural seawater² are generally omitted from artificial seawaters because their molalities are too low to influence the activity coefficients of other solutes. The development of a chemical speciation model of these buffer solutions, yielding molalities and activities of solute species for a range of salinities and temperatures, and hence total pH, has a number of potential benefits. These include the extension of the scale to a wider range of temperatures and salinities, conversion to other forms such as “free” pH³ and conventional pH,⁴ and improved metrological traceability.^{5–7}

Clegg et al.⁶ have developed a draft model of Tris buffer in artificial seawater, using the Pitzer equations⁸ for the calculation of activity coefficients, and have tabulated the unknown Pitzer interaction parameters that new thermodynamic data are needed to quantify. As the first step toward achieving this goal, Maksimov et al.⁷ have determined mean activity coefficients of HCl in aqueous HCl–TrisHCl mixtures from measured potentials of Harned cells (which yield activity

products of H⁺ and Cl[−]). This study is the second of a series which involves the National Metrology Institutes of Japan (hereinafter NMIJ), Germany, and the USA. Here we present measurements of electrochemical potentials of aqueous HCl–NaCl–TrisHCl mixtures, and Tris buffer in aqueous NaCl solutions, over a range of temperatures and ionic strengths as a further step toward developing a model of the pH buffer. The results are compared with available data for aqueous HCl–TrisHCl and HCl–NaCl solutions and for Tris buffer in artificial seawater.

2. EXPERIMENTAL METHOD

Activity products of H⁺ and Cl[−] ions were determined from measurements of the potential difference of the following electrochemical cell:



where the solutions in this study contain either H⁺, Na⁺, TrisH⁺ and Cl[−] ions, or equimolar TrisHCl and Tris (Tris

Received: May 29, 2025

Revised: July 8, 2025

Accepted: July 17, 2025

Published: August 11, 2025

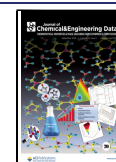


Table 1. Chemicals Used in This Study

chemical	CAS registry #	molar mass (g)	supplier or source	notes
Tris ^a	77-86-1	121.135	FUJIFILM WAKO Pure Chemical Corp.	used as NMIJ CRM 3012-a, purity 99.99 ± 0.10% (<i>k</i> = 2) determined by acidimetric coulometric titration
HCl	7647-01-0	36.4609	Kanto Chemical Co.	ultrapure grade aqueous HCl of 31.4 mass % (diluted with water and then molality determined before use)
H ₂ O	7732-18-5	18.0153	Milli-Q Ultrapure Water System (Merck)	resistivity 18.2 MΩ cm at 25 °C
NaCl	7647-14-5	58.4430	FUJIFILM WAKO Pure Chemical Corp.	used as NMIJ CRM 3008-a, purity 100.000 ± 0.047% (<i>k</i> = 2) determined by argentometric coulometric titration

^a2-Amino-2-(hydroxymethyl)propane-1,3-diol, C₄H₁₁NO₃.

Table 2. Cell Identifiers and Dates of Measurements

cells ^a	<i>m</i> Cl [−] (mol kg ^{−1})	date	cells	<i>m</i> HCl (mol kg ^{−1})	date
73–74	0.2 (Tris buffer) ^b	11/10/17	A–F	0.01	21/08/17
75–76	1.0 (Tris buffer) ^b	11/10/17	G–L	0.01	24/08/17
77–78	4.0 (Tris buffer) ^b	11/10/17	M–R	0.01	25/09/17
79–84	3.5	13/11/17	S–X	0.01	23/10/17
85–90	4.0	20/11/17	A1–F1	0.01	14/12/17
91–96	4.5	27/11/17	G1–L1	0.01	06/06/22
97–102	5.0	05/12/17	M1–R1	0.01	23/01/23
103–108	5.5	11/12/17			
1–6	1.0	20/02/23			
7–12	1.5	27/02/23			
13–18	2.0	06/03/23			

^aCells 1–18 are different from those in our previous study that have the same numbers.⁷ ^bThese are the solutions containing equimolar Tris and TrisHCl in aqueous NaCl.

buffer) in aqueous NaCl. The presence of H⁺ in the first set of solutions (at a molality of 0.1 mol kg^{−1}) is sufficient to entirely suppress the dissociation of TrisH⁺. In the buffer solutions, the H⁺ molality is controlled by the dissociation of the conjugate acid of Tris, TrisH⁺,⁹ which yields a slightly alkaline solution. The potential, *E* (V), of Cell A is given by the following expression:

$$E = E^0 - (RT/F) \cdot \ln(a\text{H}^+ \cdot a\text{Cl}^-) \quad (1)$$

where *E*⁰ (V) is the standard potential of the cell at the temperature *T* (K) of interest, *R* (8.31446 J mol^{−1} K^{−1}) is the gas constant, *F* (96 485.332 C mol^{−1}) is Faraday's constant, and prefix *a* denotes activity. The activity product of the H⁺ and Cl[−] ions can also be written *m*H⁺ · *m*Cl[−] · γ_{HCl}², where the prefix *m* indicates molality and γ_{HCl} is the mean activity coefficient of H⁺ and Cl[−] ions in the solution.

A schematic of the Harned cell (Cell A) used at NMIJ is shown in Figure 1 of Maksimov et al.⁷ A flow of dry hydrogen gas at a rate of 4 cm³ min^{−1} first passes through a set of three presaturators all of which contain an aqueous solution of the same composition as that being measured. The gas flow next passes into the half-cell of the U-shaped hydrogen measurement compartment containing the platinum hydrogen electrode and bubbles through the solution. The gas exits the cell via a hydraulic trap designed to prevent any direct contact with the air. This half-cell is connected, with a glass capillary tube, to the other half-cell which contains the same solution and the reference silver–silver chloride electrode. A set of six Harned cells is used for each measurement run. The cells are immersed in a water bath for temperature control.

A total of 18 Harned cells and 18 reference electrodes, belonging to two separate sets, were used in this study. The 12 electrodes used for measurements carried out in 2017 were the same as in our previous study,⁷ and a further six were used for

measurements made in 2023. The preparation of hydrogen and reference electrodes is described by Bates,¹⁰ and the specific procedures used at NMIJ are summarized in the Supporting Information to Maksimov et al.⁷ The ancillary equipment used (for temperature control, and measurement of pressure and potential) is also listed by Maksimov et al., and the setup for Harned cell measurements at NMIJ is described in detail by Ohata.¹¹

2.1. Solution Compositions and Preparation. The molal ionic strengths (*I*) of the HCl–NaCl–TrisHCl aqueous solutions range from 1.0 to 5.5 mol kg^{−1}, with Na⁺ cation fractions *y*Na⁺ (equal to *m*Na⁺/(*m*Na⁺ + *m*TrisH⁺)) of 0.3, 0.5 and 0.7, and a constant H⁺ molality of 0.1 mol kg^{−1}. The Tris buffer solutions contain stoichiometric molalities of 0.04 mol kg^{−1} Tris and TrisH⁺ cation (the product of half-neutralization of Tris by HCl) in an NaCl medium with ionic strengths of 0.2, 1.0, and 4.0 mol kg^{−1}. The measurement of a wide range of ionic strengths should enable unknown Pitzer model interaction parameters for this mixture to be determined accurately.

The chemicals used in the preparation of the solutions are listed in Table 1. The solid Tris, the purity of which was determined by acidimetric coulometric titration, was stored at room temperature and used directly from sealed bottles without additional drying. The concentrated HCl was diluted with ultrapure water to produce stock solutions of lower concentrations, and their exact molalities (3.6654 ± 0.0014, 3.6603 ± 0.0018, 5.7700 ± 0.0035, and 7.4143 ± 0.0044 mol kg^{−1}) were determined by coulometric titration. The purity of the NaCl reagent was determined by argentometric coulometric titration. The salt was dried at 450 °C for 2 h and cooled to room temperature in a desiccator with silica gel before the preparation of NaCl stock solutions of molalities 3.0000 ± 0.0031, 5.1025 ± 0.0031, and 5.1279 ± 0.0031 mol

kg⁻¹. The concentration uncertainties were calculated from the uncertainty of NaCl purity and the uncertainty of gravimetric preparation.

All of the studied solutions were prepared gravimetrically as weights in air of HCl and NaCl stock solution aliquots, solid Tris, and water. Buoyancy corrections were carried out using equations presented in Dickson et al.,¹² and assuming a laboratory temperature of 20 °C. A density of solid Tris of 1.328 g cm⁻³ (typical of those quoted by chemical suppliers) was adopted for the calculation of the buoyancy correction. Densities of aqueous HCl and NaCl solutions were taken from Clegg and Wexler,¹³ and those of water from Kell.¹⁴ All of the measured solutions were prepared in duplicate.

The standard potentials of the Harned cells are determined from measurements of ~0.01 mol kg⁻¹ HCl at each temperature. The preparation of the dilute aqueous HCl solutions used for measurements carried out in 2017 is described in Section 2.1 of Maksimov.⁷ For the measurements carried out in 2023, the ~0.1 mol kg⁻¹ HCl stock solution was gravimetrically diluted in the same way to obtain the required 0.01 mol kg⁻¹ solutions (0.01000012 and 0.00999946 mol kg⁻¹ in this work).

2.2. Measurements. Cell potentials were measured from 5 to 40 °C for all solutions. Identifiers for the individual cells used, the chloride or HCl molalities of the solutions, and the dates of measurement are listed in Table 2. As can be seen, the measurements for the acidic solutions were carried out in two groups: 3.5–5.5 mol kg⁻¹ ionic strength solutions in 2017, and the lower molality solutions in 2023 (and the associated HCl solutions for the determination of standard potentials in 2022 and 2023). All measurements of the 0.04 mol kg⁻¹ Tris buffers in aqueous NaCl were made in 2017.

The Harned cells at NMIJ are routinely used for the certification of buffer solutions of ionic strengths up to 0.1 mol kg⁻¹, and the measurements in this and our previous study presented some additional difficulties. One of these is related to the fact that the solubility of AgCl increases in solutions containing high concentrations of chloride ions.¹⁵ Gradual degradation of the reference electrodes due to the dissolution of the electrodeposited layer of silver chloride eventually results in irreversible damage, and it was necessary to measure the solutions in a relatively short space of time. The measurements of solutions made in 2023 (HCl–NaCl–TrisHCl solutions with ionic strengths 1.0–2.0 mol kg⁻¹) were made with a comparatively old set of electrodes having in addition a relatively small size of the original silver bulb. The quicker deterioration of those electrodes appears to have caused an offset in the measured cell potentials. This is discussed in Section 4.1, and further details are given in the Supporting Information. Also, during the measurements of some of the most concentrated solutions at the highest temperatures, salt deposition occurred in the first of the three H₂ presaturator tubes due to loss of water to the dry H₂ gas stream (see the Supporting Information). These measurements, 11 in total, were discarded.

In dilute buffer solutions, the criterion of stability of cell potential is a voltage drift not exceeding 10 μV h⁻¹. For the HCl–NaCl–TrisHCl solutions we observed a similar bias at the lower temperatures 5, 10, 15, and 20 °C, with the drift rising to 50 μV h⁻¹ at 30 °C and to 90 μV h⁻¹ at 40 °C. Compared to our previous study with HCl–TrisHCl solutions,⁷ the increase at the two last temperatures may have been caused by a stronger impact (on the recorded

voltage) of water evaporation from the more concentrated media. This is despite the partial compensation from the preceding set of three presaturators. For the 0.04 mol kg⁻¹ Tris buffer in NaCl solutions, the voltage drift was within 10 μV h⁻¹, rising slightly to 20 μV h⁻¹ at the final temperature of 40 °C.

3. TREATMENT OF THE DATA

The measured cell potentials, E_{meas} , at the ambient H₂ partial pressure in the cell are corrected to p_{H_2} equal to 1 atm using the following relationship:¹⁰

$$E(p_{\text{H}_2}, 1 \text{ atm}) = E_{\text{meas}} - RT/(2F) \cdot \ln(p_{\text{H}_2}) \quad (2)$$

where

$$p_{\text{H}_2} = P - p_{\text{H}_2\text{O}} - p_{\text{HCl}} + 0.4 \cdot \rho \cdot h \cdot g \cdot C \quad (3)$$

P (atm) is atmospheric pressure at the time of the measurement, and $p_{\text{H}_2\text{O}}$ (atm) and p_{HCl} (atm) are the equilibrium partial pressures of water and of HCl, respectively, above the solution at the temperature of the measurement. The final term in eq 3 is a further correction in which 0.4 is an empirical factor,¹⁶ ρ (g cm⁻³) is the density of the solution, h (mm) is the depth of immersion of the H₂ electrode, g (9.81 m s⁻²) is the gravitational constant, and C (1/101 325 atm Pa⁻¹) is a conversion factor from Pa to atm. The influences of the different terms in eq 3 on the adjustment to the measured potentials are given in Table 4 of Maksimov et al.⁷ The contribution of p_{HCl} is very small at all temperatures (its maximum calculated value for the acidic solutions measured in this study is 1.9×10^{-6} atm). The values of $p_{\text{H}_2\text{O}}$ are equal to $a_{\text{H}_2\text{O}} \cdot p^\circ(\text{H}_2\text{O})$, neglecting the small difference between partial pressure and fugacity, where $a_{\text{H}_2\text{O}}$ is the water activity of the solution and $p^\circ(\text{H}_2\text{O})$ (atm) the vapor pressure of pure water at the temperature of the measurement. The estimation of p_{HCl} , $a_{\text{H}_2\text{O}}$, and ρ and their associated uncertainties is summarized in the Supporting Information.

3.1. Standard Potentials. Standard potentials, E^0 , of Cell A at each temperature were obtained from the measurements of 0.01 mol kg⁻¹ HCl solutions, adjusted to 1 atm p_{H_2} , together with mean activity coefficients of HCl listed by Bates and Robinson.¹⁷ The effects of the very small deviations of the solution compositions from exactly 0.01 mol kg⁻¹ were compensated for by adjusting the potentials E as described in Section 3.1 of Maksimov et al.⁷ Information concerning the cells used to determine the standard potentials at each temperature, and the values of E^0 (with uncertainties) determined in this study, can be found in the Supporting Information. The standard potentials of the cells used for measurements made in 2017 are the same as those presented by Maksimov et al.⁷

The potentials of the measurement solutions, after adjustment to 1 atm p_{H_2} , were further adjusted as described by Maksimov et al.⁷ to be consistent with the standard potentials of Bates and Bower¹⁸ (column 7 of their Table 1) for ease of comparability. It is these adjusted potentials, $E(\text{adj.})$, that are tabulated in this work.

3.2. Uncertainties. The overall uncertainty of the measured potential is dominated by that of the voltage measurement. In comparison with our previous study, we estimate that the contribution of the uncertainty of the water activity $u(a_{\text{H}_2\text{O}})$ to the total, for the most concentrated HCl–NaCl–TrisHCl solutions at the highest temperatures, was greater by about 2 orders of magnitude but was still equal to

Table 3. Harned Cell Results for HCl–NaCl–TrisHCl Solutions at Ionic Strengths of 3.5 mol kg^{−1} and above, Including Calculated Mean Activity Coefficients of HCl^a

<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (E) ^b (mV)	<i>γ</i> HCl	<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (E) ^b (mV)	<i>γ</i> HCl
5	3.5	0.30	0.10012	2.37995	1.02003	0.26089	0.130	0.9656	20	4.5	0.30	0.10026	3.07973	1.32007	0.24370	0.011	1.0399
5	3.5	0.30	0.10011	2.37985	1.02004	0.26071	0.130	0.9693	20	4.5	0.30	0.10020	3.07987	1.32003	0.24370	0.011	1.0403
5	3.5	0.50	0.10005	1.70001	1.70007	0.25762	0.011	1.0342	20	4.5	0.50	0.10014	2.19992	2.20003	0.23878	0.011	1.1470
5	3.5	0.50	0.10007	1.69994	1.70007	0.25762	0.011	1.0341	20	4.5	0.50	0.10018	2.19982	2.20002	0.23878	0.011	1.1466
5	3.5	0.70	0.10002	1.01997	2.38012	0.25423	0.075	1.1101	20	4.5	0.70	0.10010	1.31994	3.08015	0.23329	0.011	1.2788
5	3.5	0.70	0.10007	1.01992	2.38007	0.25413	0.075	1.1122	20	4.5	0.70	0.10012	1.31984	3.08009	0.23329	0.011	1.2788
10	3.5	0.30	0.10012	2.37995	1.02003	0.25925	0.140	0.9547	25	4.5	0.30	0.10026	3.07973	1.32007	0.24170	0.020	1.0226
10	3.5	0.30	0.10011	2.37985	1.02004	0.25905	0.140	0.9586	25	4.5	0.30	0.10020	3.07987	1.32003	0.24170	0.020	1.0230
10	3.5	0.50	0.10005	1.70001	1.70007	0.25585	0.011	1.0239	25	4.5	0.50	0.10014	2.19992	2.20003	0.23668	0.020	1.1283
10	3.5	0.50	0.10007	1.69994	1.70007	0.25586	0.011	1.0236	25	4.5	0.50	0.10018	2.19982	2.20002	0.23668	0.020	1.1279
10	3.5	0.70	0.10002	1.01997	2.38012	0.25234	0.012	1.1004	25	4.5	0.70	0.10010	1.31994	3.08015	0.23104	0.020	1.2594
10	3.5	0.70	0.10007	1.01992	2.38007	0.25233	0.012	1.1003	25	4.5	0.70	0.10012	1.31984	3.08009	0.23104	0.020	1.2592
15	3.5	0.30	0.10012	2.37995	1.02003	0.25755	0.140	0.9423	30	4.5	0.30	0.10026	3.07973	1.32007	0.23957	0.050	1.0062
15	3.5	0.30	0.10011	2.37985	1.02004	0.25735	0.140	0.9462	30	4.5	0.30	0.10020	3.07987	1.32003	0.23957	0.050	1.0065
15	3.5	0.50	0.10005	1.70001	1.70007	0.25404	0.011	1.0116	30	4.5	0.50	0.10014	2.19992	2.20003	0.23446	0.050	1.1102
15	3.5	0.50	0.10007	1.69994	1.70007	0.25405	0.011	1.0114	30	4.5	0.50	0.10018	2.19982	2.20002	0.23446	0.050	1.1099
15	3.5	0.70	0.10002	1.01997	2.38012	0.25042	0.011	1.0883	30	4.5	0.70	0.10012	1.31984	3.08009	0.22880	0.180	1.2373
15	3.5	0.70	0.10007	1.01992	2.38007	0.25041	0.011	1.0882	40	4.5	0.30	0.10026	3.07973	1.32007	0.23513	0.200	0.9710
20	3.5	0.30	0.10012	2.37995	1.02003	0.25569	0.140	0.9306	40	4.5	0.50	0.10014	2.19992	2.20003	0.22987	0.090	1.0712
20	3.5	0.30	0.10011	2.37985	1.02004	0.25549	0.140	0.9344	40	4.5	0.50	0.10018	2.19982	2.20002	0.22988	0.090	1.0708
20	3.5	0.50	0.10005	1.70001	1.70007	0.25211	0.011	0.9993	40	4.5	0.70	0.10012	1.31984	3.08009	0.22405	0.200	1.1932
20	3.5	0.50	0.10007	1.69994	1.70007	0.25212	0.011	0.9991	5	5.0	0.30	0.10035	3.42967	1.47001	0.24328	0.076	1.1653
20	3.5	0.70	0.10002	1.01997	2.38012	0.24835	0.011	1.0766	5	5.0	0.30	0.10032	3.42990	1.47001	0.24317	0.076	1.1680
20	3.5	0.70	0.10007	1.01992	2.38007	0.24835	0.011	1.0764	5	5.0	0.50	0.10021	2.44982	2.45002	0.23792	0.010	1.3039
25	3.5	0.30	0.10012	2.37995	1.02003	0.25377	0.150	0.9174	5	5.0	0.50	0.10024	2.44979	2.45005	0.23792	0.010	1.3037
25	3.5	0.30	0.10011	2.37985	1.02004	0.25356	0.150	0.9212	5	5.0	0.70	0.10014	1.46982	3.42988	0.23178	0.010	1.4826
25	3.5	0.50	0.10005	1.70001	1.70007	0.25011	0.021	0.9856	5	5.0	0.70	0.10013	1.46993	3.43008	0.23179	0.010	1.4825
25	3.5	0.50	0.10007	1.69994	1.70007	0.25011	0.021	0.9853	10	5.0	0.30	0.10035	3.42967	1.47001	0.24146	0.093	1.1488
25	3.5	0.70	0.10002	1.01997	2.38012	0.24621	0.020	1.0633	10	5.0	0.30	0.10032	3.42990	1.47001	0.24133	0.093	1.1520
25	3.5	0.70	0.10007	1.01992	2.38007	0.24621	0.020	1.0630	10	5.0	0.50	0.10021	2.44982	2.45002	0.23600	0.010	1.2857
30	3.5	0.30	0.10012	2.37995	1.02003	0.25170	0.140	0.9052	10	5.0	0.50	0.10024	2.44979	2.45005	0.23600	0.010	1.2855
30	3.5	0.30	0.10011	2.37985	1.02004	0.25151	0.140	0.9085	10	5.0	0.70	0.10014	1.46982	3.42988	0.22977	0.010	1.4613
30	3.5	0.50	0.10005	1.70001	1.70007	0.24797	0.050	0.9725	10	5.0	0.70	0.10013	1.46993	3.43008	0.22977	0.010	1.4613
30	3.5	0.50	0.10007	1.69994	1.70007	0.24798	0.050	0.9723	15	5.0	0.30	0.10035	3.42967	1.47001	0.23961	0.110	1.1300
30	3.5	0.70	0.10002	1.01997	2.38012	0.24393	0.050	1.0507	15	5.0	0.30	0.10032	3.42990	1.47001	0.23946	0.110	1.1336
30	3.5	0.70	0.10007	1.01992	2.38007	0.24394	0.050	1.0503	15	5.0	0.50	0.10021	2.44982	2.45002	0.23405	0.010	1.2650
40	3.5	0.30	0.10012	2.37995	1.02003	0.24733	0.200	0.8790	15	5.0	0.50	0.10024	2.44979	2.45005	0.23405	0.010	1.2648
40	3.5	0.30	0.10011	2.37985	1.02004	0.24707	0.200	0.8832	15	5.0	0.70	0.10014	1.46982	3.42988	0.22772	0.010	1.4374
40	3.5	0.50	0.10005	1.70001	1.70007	0.24354	0.090	0.9432	15	5.0	0.70	0.10013	1.46993	3.43008	0.22772	0.010	1.4374
40	3.5	0.50	0.10007	1.69994	1.70007	0.24354	0.090	0.9431	20	5.0	0.30	0.10035	3.42967	1.47001	0.23767	0.012	1.1112
40	3.5	0.70	0.10002	1.01997	2.38012	0.23906	0.250	1.0251	20	5.0	0.30	0.10032	3.42990	1.47001	0.23766	0.012	1.1115
40	3.5	0.70	0.10007	1.01992	2.38007	0.23939	0.250	1.0185	20	5.0	0.50	0.10021	2.44982	2.45002	0.23202	0.010	1.2433

Table 3. continued

<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^{<i>b</i>} (V)	<i>u</i> (<i>E</i>) ^{<i>b</i>} (mV)	<i>γ</i> _{HCl}	<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^{<i>b</i>} (V)	<i>u</i> (<i>E</i>) ^{<i>b</i>} (mV)	<i>γ</i> _{HCl}
5	4.0	0.30	0.10022	2.72986	1.17003	0.25494	0.088	1.0222	20	5.0	0.50	0.10024	2.44979	2.45005	0.23202	0.010	1.2431
5	4.0	0.30	0.10021	2.72974	1.16997	0.25481	0.088	1.0250	20	5.0	0.70	0.10014	1.46982	3.42988	0.22559	0.010	1.4127
5	4.0	0.50	0.10016	1.94991	1.95005	0.25098	0.012	1.1106	20	5.0	0.70	0.10013	1.46993	3.43008	0.22559	0.010	1.4127
5	4.0	0.50	0.10016	1.94975	1.94994	0.25099	0.012	1.1104	25	5.0	0.30	0.10035	3.42967	1.47001	0.23562	0.021	1.0914
5	4.0	0.70	0.10006	1.16994	2.73009	0.24657	0.074	1.2182	25	5.0	0.30	0.10032	3.42990	1.47001	0.23562	0.021	1.0917
5	4.0	0.70	0.10008	1.16994	2.73009	0.24667	0.074	1.2154	25	5.0	0.50	0.10021	2.44982	2.45002	0.22988	0.020	1.2213
10	4.0	0.30	0.10022	2.72986	1.17003	0.25323	0.099	1.0097	25	5.0	0.50	0.10024	2.44979	2.45005	0.22988	0.020	1.2211
10	4.0	0.30	0.10021	2.72974	1.16997	0.25309	0.099	1.0127	25	5.0	0.70	0.10014	1.46982	3.42988	0.22321	0.140	1.3911
10	4.0	0.50	0.10016	1.94991	1.95005	0.24916	0.012	1.0978	25	5.0	0.70	0.10013	1.46993	3.43008	0.22340	0.140	1.3859
10	4.0	0.50	0.10016	1.94975	1.94994	0.24917	0.012	1.0977	30	5.0	0.30	0.10035	3.42967	1.47001	0.23343	0.050	1.0731
10	4.0	0.70	0.10006	1.16994	2.73009	0.24464	0.076	1.2052	30	5.0	0.30	0.10032	3.42990	1.47001	0.23343	0.050	1.0733
10	4.0	0.70	0.10008	1.16994	2.73009	0.24474	0.076	1.2024	30	5.0	0.50	0.10021	2.44982	2.45002	0.22762	0.050	1.2001
15	4.0	0.30	0.10022	2.72986	1.17003	0.25148	0.130	0.9955	30	5.0	0.50	0.10024	2.44979	2.45005	0.22763	0.050	1.1999
15	4.0	0.30	0.10021	2.72974	1.16997	0.25129	0.130	0.9993	30	5.0	0.70	0.10013	1.46993	3.43008	0.22110	0.180	1.3603
15	4.0	0.50	0.10016	1.94991	1.95005	0.24731	0.012	1.0831	40	5.0	0.30	0.10035	3.42967	1.47001	0.22889	0.200	1.0338
15	4.0	0.50	0.10016	1.94975	1.94994	0.24732	0.012	1.0830	40	5.0	0.50	0.10021	2.44982	2.45002	0.22293	0.090	1.1552
15	4.0	0.70	0.10006	1.16994	2.73009	0.24265	0.086	1.1902	40	5.0	0.50	0.10024	2.44979	2.45005	0.22294	0.090	1.1549
15	4.0	0.70	0.10008	1.16994	2.73009	0.24277	0.086	1.1872	40	5.0	0.70	0.10013	1.46993	3.43008	0.21633	0.200	1.3061
20	4.0	0.30	0.10022	2.72986	1.17003	0.24960	0.130	0.9817	5	5.5	0.30	0.10034	3.77981	1.61999	0.23815	0.150	1.2365
20	4.0	0.30	0.10021	2.72974	1.16997	0.24941	0.130	0.9854	5	5.5	0.30	0.10010	3.77057	1.61614	0.23836	0.150	1.2340
20	4.0	0.50	0.10016	1.94991	1.95005	0.24535	0.011	1.0681	5	5.5	0.50	0.10026	2.69965	2.70002	0.23202	0.160	1.4057
20	4.0	0.50	0.10016	1.94975	1.94994	0.24535	0.011	1.0681	5	5.5	0.50	0.10027	2.69969	2.70005	0.23224	0.160	1.3991
20	4.0	0.70	0.10006	1.16994	2.73009	0.24059	0.085	1.1742	5	5.5	0.70	0.10016	1.61984	3.78003	0.22509	0.150	1.6253
20	4.0	0.70	0.10008	1.16994	2.73009	0.24070	0.085	1.1714	5	5.5	0.70	0.10015	1.61985	3.77996	0.22488	0.150	1.6325
25	4.0	0.30	0.10022	2.72986	1.17003	0.24762	0.120	0.9667	10	5.5	0.30	0.10034	3.77981	1.61999	0.23631	0.150	1.2173
25	4.0	0.30	0.10021	2.72974	1.16997	0.24745	0.120	0.9701	10	5.5	0.30	0.10010	3.77057	1.61614	0.23652	0.150	1.2150
25	4.0	0.50	0.10016	1.94991	1.95005	0.24327	0.020	1.0525	10	5.5	0.50	0.10026	2.69965	2.70002	0.23007	0.150	1.3837
25	4.0	0.50	0.10016	1.94975	1.94994	0.24327	0.020	1.0525	10	5.5	0.50	0.10027	2.69969	2.70005	0.23029	0.150	1.3775
25	4.0	0.70	0.10006	1.16994	2.73009	0.23841	0.100	1.1576	10	5.5	0.70	0.10016	1.61984	3.78003	0.22303	0.130	1.5994
25	4.0	0.70	0.10008	1.16994	2.73009	0.23854	0.100	1.1544	10	5.5	0.70	0.10015	1.61985	3.77996	0.22285	0.130	1.6055
30	4.0	0.30	0.10022	2.72986	1.17003	0.24551	0.120	0.9527	15	5.5	0.30	0.10034	3.77981	1.61999	0.23443	0.130	1.1959
30	4.0	0.30	0.10021	2.72974	1.16997	0.24536	0.120	0.9555	15	5.5	0.30	0.10010	3.77057	1.61614	0.23462	0.130	1.1944
30	4.0	0.50	0.10016	1.94991	1.95005	0.24107	0.050	1.0374	15	5.5	0.50	0.10026	2.69965	2.70002	0.22811	0.140	1.3590
30	4.0	0.50	0.10016	1.94975	1.94994	0.24108	0.050	1.0374	15	5.5	0.50	0.10027	2.69969	2.70005	0.22831	0.140	1.3535
30	4.0	0.70	0.10006	1.16994	2.73009	0.23598	0.200	1.1443	15	5.5	0.70	0.10016	1.61984	3.78003	0.22095	0.085	1.5703
30	4.0	0.70	0.10008	1.16994	2.73009	0.23625	0.200	1.1382	15	5.5	0.70	0.10015	1.61985	3.77996	0.22084	0.085	1.5742
40	4.0	0.30	0.10022	2.72986	1.17003	0.24110	0.170	0.9223	20	5.5	0.30	0.10034	3.77981	1.61999	0.23247	0.074	1.1742
40	4.0	0.30	0.10021	2.72974	1.16997	0.24090	0.170	0.9259	20	5.5	0.30	0.10010	3.77057	1.61614	0.23258	0.074	1.1746
40	4.0	0.50	0.10016	1.94991	1.95005	0.23653	0.200	1.0041	20	5.5	0.50	0.10026	2.69965	2.70002	0.22606	0.120	1.3337
40	4.0	0.70	0.10008	1.16994	2.73009	0.23159	0.200	1.1009	20	5.5	0.50	0.10027	2.69969	2.70005	0.22623	0.120	1.3292
5	4.5	0.30	0.10026	3.07973	1.32007	0.24919	0.110	1.0863	20	5.5	0.70	0.10016	1.61984	3.78003	0.21881	0.011	1.5403
5	4.5	0.30	0.10020	3.07987	1.32003	0.24904	0.110	1.0901	20	5.5	0.70	0.10015	1.61985	3.77996	0.21880	0.011	1.5405

Table 3. continued

t (°C)	$m\text{Cl}^-$ (mol kg ⁻¹)	γ_{Na^+}	$m\text{HCl}$ (mol kg ⁻¹)	$m\text{TrisHCl}$ (mol kg ⁻¹)	$m\text{NaCl}$ (mol kg ⁻¹)	$E(\text{adj.})^b$ (V)	$u(E)^b$ (mV)	γ_{HCl}	t (°C)	$m\text{Cl}^-$ (mol kg ⁻¹)	γ_{Na^+}	$m\text{HCl}$ (mol kg ⁻¹)	$m\text{TrisHCl}$ (mol kg ⁻¹)	$m\text{NaCl}$ (mol kg ⁻¹)	$E(\text{adj.})^b$ (V)	$u(E)^b$ (mV)	γ_{HCl}
5	4.5	0.50	0.10014	2.19992	2.20003	0.24454	0.073	1.1976	25	5.5	0.30	0.10034	3.77981	1.61999	0.23040	0.079	1.1520
5	4.5	0.50	0.10018	2.19982	2.20002	0.24464	0.073	1.1948	25	5.5	0.30	0.10010	3.77057	1.61614	0.23051	0.079	1.1524
5	4.5	0.70	0.10010	1.31994	3.08015	0.23935	0.010	1.3348	25	5.5	0.50	0.10026	2.69965	2.70002	0.22389	0.120	1.3081
5	4.5	0.70	0.10012	1.31984	3.08009	0.23935	0.010	1.3347	25	5.5	0.50	0.10027	2.69969	2.70005	0.22406	0.120	1.3039
10	4.5	0.30	0.10026	3.07973	1.32007	0.24743	0.096	1.0719	25	5.5	0.70	0.10016	1.61984	3.78003	0.21642	0.088	1.5137
10	4.5	0.30	0.10020	3.07987	1.32003	0.24730	0.096	1.0752	25	5.5	0.70	0.10015	1.61985	3.77996	0.21654	0.088	1.5102
10	4.5	0.50	0.10014	2.19992	2.20003	0.24270	0.011	1.1817	30	5.5	0.30	0.10034	3.77981	1.61999	0.22824	0.051	1.1301
10	4.5	0.50	0.10018	2.19982	2.20002	0.24271	0.011	1.1813	30	5.5	0.30	0.10010	3.77057	1.61614	0.22825	0.051	1.1326
10	4.5	0.70	0.10010	1.31994	3.08015	0.23737	0.010	1.3183	30	5.5	0.50	0.10026	2.69965	2.70002	0.22159	0.150	1.2840
10	4.5	0.70	0.10012	1.31984	3.08009	0.23737	0.010	1.3182	30	5.5	0.50	0.10027	2.69969	2.70005	0.22179	0.150	1.2790
15	4.5	0.30	0.10026	3.07973	1.32007	0.24562	0.110	1.0559	30	5.5	0.70	0.10015	1.61985	3.77996	0.21429	0.180	1.4773
15	4.5	0.30	0.10020	3.07987	1.32003	0.24547	0.110	1.0593	40	5.5	0.30	0.10034	3.77981	1.61999	0.22377	0.090	1.0838
15	4.5	0.50	0.10014	2.19992	2.20003	0.24078	0.011	1.1647	40	5.5	0.30	0.10010	3.77057	1.61614	0.22377	0.090	1.0864
15	4.5	0.50	0.10018	2.19982	2.20002	0.24079	0.011	1.1644	40	5.5	0.50	0.10026	2.69965	2.70002	0.21690	0.190	1.2313
15	4.5	0.70	0.10010	1.31994	3.08015	0.23537	0.011	1.2991	40	5.5	0.50	0.10027	2.69969	2.70005	0.21715	0.190	1.2257
15	4.5	0.70	0.10012	1.31984	3.08009	0.23536	0.011	1.2991									

^aThe first nine entries on each row is one set of results, and the second nine entries (also starting with temperature t) is a second set. Columns $m\text{Cl}^-$ and γ_{Na^+} contain rounded values, and exact molalities can be calculated from the listed $m\text{HCl}$, $m\text{NaCl}$ and $m\text{TrisHCl}$. More complete results, including estimated uncertainties of γ_{HCl} , can be found in the [Supporting Information](#). ^bCell potentials and their uncertainties are listed here to a fixed 5 digits and 3 digits following the decimal point, respectively. This was done for simplicity. In some cases (uncertainties of around 0.01 mV) an extra digit in $E(\text{adj.})$ is appropriate, ²⁸ or (for uncertainties of around 0.1 mV or higher) the removal of a final zero ($u(E)$).

Table 4. Harned Cell Results For HCl–NaCl–TrisHCl Solutions at Ionic Strengths of 2.0 mol kg^{−1} and below, Including Calculated Mean Activity Coefficients of HCl^a

<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (<i>E</i>) ^b (mV)	<i>γ</i> _{HCl}	<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (<i>E</i>) ^b (mV)	<i>γ</i> _{HCl}
5	1.0	0.30	0.10000	0.62997	0.26993	0.30334	0.012	0.7457	25	1.5	0.30	0.09990	0.98005	0.41996	0.28578	0.100	0.7525
5	1.0	0.30	0.10001	0.63004	0.26995	0.30335	0.012	0.7455	25	1.5	0.30	0.09994	0.98001	0.42001	0.28592	0.100	0.7503
5	1.0	0.50	0.10002	0.44999	0.45001	0.30287	0.013	0.7529	25	1.5	0.50	0.09995	0.69999	0.70001	0.28461	0.021	0.7697
5	1.0	0.50	0.10024	0.44997	0.44998	0.30286	0.013	0.7522	25	1.5	0.50	0.09998	0.69998	0.70002	0.28460	0.021	0.7697
5	1.0	0.70	0.10010	0.27001	0.62991	0.30210	0.011	0.7648	25	1.5	0.70	0.10000	0.42001	0.97997	0.28320	0.020	0.7908
5	1.0	0.70	0.09993	0.27002	0.62997	0.30210	0.011	0.7654	25	1.5	0.70	0.10002	0.42000	0.97998	0.28321	0.020	0.7907
10	1.0	0.30	0.10000	0.62997	0.26993	0.30213	0.072	0.7422	30	1.5	0.30	0.09990	0.98005	0.41996	0.28394	0.120	0.7468
10	1.0	0.30	0.10001	0.63004	0.26995	0.30223	0.072	0.7406	30	1.5	0.30	0.09994	0.98001	0.42001	0.28409	0.120	0.7444
10	1.0	0.50	0.10002	0.44999	0.45001	0.30163	0.073	0.7498	30	1.5	0.50	0.09995	0.69999	0.70001	0.28272	0.050	0.7642
10	1.0	0.50	0.10024	0.44997	0.44998	0.30153	0.073	0.7505	30	1.5	0.50	0.09998	0.69998	0.70002	0.28272	0.050	0.7642
10	1.0	0.70	0.10010	0.27001	0.62991	0.30081	0.010	0.7623	30	1.5	0.70	0.10000	0.42001	0.97997	0.28128	0.050	0.7854
10	1.0	0.70	0.09993	0.27002	0.62997	0.30081	0.010	0.7629	30	1.5	0.70	0.10002	0.42000	0.97998	0.28128	0.050	0.7853
15	1.0	0.30	0.10000	0.62997	0.26993	0.30084	0.077	0.7378	40	1.5	0.30	0.09990	0.98005	0.41996	0.28026	0.140	0.7302
15	1.0	0.30	0.10001	0.63004	0.26995	0.30094	0.077	0.7362	40	1.5	0.30	0.09994	0.98001	0.42001	0.28041	0.140	0.7281
15	1.0	0.50	0.10002	0.44999	0.45001	0.30030	0.013	0.7458	40	1.5	0.50	0.09995	0.69999	0.70001	0.27897	0.090	0.7477
15	1.0	0.50	0.10024	0.44997	0.44998	0.30029	0.013	0.7450	40	1.5	0.50	0.09998	0.69998	0.70002	0.27896	0.090	0.7477
15	1.0	0.70	0.10010	0.27001	0.62991	0.29945	0.010	0.7583	40	1.5	0.70	0.10000	0.42001	0.97997	0.27744	0.090	0.7690
15	1.0	0.70	0.09993	0.27002	0.62997	0.29945	0.010	0.7590	40	1.5	0.70	0.10002	0.42000	0.97998	0.27745	0.090	0.7688
20	1.0	0.30	0.10000	0.62997	0.26993	0.29938	0.085	0.7338	5	2.0	0.30	0.10006	1.33000	0.56996	0.28222	0.140	0.8190
20	1.0	0.30	0.10001	0.63004	0.26995	0.29949	0.085	0.7321	5	2.0	0.30	0.10004	1.32995	0.56999	0.28241	0.140	0.8157
20	1.0	0.50	0.10002	0.44999	0.45001	0.29879	0.012	0.7423	5	2.0	0.50	0.10009	0.94979	0.95026	0.28070	0.160	0.8452
20	1.0	0.50	0.10024	0.44997	0.44998	0.29878	0.012	0.7415	5	2.0	0.50	0.10001	0.95002	0.94994	0.28092	0.160	0.8417
20	1.0	0.70	0.10010	0.27001	0.62991	0.29793	0.010	0.7547	5	2.0	0.70	0.10000	0.57000	1.32998	0.27928	0.140	0.8710
20	1.0	0.70	0.09993	0.27002	0.62997	0.29793	0.010	0.7554	5	2.0	0.70	0.09995	0.57006	1.32999	0.27909	0.140	0.8747
25	1.0	0.30	0.10000	0.62997	0.26993	0.29783	0.082	0.7286	10	2.0	0.30	0.10006	1.33000	0.56996	0.28077	0.140	0.8128
25	1.0	0.30	0.10001	0.63004	0.26995	0.29794	0.082	0.7270	10	2.0	0.30	0.10004	1.32995	0.56999	0.28096	0.140	0.8097
25	1.0	0.50	0.10002	0.44999	0.45001	0.29721	0.021	0.7373	10	2.0	0.50	0.10009	0.94979	0.95026	0.27916	0.160	0.8400
25	1.0	0.50	0.10024	0.44997	0.44998	0.29720	0.021	0.7366	10	2.0	0.50	0.10001	0.95002	0.94994	0.27938	0.160	0.8365
25	1.0	0.70	0.10010	0.27001	0.62991	0.29631	0.020	0.7501	10	2.0	0.70	0.10000	0.57000	1.32998	0.27767	0.140	0.8664
25	1.0	0.70	0.09993	0.27002	0.62997	0.29631	0.020	0.7507	10	2.0	0.70	0.09995	0.57006	1.32999	0.27748	0.140	0.8700
30	1.0	0.30	0.10000	0.62997	0.26993	0.29611	0.097	0.7243	15	2.0	0.30	0.10006	1.33000	0.56996	0.27924	0.140	0.8057
30	1.0	0.30	0.10001	0.63004	0.26995	0.29623	0.097	0.7226	15	2.0	0.30	0.10004	1.32995	0.56999	0.27943	0.140	0.8026
30	1.0	0.50	0.10002	0.44999	0.45001	0.29546	0.050	0.7332	15	2.0	0.50	0.10009	0.94979	0.95026	0.27755	0.170	0.8333
30	1.0	0.50	0.10024	0.44997	0.44998	0.29545	0.050	0.7324	15	2.0	0.50	0.10001	0.95002	0.94994	0.27779	0.170	0.8297
30	1.0	0.70	0.10010	0.27001	0.62991	0.29454	0.050	0.7459	15	2.0	0.70	0.10000	0.57000	1.32998	0.27600	0.140	0.8602
30	1.0	0.70	0.09993	0.27002	0.62997	0.29454	0.050	0.7466	15	2.0	0.70	0.09995	0.57006	1.32999	0.27580	0.140	0.8639
40	1.0	0.30	0.10000	0.62997	0.26993	0.29265	0.120	0.7106	20	2.0	0.30	0.10006	1.33000	0.56996	0.27755	0.150	0.7989
40	1.0	0.30	0.10001	0.63004	0.26995	0.29276	0.120	0.7090	20	2.0	0.30	0.10004	1.32995	0.56999	0.27776	0.150	0.7957
40	1.0	0.50	0.10002	0.44999	0.45001	0.29195	0.120	0.7197	20	2.0	0.50	0.10009	0.94979	0.95026	0.27581	0.170	0.8269
40	1.0	0.50	0.10024	0.44997	0.44998	0.29185	0.120	0.7202	20	2.0	0.50	0.10001	0.95002	0.94994	0.27604	0.170	0.8234
40	1.0	0.70	0.10010	0.27001	0.62991	0.29097	0.090	0.7326	20	2.0	0.70	0.10000	0.57000	1.32998	0.27419	0.150	0.8542
40	1.0	0.70	0.09993	0.27002	0.62997	0.29097	0.090	0.7333	20	2.0	0.70	0.09995	0.57006	1.32999	0.27397	0.150	0.8581

Table 4. continued

<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (<i>E</i>) ^b (mV)	<i>γ</i> _{HCl}	<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>y</i> Na ⁺	<i>m</i> HCl (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) ^b (V)	<i>u</i> (<i>E</i>) ^b (mV)	<i>γ</i> _{HCl}
5	1.5	0.30	0.09990	0.98005	0.41996	0.29181	0.110	0.7747	25	2.0	0.30	0.10006	1.33000	0.56996	0.27580	0.020	0.7907
5	1.5	0.30	0.09994	0.98001	0.42001	0.29197	0.110	0.7721	25	2.0	0.30	0.10004	1.32995	0.56999	0.27581	0.020	0.7907
5	1.5	0.50	0.09995	0.69999	0.70001	0.29082	0.011	0.7908	25	2.0	0.50	0.10009	0.94979	0.95026	0.27399	0.170	0.8189
5	1.5	0.50	0.09998	0.69998	0.70002	0.29081	0.011	0.7908	25	2.0	0.50	0.10001	0.95002	0.94994	0.27423	0.170	0.8155
5	1.5	0.70	0.10000	0.42001	0.97997	0.28965	0.010	0.8101	25	2.0	0.70	0.10000	0.57000	1.32998	0.27230	0.150	0.8466
5	1.5	0.70	0.10002	0.42000	0.97998	0.28965	0.010	0.8100	25	2.0	0.70	0.09995	0.57006	1.32999	0.27209	0.150	0.8504
10	1.5	0.30	0.09990	0.98005	0.41996	0.29046	0.110	0.7701	30	2.0	0.30	0.10006	1.33000	0.56996	0.27388	0.160	0.7835
10	1.5	0.30	0.09994	0.98001	0.42001	0.29061	0.110	0.7676	30	2.0	0.30	0.10004	1.32995	0.56999	0.27409	0.160	0.7804
10	1.5	0.50	0.09995	0.69999	0.70001	0.28941	0.011	0.7867	30	2.0	0.50	0.10009	0.94979	0.95026	0.27202	0.180	0.8117
10	1.5	0.50	0.09998	0.69998	0.70002	0.28941	0.011	0.7866	30	2.0	0.50	0.10001	0.95002	0.94994	0.27226	0.180	0.8083
10	1.5	0.70	0.10000	0.42001	0.97997	0.28817	0.011	0.8068	30	2.0	0.70	0.10000	0.57000	1.32998	0.27029	0.170	0.8394
10	1.5	0.70	0.10002	0.42000	0.97998	0.28817	0.011	0.8066	30	2.0	0.70	0.09995	0.57006	1.32999	0.27006	0.170	0.8434
15	1.5	0.30	0.09990	0.98005	0.41996	0.28904	0.110	0.7643	40	2.0	0.30	0.10006	1.33000	0.56996	0.27003	0.190	0.7638
15	1.5	0.30	0.09994	0.98001	0.42001	0.28920	0.110	0.7618	40	2.0	0.30	0.10004	1.32995	0.56999	0.27027	0.190	0.7605
15	1.5	0.50	0.09995	0.69999	0.70001	0.28795	0.011	0.7811	40	2.0	0.50	0.10009	0.94979	0.95026	0.26809	0.200	0.7916
15	1.5	0.50	0.09998	0.69998	0.70002	0.28794	0.011	0.7811	40	2.0	0.50	0.10001	0.95002	0.94994	0.26834	0.200	0.7882
15	1.5	0.70	0.10000	0.42001	0.97997	0.28664	0.011	0.8018	40	2.0	0.70	0.10000	0.57000	1.32998	0.26627	0.200	0.8191
15	1.5	0.70	0.10002	0.42000	0.97998	0.28664	0.011	0.8016	40	2.0	0.70	0.09995	0.57006	1.32999	0.26602	0.200	0.8231
20	1.5	0.30	0.09990	0.98005	0.41996	0.28745	0.120	0.7591									
20	1.5	0.30	0.09994	0.98001	0.42001	0.28762	0.120	0.7564									
20	1.5	0.50	0.09995	0.69999	0.70001	0.28631	0.011	0.7761									
20	1.5	0.50	0.09998	0.69998	0.70002	0.28631	0.011	0.7761									
20	1.5	0.70	0.10000	0.42001	0.97997	0.28497	0.011	0.7967									
20	1.5	0.70	0.10002	0.42000	0.97998	0.28498	0.011	0.7966									

^aThe first nine entries on each row is one set of results, and the second nine entries (also starting with temperature *t*) is a second set. Columns *m*Cl[−] and *y*Na⁺ contain rounded values, and exact molalities can be calculated from the listed *m*HCl, *m*NaCl, and *m*TrisHCl. More complete results, including estimated uncertainties of *γ*_{HCl}, can be found in the Supporting Information. ^bCell potentials and their uncertainties are listed here to a fixed 5 digits and 3 digits following the decimal point, respectively. This was done for simplicity. In some cases (uncertainties of around 0.01 mV) an extra digit in *E*(adj.) is appropriate,²⁸ or (for uncertainties of around 0.1 mV or higher) the removal of a final zero (*u*(*E*)).

only $\sim 0.6\%$ of the total uncertainty of the cell potential. The uncertainty of the voltage measurement was calculated as a combined value of cell potential drift (see Section 2.2 for its numeric values) at the experimental temperature and the standard deviation (SD) of two duplicate measurements:

$$u(E) = [(drift)^2 + (SD)^2]^{1/2} \quad (4)$$

In general, the $u(E)$ values for the HCl–NaCl–TrisHCl solutions were found to be larger than the uncertainties of the measurements in our previous study. They increase with temperature, reaching quite a significant value of $200 \mu\text{V}$ at 40°C for solutions with ionic strengths of 3.5 mol kg^{-1} and above. In addition to the more difficult nature of the measurand, slight differences in the geometrical design of duplicate cells (the diameter of the inner capillary tubes, especially) seem likely to be an important influence on the repeatability of measurements for concentrated solutions at temperatures above 25°C due to water evaporation and transfer.

The $u(E)$ for 0.04 mol kg^{-1} Tris buffer in a NaCl medium was approximately $100 \mu\text{V}$ for all studied temperatures.

4. RESULTS AND DISCUSSION

In this section, we discuss the results for the two types of solutions and compare them with existing literature data and with model calculations.

4.1. Aqueous HCl–NaCl–TrisHCl Solutions. Measured cell potentials, corrected to $p\text{H}_2$ equal to 1 atm and adjusted to be consistent with the standard potentials of Bates and Bower,¹⁸ are listed in Tables 3 and 4 together with values of γ_{HCl} determined from the data. In Tables S6 and S7 of the Supporting Information the original measured potentials are listed, together with other information needed in eqs 2 and 3 to adjust the data to 1 atm $p\text{H}_2$, and also the estimated uncertainties in γ_{HCl} .

Results at 25°C are shown in Figure 1, distinguishing the data for each of the three Na^+ fractions (y_{Na^+}). The solid line represents mean activity coefficients for aqueous HCl–TrisHCl calculated using the same Pitzer model as Maksimov et al.⁷ in their Figure 2b. For compositions corresponding to y_{Na^+} equal to unity, i.e., aqueous HCl–NaCl, we show model-calculated values at low ionic strengths and also data from several other studies, some of which derive from the application of Harned's rule to the original measurements (cited in the caption to Figure 1). Our results in Table 4 for low ionic strengths, plotted in the inset of Figure 1, show that measured values (the solid symbols) are not equidistant between the lines for the two end-member cases of y_{Na^+} equal to zero and one. This appears to suggest that the substitution of TrisH^+ by Na^+ in these dilute solutions yields a steep increase in γ_{HCl} that is not apparent in the measurements for the higher ionic strengths, also shown in Figure 1, that were carried out several years before. This behavior is examined below.

Figure 2, parts a–d, shows values of γ_{HCl} at three different temperatures, as a function of y_{Na^+} for fixed ionic strengths. At ionic strengths and temperatures for which there are also data for the end-member solutions (y_{Na^+} equal to zero and one), dotted lines are used to link all the values. The results show that γ_{HCl} is the highest at the lowest temperatures, and the slope with respect to y_{Na^+} increases with ionic strength.

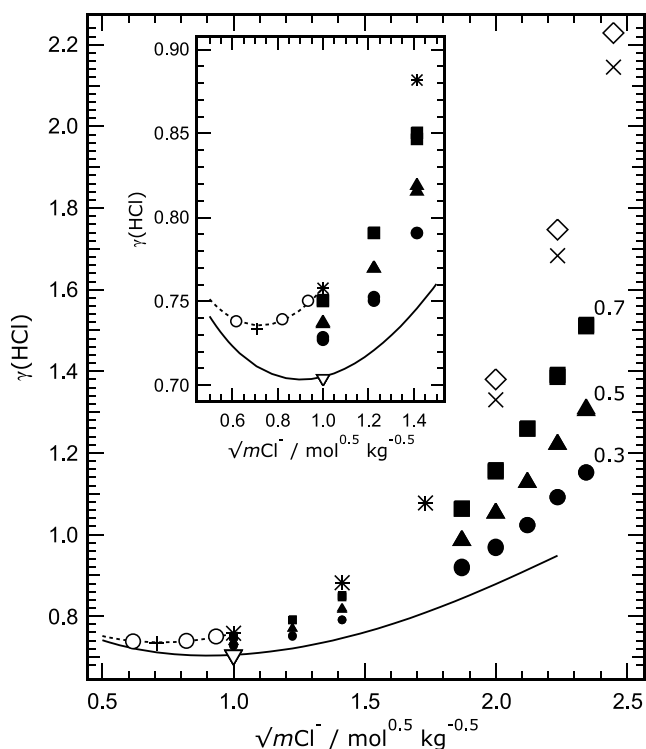


Figure 1. Measured and calculated mean activity coefficients γ_{HCl} (labeled $\gamma(\text{HCl})$ for clarity) at 25°C , plotted against the square root of total Cl^- molality ($m\text{Cl}^-$). All data are for solutions containing 0.1 mol kg^{-1} of H^+ . Symbols: dot, solid triangle, and solid square – results of this study at the three Na^+ cation fractions (y_{Na^+}) indicated on the plot; inverted triangle – measurement from Maksimov et al.⁷ for aqueous HCl–TrisHCl (hence $y_{\text{Na}^+} = 0$). Other symbols are for aqueous HCl–NaCl solutions ($y_{\text{Na}^+} = 1$): open circle – Macaskill et al.²² (calculated using Harned's rule coefficients in their Table II); plus – from Harned's rule coefficients in Table 14-6-2 of Harned and Owen;²³ asterisk – from Harned's rule coefficients in Table 1 of Harned;²⁴ cross – measurements of Hawkins;²⁵ diamond – from Harned's rule coefficients in Table 4 of Jiang.²⁶ Solid symbols at low chloride molalities are reduced in size for clarity. Lines: solid – for aqueous HCl–TrisHCl ($y_{\text{Na}^+} = 0$) calculated using the Pitzer model of Clegg et al.⁶ including values of parameters $\theta_{\text{H,TrisH}}$ and $\psi_{\text{H,TrisH,Cl}}$ as described in the text; dotted – for aqueous HCl–NaCl calculated using the same Pitzer model. The inset shows the same results up to a 2.0 mol kg^{-1} Cl^- molality.

In Figure 2b we compare model-calculated γ_{HCl} with measured values at 25°C and an ionic strength of 1.0 mol kg^{-1} as a typical example of the results at low ionic strengths. The dashed-dotted line was calculated using Pitzer model parameters for $\text{H}^+ - \text{Cl}^-$, $\text{TrisH}^+ - \text{Cl}^-$, and $\text{Na}^+ - \text{Cl}^-$ interactions only. The addition of ternary parameters for $\text{H}^+ - \text{Na}^+ - \text{Cl}^-$ interactions (as used by Clegg et al.⁶), and $\text{H}^+ - \text{TrisH}^+ - \text{Cl}^-$ interactions (from Bates and Macaskill¹⁹), can be shown to yield more accurate predictions of both end-member solutions. However, our measured γ_{HCl} for intermediate values of y_{Na^+} are consistently higher than predicted, by about 0.0075 , even using recently determined parameters for $\text{Na}^+ - \text{TrisH}^+ - \text{Cl}^-$ interactions (J. Miladinovic, Pers. comm.). This is equivalent to a difference in potential of about 0.5 mV . No plausible values of the ternary mixture parameters in the Pitzer model for these solutions seem able to account for the observed difference, and we attribute it to the condition of the electrodes

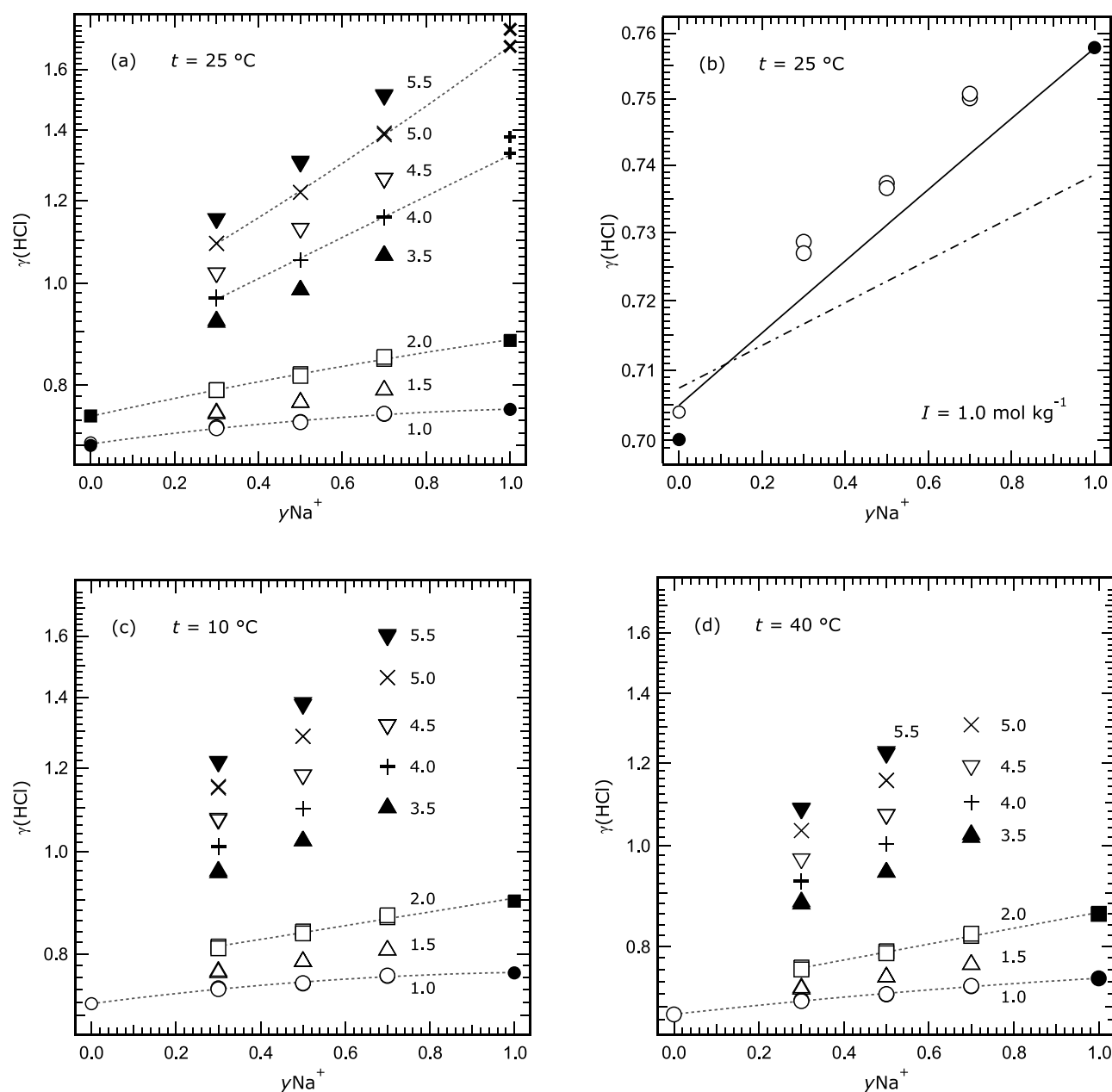


Figure 2. Measured mean activity coefficients γ_{HCl} (labeled $\gamma(\text{HCl})$ for clarity) plotted against the Na^+ cation fraction y_{Na^+} for different temperatures and ionic strengths as indicated on the plots. Symbols and ionic strengths: dot and open circle – 1.0; triangle – 1.5; square and solid square – 2.0; solid triangle – 3.5; plus – 4.0; inverted triangle – 4.5; cross – 5.0; solid inverted triangle – 5.5 mol kg^{-1} . The open circles at $y_{\text{Na}^+} = 0$ are values from our previous study.⁷ (a) Results at 25 °C, including measurements of Macaskill and Bates²⁷ and Bates and Macaskill¹⁹ (solid symbols at $y_{\text{Na}^+} = 0.0$), Harned²⁴ (solid square and circle at $y_{\text{Na}^+} = 1.0$), and Hawkins²⁵ and Jiang²⁶ (bold plus and cross at $y_{\text{Na}^+} = 1.0$). Dotted lines are visual guides only. (b) Results for ionic strength 1.0 mol kg^{-1} from plot (a). Lines were calculated using the model of Clegg et al.,⁶ as follows: dash-dot – without ternary mixture parameters; solid – with ternary mixture parameters as described in the text. (c, d) Results at 10 and 40 °C, with symbols denoting different ionic strengths as in (a). Data for the other temperatures (5, 15, 20, and 30 °C) are similar and are not shown.

used for the low ionic strength measurements, as noted in Section 2.2.

Further examination of this behavior in Figure 3a shows, first, that the offset of the measured γ_{HCl} from the predicted values is similar at all three ionic strengths and does not appear to have a relationship with y_{Na^+} . Second, the modeled γ_{HCl} for aqueous HCl-NaCl (i.e., y_{Na^+} equal to 1.0) at 2.0 mol kg^{-1} ionic strength is lower than the measured value. Calculations for higher ionic strengths (not shown) yield similar behavior, which suggests that this underprediction may represent small

errors in the model for $\text{H}^+-\text{Na}^+-\text{Cl}^-$ interactions, or perhaps those for Na^+-Cl^- (or H^+-Cl^- in the most concentrated solutions). In Figure 3b we show the difference between adjusted values of γ_{HCl} obtained from our measurements (at y_{Na^+} equal to 0.3, 0.5, and 0.7) and modeled values. The adjustment is equivalent to a change in the measured potential by 0.5 mV, as determined from the data for the 1.0 mol kg^{-1} ionic strength and noted above. There is quite good agreement, in most cases, to within about ± 0.002 in γ_{HCl} . The fact that the deviations of $\Delta\gamma_{\text{HCl}}$ increase with y_{Na^+} for the

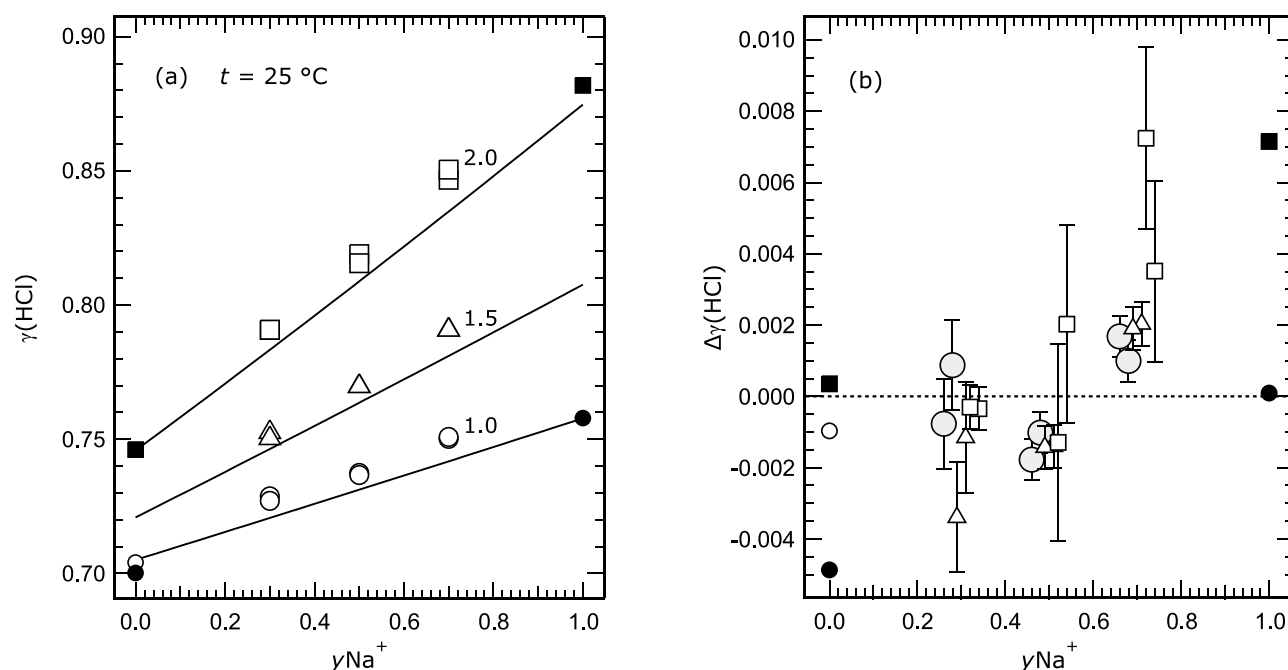


Figure 3. Measured and calculated mean activity coefficients γ_{HCl} (labeled $\gamma(\text{HCl})$ for clarity) at 25°C , for solutions with ionic strengths 1.0, 1.5, and 2.0 mol kg⁻¹, plotted against Na^+ cation fraction (y_{Na^+}). (a) Symbols: open circle, triangle, and square – results of this study for 1.0, 1.5, and 2.0 mol kg⁻¹ ionic strength as indicated; open circle at y_{Na^+} equal to 0 – measurement of Maksimov et al.;⁷ solid symbols at y_{Na^+} equal to 0 – measurements of Macaskill and Bates²⁷ ($I = 1.0$ mol kg⁻¹) and Bates and Macaskill¹⁹ ($I = 2.0$ mol kg⁻¹); solid symbols at y_{Na^+} equal to 1.0 – from Harned's rule coefficients in Table I of Harned.²⁴ Lines: calculated using the Pitzer model, including values of ternary mixture parameters as described in the text. (b) The same data as in (a), but shown as the difference between measured and model-calculated activity coefficients ($\Delta\gamma(\text{HCl})$), with the measurements from this study adjusted by an equivalent of 0.5 mV (a factor of about 0.99 in γ_{HCl}). Values of γ_{HCl} from other studies (at y_{Na^+} equal to 0 and 1) are not adjusted. Symbols: circles, triangle, and square – all values for 1.0, 1.5, and 2.0 mol kg⁻¹ ionic strength, respectively. The symbols for 1.0 mol kg⁻¹ (circles), the measurements from which the adjustment was determined, are enlarged and shaded to contrast them with the other data. Error bars (Table S4) are included.

solutions at 2.0 mol kg⁻¹ ionic strength (relative to values at the two lower ionic strengths) is consistent with the small error in the model mentioned above. Past experience suggests that the ΔE values that we observe here, related to the condition of the electrodes, are likely to be roughly constant with temperature. If this is so then these data will still be valuable for constraining a future Pitzer model of these solutions.

Figure 4a–c shows the approximately linear change of measured γ_{HCl} with temperature at all ionic strengths for the three values of y_{Na^+} . Figure 4d, for y_{Na^+} equal to 0.5, presents values of γ_{HCl} at each temperature divided by the corresponding value at 40°C . This normalization enables the relative slopes of γ_{HCl} with respect to temperature to be compared across all ionic strengths. The change in γ_{HCl} with temperature, for constant composition, is greatest at the highest ionic strength and appears to decrease smoothly: at ionic strength 5.5 mol kg⁻¹ the value of γ_{HCl} at 5°C is about 1.14 times that at 40°C , whereas at 1.0 mol kg⁻¹, the increase is only a factor of about 1.05.

4.2. Tris Buffer (Equimolar TrisHCl and Tris) in Aqueous NaCl. For the aqueous HCl–NaCl–TrisHCl solutions discussed above, the molalities of both H^+ and Cl^- are known and eq 1 was used to calculate the mean activity coefficient of HCl from the measured potentials. This is not possible for the solutions containing Tris buffer (0.04 mol kg⁻¹ TrisHCl and Tris). In these alkaline solutions, the H^+ content of the solutions is determined from the very slight dissociation of weak acid TrisH^+ (to yield H^+ and Tris), which is a function of the values of the thermodynamic equilibrium constant and

activity coefficients of the three species. When considering the results of the measurements for these solutions, it is therefore helpful to define the following acidity function, Q , which can be calculated directly from the measured cell potentials:

$$Q = \ln(m\text{H}^+ \cdot \gamma_{\text{HCl}}^2) = (E^0 - E) \cdot (F/RT) - \ln(m\text{Cl}^-) \quad (5)$$

Measured and adjusted cell potentials for these solutions are given in Table 5 together with values of the acidity function calculated from them. Table S8 of the Supporting Information contains the estimated uncertainties in the acidity function and information relevant to the adjustment of the measured potentials. Note that this function is a natural logarithm rather than decadal, and is without a reversal of sign so that all calculated values are negative.

Figure 5a shows the acidity function (on a log₁₀ basis) at all temperatures, together with values determined from measurements of DelValls and Dickson¹ for artificial seawater containing the same stoichiometric molalities of TrisHCl and Tris as in our work. The top axis indicates the nominal practical salinities of artificial seawater corresponding to the ionic strengths on the bottom x -axis. The line on the plot represents values of the acidity function calculated for the Tris buffer in aqueous NaCl over a very wide range of ionic strength using the draft model of these solutions of Clegg et al.⁶ This includes parameters for the interaction of Tris with Na^+ and a number of other ions, but not parameters for Na^+ – TrisH^+ – Cl^- or H^+ – TrisH^+ – Cl^- interactions (the latter do not

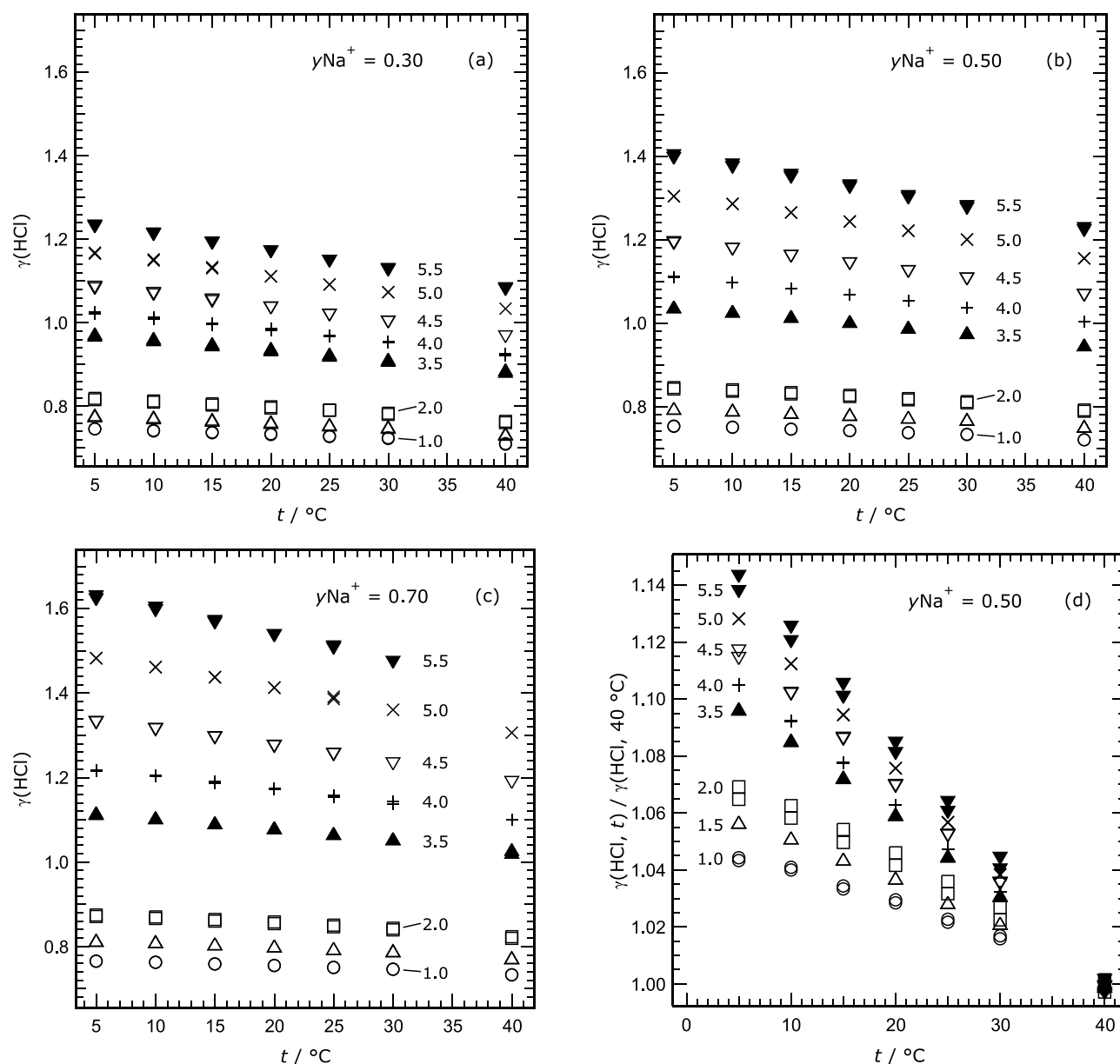


Figure 4. Measured mean activity coefficients γ_{HCl} (labeled $\gamma(\text{HCl})$ for clarity) plotted against temperature (t) for different cation fractions y_{Na^+} and ionic strengths as indicated on the plots. Symbols and ionic strengths: open circle – 1.0; triangle – 1.5; square and solid square – 2.0; solid triangle – 3.5; plus – 4.0; inverted triangle – 4.5; cross – 5.0; solid inverted triangle – 5.5 mol kg^{-1} . Plots (a)–(c): for $y_{\text{Na}^+} = 0.30, 0.50$, and 0.70 , respectively. (d) The ratio of each γ_{HCl} to its value at 40°C (for the same ionic strength and y_{Na^+}), to show how the variation of γ_{HCl} with temperature increases with ionic strength.

influence the calculated acidity function for reasons explained in the following section).

Figure 5b, which is for 25°C only, demonstrates that our results for the Tris buffer in aqueous NaCl are quite close to those for an artificial seawater medium. The draft model yields values of the acidity function that are slightly lower than measured values, but the results are encouraging.

4.3. Modeling. In this work, as in our previous study, we do not attempt to develop a Pitzer model of the solutions from the results. This is because such a model requires the consideration of a large range of literature information, and because further Harned cell data sets are still in preparation. Here we summarize the requirements for Pitzer models of the solutions studied in this work. In Table 6 we list the binary and

ternary interactions for which the Pitzer model contains parameters.

For aqueous HCl–NaCl–TrisHCl, there are existing data from which most interactions can be quantified, although in two cases ($\text{TrisH}^+ - \text{Cl}^-$ and $\text{Na}^+ - \text{TrisH}^+ - \text{Cl}^-$) the information is mostly restricted to 25°C . We note that Tishchenko²⁰ has developed a Pitzer chemical speciation model of Tris buffer in aqueous NaCl, based largely on measurements made in the same study. Some of the results of Tishchenko have been examined by Lodeiro et al.,²¹ and seem likely to be erroneous—notably osmotic and activity coefficients of aqueous Tris solutions—or were found to be inconsistent with solubility measurements.

When considering a model for the Tris buffer in aqueous NaCl solutions and what can be determined from Harned cell

Table 5. Harned Cell Results for 0.04 mol kg^{−1} Tris Buffer in Aqueous NaCl at Ionic Strengths of 0.2, 1.0, and 4.0 mol kg^{−1}, Including Values of the Acidity Function (Equation 5)^a

cell	<i>t</i> (°C)	<i>m</i> Cl [−] (mol kg ^{−1})	<i>m</i> Tris (mol kg ^{−1})	<i>m</i> TrisHCl (mol kg ^{−1})	<i>m</i> NaCl (mol kg ^{−1})	<i>E</i> (adj.) (V)	<i>u</i> (<i>E</i>) ^b (mV)	acidity function <i>Q</i> ^c	<i>u</i> (<i>Q</i>)
73	5	0.20	0.03998	0.04004	0.16000	0.76791	0.096	−20.6624	0.0042
74	5	0.20	0.04001	0.04001	0.16000	0.76778	0.096	−20.6567	0.0042
75	5	1.00	0.04001	0.04000	0.96004	0.73758	0.020	−21.0062	0.0014
76	5	1.00	0.04001	0.04001	0.96001	0.73757	0.020	−21.0060	0.0014
77	5	4.00	0.04001	0.03999	3.96013	0.70718	0.150	−21.1242	0.0064
78	5	4.00	0.03995	0.04003	3.96006	0.70697	0.150	−21.1155	0.0064
73	10	0.20	0.03998	0.04004	0.16000	0.76581	0.098	−20.2930	0.0042
74	10	0.20	0.04001	0.04001	0.16000	0.76568	0.098	−20.2872	0.0042
75	10	1.00	0.04001	0.04000	0.96004	0.73485	0.021	−20.6334	0.0014
76	10	1.00	0.04001	0.04001	0.96001	0.73485	0.021	−20.6331	0.0014
77	10	4.00	0.04001	0.03999	3.96013	0.70370	0.140	−20.7430	0.0059
78	10	4.00	0.03995	0.04003	3.96006	0.70351	0.140	−20.7351	0.0059
73	15	0.20	0.03998	0.04004	0.16000	0.76368	0.110	−19.9414	0.0046
74	15	0.20	0.04001	0.04001	0.16000	0.76353	0.110	−19.9352	0.0046
75	15	1.00	0.04001	0.04000	0.96004	0.73210	0.021	−20.2790	0.0014
76	15	1.00	0.04001	0.04001	0.96001	0.73209	0.021	−20.2786	0.0014
77	15	4.00	0.04001	0.03999	3.96013	0.70021	0.110	−20.3809	0.0046
78	15	4.00	0.03995	0.04003	3.96006	0.70006	0.110	−20.3748	0.0046
73	20	0.20	0.03998	0.04004	0.16000	0.76145	0.110	−19.6039	0.0045
74	20	0.20	0.04001	0.04001	0.16000	0.76130	0.110	−19.5979	0.0045
75	20	1.00	0.04001	0.04000	0.96004	0.72927	0.130	−19.9394	0.0053
76	20	1.00	0.04001	0.04001	0.96001	0.72909	0.130	−19.9320	0.0053
77	20	4.00	0.04001	0.03999	3.96013	0.69671	0.100	−20.0365	0.0042
78	20	4.00	0.03995	0.04003	3.96006	0.69657	0.100	−20.0310	0.0042
73	25	0.20	0.03998	0.04004	0.16000	0.75912	0.110	−19.2810	0.0045
74	25	0.20	0.04001	0.04001	0.16000	0.75897	0.110	−19.2750	0.0045
75	25	1.00	0.04001	0.04000	0.96004	0.72638	0.140	−19.6157	0.0056
76	25	1.00	0.04001	0.04001	0.96001	0.72618	0.140	−19.6081	0.0056
77	25	4.00	0.04001	0.03999	3.96013	0.69312	0.067	−19.7075	0.0029
78	25	4.00	0.03995	0.04003	3.96006	0.69311	0.067	−19.7071	0.0029
73	30	0.20	0.03998	0.04004	0.16000	0.75672	0.110	−18.9706	0.0044
74	30	0.20	0.04001	0.04001	0.16000	0.75656	0.110	−18.9646	0.0044
75	30	1.00	0.04001	0.04000	0.96004	0.72341	0.150	−19.3048	0.0059
76	30	1.00	0.04001	0.04001	0.96001	0.72319	0.150	−19.2966	0.0059
77	30	4.00	0.04001	0.03999	3.96013	0.68930	0.100	−19.3856	0.0040
78	30	4.00	0.03995	0.04003	3.96006	0.68944	0.100	−19.3910	0.0040
73	40	0.20	0.03998	0.04004	0.16000	0.75180	0.110	−18.3919	0.0046
74	40	0.20	0.04001	0.04001	0.16000	0.75165	0.110	−18.3861	0.0046
75	40	1.00	0.04001	0.04000	0.96004	0.71744	0.170	−18.7277	0.0066
76	40	1.00	0.04001	0.04001	0.96001	0.71720	0.170	−18.7188	0.0066
77	40	4.00	0.04001	0.03999	3.96013	0.68159	0.490	−18.7856	0.0183
78	40	4.00	0.03995	0.04003	3.96006	0.68228	0.490	−18.8111	0.0183

^aColumn *m*Cl[−] contains rounded values, and exact molalities can be calculated from the listed *m*NaCl and *m*TrisHCl. Prefix “*u*” in the column headers denotes an uncertainty. More complete results can be found in the [Supporting Information](#). ^bCell potentials and their uncertainties are listed here to a fixed 5 digits and 3 digits following the decimal point, respectively. This was done for simplicity. In some cases the removal of a final zero in *u*(*E*) is preferred.²⁸ ^cThe acidity function *Q* is equal to ln(*m*H⁺·*γ*_{HCl}²), see [eq 5](#). In the same way as for *E*(adj.) and *u*(*E*) we report both *Q* and *u*(*Q*) to a fixed 4 digits following the decimal point.

measurements, it is helpful to substitute for *a*H⁺ in [eq 1](#) as follows:

$$E = E^0 - RT/F \cdot \ln(K(\text{TrisH}^+) \cdot (m_{\text{TrisH}^+} \cdot m_{\text{Cl}^-} / m_{\text{Tris}}) \cdot \gamma_{\text{TrisHCl}}^2 / \gamma_{\text{Tris}}) \quad (6)$$

and, substituting from [eq 5](#)

$$Q - \ln(K(\text{TrisH}^+)) = \ln((m_{\text{TrisH}^+} / m_{\text{Tris}}) \cdot \gamma_{\text{TrisHCl}}^2 / \gamma_{\text{Tris}}) \quad (7)$$

where *K*(TrisH⁺) (mol kg^{−1}) is the acid dissociation constant of TrisH⁺. The value of this dissociation constant is known,⁹ and the molalities of TrisH⁺ and Tris at equilibrium will differ very little from their stoichiometric values (known from the preparation of the solutions). Consequently, the measured cell potentials can be used in [eq 6](#) or [eq 7](#) to obtain the quantity *γ*_{TrisHCl}²/*γ*_{Tris}. The list of Pitzer model interactions in [Table 6](#) for the Tris buffer solutions is longer than that for aqueous HCl–NaCl–TrisHCl, but three of these interactions—the ones involving H⁺—do not influence the calculated cell

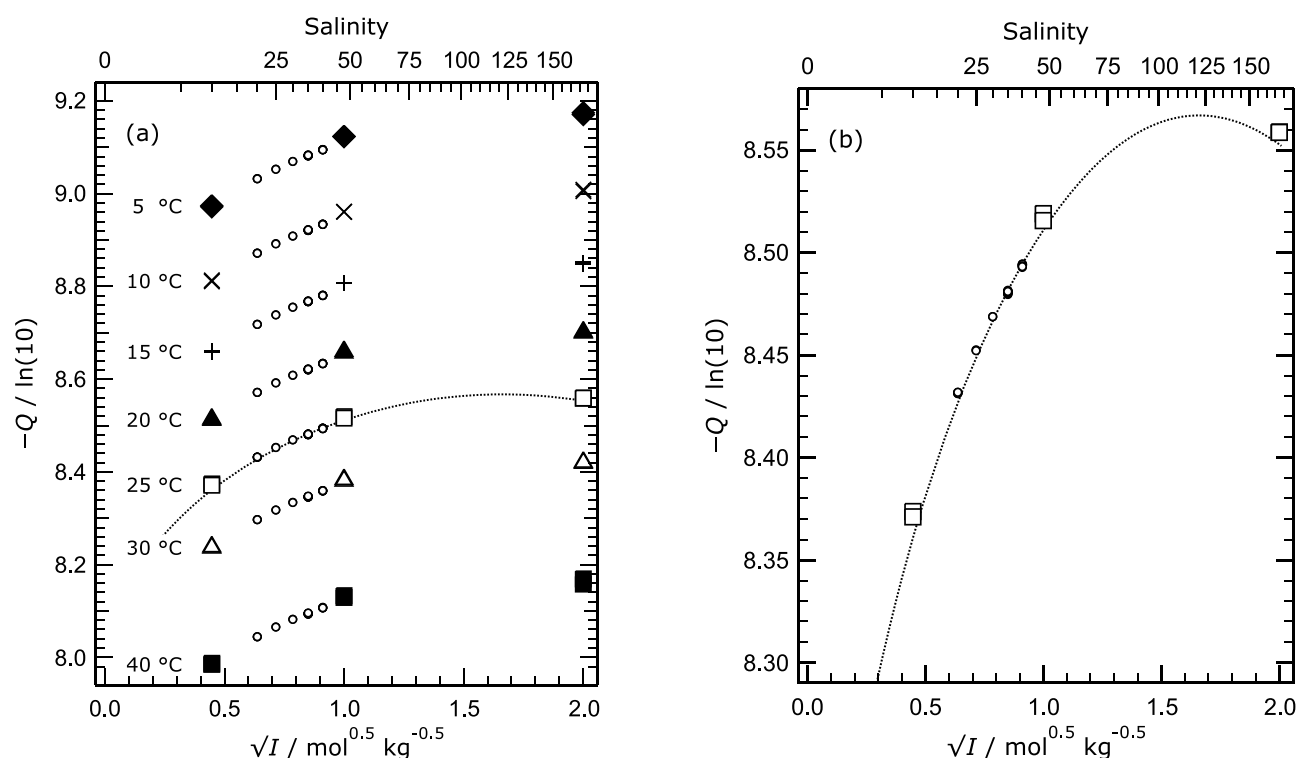


Figure 5. Values of the acidity function quantity $-Q/\ln(10)$ (equivalent to $-\log_{10}(m\text{H}^+ \cdot \gamma_{\text{HCl}}^2)$, see eq 5), calculated from measured potentials and plotted against the square root of ionic strength I (mol kg^{-1}). The upper x -axis is the salinity of an artificial seawater of the same ionic strength. (a) Symbols (data from this study): solid diamond – 5 °C; cross – 10 °C; plus – 15 °C; solid triangle – 20 °C; square – 25 °C; triangle – 30 °C; solid square – 40 °C. Symbols (data from DelValls and Dickson¹ for Tris buffer in artificial seawater): small circles – values at all the indicated temperatures. Dotted line: values calculated using the model of Clegg et al.⁶ for 25 °C as described in the text. (a) For temperatures from 5 to 40 °C, as indicated. (b) Results for 25 °C only.

Table 6. Binary and Ternary Interactions in the Pitzer Model for the Two Solutions Studied

(1) aqueous HCl–NaCl–TrisHCl		(2) Tris buffer in aqueous NaCl	
interactions	data available ^a	interactions ^b	data available ^a
$\text{H}^+ - \text{Cl}^-$	yes	$(\text{H}^+ - \text{Cl}^-)$	yes
$\text{Na}^+ - \text{Cl}^-$	yes	$\text{Na}^+ - \text{Cl}^-$	yes
$\text{TrisH}^+ - \text{Cl}^-$	yes ^c	$\text{TrisH}^+ - \text{Cl}^-$	yes ^c
$\text{H}^+ - \text{Na}^+ - \text{Cl}^-$	yes	$(\text{H}^+ - \text{Na}^+ - \text{Cl}^-)$	yes
$\text{H}^+ - \text{TrisH}^+ - \text{Cl}^-$	yes ^d	$(\text{H}^+ - \text{TrisH}^+ - \text{Cl}^-)$	yes ^d
$\text{Na}^+ - \text{TrisH}^+ - \text{Cl}^-$	^e	$\text{Na}^+ - \text{TrisH}^+ - \text{Cl}^-$	^e
		Tris–NaCl	yes ^f
		Tris–TrisHCl	yes ^f

^aA “yes” in this column means that there are published data from which the Pitzer interaction parameters can be determined and/or values of the parameters available in the literature. ^bThe values in parentheses are needed for a calculation of speciation in the solution, but not for the cell potential (see eq 6). ^cCurrently available for 25 °C only.¹⁹ ^dSee study of Maksimov et al.⁷ ^eCurrently the subject of isopiestic measurements to determine osmotic coefficients (J. Miladinovic, pers. comm.), also studied by Tishchenko²⁰ (see text). ^fStudied by Lodeiro et al.²¹

potential (although they are required to calculate the H^+ molality).

The availability of data that can be used to determine the value of the Pitzer model parameters for the various interactions in the buffer solutions is similar to that for aqueous HCl–NaCl–TrisHCl, as many interactions are common to both (Table 6). The additional ones, involving dissolved Tris, are either currently being measured (J.

Miladinovic, pers. comm.), or have already been studied as a part of our project.²¹

The Harned cell measurements yield products and quotients of activity coefficients and, consequently, only sums and differences of a number of the Pitzer model interaction parameters can be determined from the data. We have listed these in Table 7 for both solutions.

Typically, parameters for cation–anion interactions (e.g., $\text{Na}^+ - \text{Cl}^-$, $\text{TrisH}^+ - \text{Cl}^-$) will be known from other measurements, but this is not always true for other types of interaction. Consequently it is sometimes the case, for example in the analysis of various types of data by Lodeiro et al.²¹ for solutions containing Tris and/or TrisH^+ , that only the total value of a pair or set of three parameters can be determined. This must be taken into account in the development of models of the solutions.

5. CONCLUSIONS

We have measured cell potentials and obtained mean activity coefficients of HCl in aqueous HCl–NaCl–TrisHCl solutions at ionic strengths from 1.0 to 5.5 mol kg^{-1} and from 5 to 40 °C. Our two sets of measurements—for ionic strengths up to 2.0 mol kg^{-1} , and for 3.5 mol kg^{-1} and above—were carried out several years apart, and the lower ionic strength measurements appear to have a small offset in the measured potentials. This deviation is likely related to the condition of the electrodes used for these particular solutions, and calculations presented here suggest that this can be corrected for. On the basis of comparisons made using data for 25 °C, our results are consistent with literature data for aqueous

Table 7. Pitzer Interaction Parameters That Occur as Sums and Differences in the Expressions for the Activity Products in the Equations for Cell Potentials

aqueous HCl–NaCl–TrisHCl		Tris buffer in aqueous NaCl	
interactions	parameters	interactions	parameters
$\text{Na}^+ - \text{Cl}^-$, $\text{Na}^+ - \text{H}^+$	$\beta_{\text{Na,Cl}}^{(0)} + \theta_{\text{Na,H}}^a$	$\text{Na}^+ - \text{Cl}^-$, $\text{Na}^+ - \text{TrisH}^+$, $\text{Tris} - \text{Na}^+$	$\beta_{\text{Na,Cl}}^{(0)} + \theta_{\text{Na,TrisH}} - \lambda_{\text{Tris,Na}}^c$
$\text{Na}^+ - \text{Cl}^-$, $\text{Na}^+ - \text{H}^+ - \text{Cl}^-$	$4C_{\text{Na,Cl}}^{(0)} + \psi_{\text{H,Na,Cl}}^a$	$\text{Na}^+ - \text{Cl}^-$, $\text{Na}^+ - \text{TrisH}^+$, $\text{Tris} - \text{Na}^+ - \text{Cl}^-$	$4C_{\text{Na,Cl}}^{(0)} + \psi_{\text{Na,TrisH,Cl}} - \zeta_{\text{Tris,Na,Cl}}^c$
$\text{TrisH}^+ - \text{Cl}^-$, $\text{TrisH}^+ - \text{H}^+$	$\beta_{\text{TrisH,Cl}}^{(0)} + \theta_{\text{TrisH,H}}^b$	$\text{Na}^+ - \text{TrisH}^+ - \text{Cl}^-$, $\text{Tris} - \text{Na}^+ - \text{Cl}^-$	$\psi_{\text{Na,TrisH,Cl}} + \zeta_{\text{Tris,Na,Cl}}^d$
$\text{TrisH}^+ - \text{Cl}^-$, $\text{TrisH}^+ - \text{H}^+ - \text{Cl}^-$	$4C_{\text{TrisH,Cl}}^{(0)} + \psi_{\text{H,TrisH,Cl}}^b$	$\text{TrisH}^+ - \text{Cl}^-$, $\text{Tris} - \text{TrisH}^+ - \text{Cl}^-$	$4C_{\text{TrisH,Cl}}^{(0)} - \zeta_{\text{Tris,TrisH,Cl}}^e$

^aAlready known, and parameters are available in the literature. ^bCan be determined from the study of Maksimov et al.,⁷ and other data for aqueous TrisHCl solutions. ^cParameters $\theta_{\text{Na,TrisH}}$ and $\psi_{\text{Na,TrisH,Cl}}$ can be determined from osmotic coefficient measurements of NaCl–TrisHCl solutions currently underway (J. Miladinovic, pers. comm.), and $\lambda_{\text{Tris,Na}}$ and $\zeta_{\text{Tris,Na,Cl}}$ from measurements of solubilities in aqueous NaCl–Tris solutions.²¹ ^dThese parameters occur as a sum because $m\text{TrisH}^+$ is equal to $m\text{Tris}$ in the solutions. ^eParameters $\lambda_{\text{Tris,TrisH}}$ and $\zeta_{\text{Tris,TrisH,Cl}}$ can be determined from measurements of solubilities in aqueous TrisHCl–Tris solutions.²¹

HCl–TrisHCl and HCl–NaCl solutions. The mean activity coefficients of HCl show smooth changes with temperature, as expected, and values are greatest at the highest ionic strengths and lowest temperatures.

We also measured cell potentials of a smaller number of aqueous solutions of NaCl containing equal stoichiometric molalities of Tris and TrisHCl, for the same range of temperatures and ionic strengths as those of aqueous HCl–NaCl–TrisHCl. The results, expressed in terms of an acidity function, are quite similar to those obtained for the same Tris buffer in artificial seawater by DelValls and Dickson¹ and also agree satisfactorily with values predicted by the draft Pitzer model of Clegg et al.⁶ We have summarized interactions in the Pitzer model that apply to the solutions studied here, noting whether the corresponding parameters in the model (or data from which they can be determined) are available.

In combination with other literature data, including our previous study,⁷ these new measurements should enable a Pitzer ion-interaction model of the HCl–NaCl–TrisHCl solutions to be developed. This, together with the data for Tris buffer in aqueous NaCl, is an important step toward the development of a speciation model of acid–base equilibrium of Tris buffers in NaCl media and in artificial seawater solutions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.5c00369>.

Description of electrode preparation; determination of standard potentials; densities, water activities, and pHCl of the measurement solutions; tabulation of original measured potentials; tabulation of derived γ_{HCl} and acidity function values including uncertainties (PDF)

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<https://pubs.acs.org/doi/10.1021/acs.jced.5c00369>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The measurements and work of I.M., T.A., and Y.H. were generously supported by the National Metrology Institute of Japan. The contribution of S.L.C. was supported by the Natural Environment Research Council of the UK (award NE/P012361/1). This publication is a contribution of SCOR Working Group 145 (SCOR is the Scientific Committee on Oceanic Research) and of the Joint Committee on the Properties of 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 WG145 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). The authors are grateful to SCOR WG145 members David Turner, Andrew Dickson, and Regina Easley, and also to Jason Waters (National Institute of Standards and Technology, USA) and Jelena Miladinovic (University of Belgrade, Serbia) for helpful discussions and access to measurements in progress.

■ REFERENCES

- (1) 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.
- (2) Millero, F. J.; Feistel, R.; Wright, D. G.; McDougall, T. J. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep Sea Res., Part I* **2008**, *55*, 50–72.
- (3) Johnson, K. S.; Jannasch, H. W.; Coletti, L. J.; Elrod, V. A.; Martz, T. A.; Takeshita, Y.; Carlson, R. J.; Connery, J. G. Deep-sea DuraFET: a pressure tolerant pH sensor designed for global sensor networks. *Anal. Chem.* **2016**, *88*, 3249–3256.

- (4) 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* (11), 2169–2200.
- (5) Dickson, A. G.; Camões, M. F.; Spitzer, P.; Fiescaro, P.; Stoica, D.; Pawlowicz, R.; Feistel, R. Metrological challenges for measurements of key climatological observables. Part 3: Seawater. *Metrologia* **2016**, *53*, R26–R39.
- (6) Clegg, S. L.; Humphreys, M. P.; Waters, J. F.; Turner, D. R.; Dickson, A. G. Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties. II. Tris buffers in artificial seawater at 25 °C, and an assessment of the seawater 'Total' pH scale. *Mar. Chem.* **2022**, *244*, No. 104096.
- (7) Maksimov, I.; Asakai, T.; Hibino, Y.; Clegg, S. L. Activity coefficients of HCl in solutions related to 'Tris' Buffers in artificial seawater. I. HCl + TrisHCl + H₂O from 1.0 to 5.0 mol kg⁻¹ ionic strength, and from 5 to 45 °C. *J. Chem. Eng. Data* **2025**, *70*, 1994–2005.
- (8) 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, 1991; pp 75–153.
- (9) 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. Phys. Chem. A* **1961**, *65*, 667–671.
- (10) Bates, R. G. *Determination of pH, Theory and Practice*; Wiley: New York, 1973.
- (11) Ohata, M. A survey on measurement technique to establish and supply pH primary standard. *AIST Bull. Metrol.* **2005**, *3*, 657–666.
- (12) Dickson, A. G.; Sabine, C. L.; Christian, J. R., Eds. *Guide to Best Practices for Ocean CO₂ Measurements*; North Pacific Marine Science Organisation, 2007.
- (13) Clegg, S. L.; Wexler, A. S. Densities and apparent molar volumes of atmospherically important electrolyte solutions. I. 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.
- (14) Kell, G. S. Density, thermal expansibility and compressibility of liquid water from 0° to 150 °C: corrections and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
- (15) Forbes, G. S. The solubility of silver chloride in chloride solutions and the existence of complex argentichloride ions. *J. Am. Chem. Soc.* **1911**, *33*, 1937–1946.
- (16) Hills, G. J.; Ives, D. J. G. The hydrogen electrode. *Nature* **1949**, *163* (4156), 997.
- (17) Bates, R. G.; Robinson, R. A. Standardization of silver-silver chloride electrodes from 0 to 60 °C. *J. Solution Chem.* **1980**, *9*, 455–456.
- (18) Bates, R. G.; Bower, V. E. Standard potential of the silver-silver chloride electrode from 0 to 95 °C and the thermodynamic properties of dilute hydrochloric acid solutions. *J. Res. Natl. Bur. Stand.* **1954**, *53*, 283–290.
- (19) Bates, R. G.; Macaskill, J. B. Activity and osmotic coefficients of t-butylammonium chloride: activity of HCl in mixtures with TRIS hydrochloride and t-butylammonium chloride at 25 °C. *J. Solution Chem.* **1985**, *14*, 723–734.
- (20) Tishchenko, P. Y. Non-ideal properties of the TRIS-TRIS.HCl-NaCl-H₂O buffer system in the 0–40 °C temperature interval. Application of the Pitzer equations. *Russ. Chem. Bull.* **2000**, *49* (4), 674–679.
- (21) Lodeiro, P.; Turner, D. R.; Achterberg, E. P.; Gregson, F. K. A.; Reid, J. P.; Clegg, S. L. Solid–liquid equilibria in aqueous solutions of Tris, Tris-NaCl, Tris-TrisHCl, and Tris-(TrisH)₂SO₄ at temperatures from 5 to 45 °C. *J. Chem. Eng. Data* **2021**, *66*, 437–455.
- (22) Macaskill, J. B.; Robinson, R. A.; Bates, R. G. Activity coefficient of hydrochloric acid in aqueous solutions of sodium chloride. *J. Solution Chem.* **1977**, *6*, 385–392.
- (23) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*; Reinhold: New York, 1958.
- (24) Harned, H. S. The thermodynamic properties of the system: hydrochloric acid, sodium chloride and water from 0 to 50°. *J. Phys. Chem. A* **1959**, *63*, 1299–1302.
- (25) Hawkins, J. E. The activity coefficients of hydrochloric acid in uni-univalent chloride solutions at constant total molality. *J. Am. Chem. Soc.* **1932**, *54*, 4480–4487.
- (26) Jiang, C. Activity coefficients of hydrochloric acid in concentrated electrolyte solutions. 1. HCl + NaCl + H₂O, HCl + LiCl + H₂O, and HCl + BaCl₂ + H₂O at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 113–116.
- (27) Macaskill, J. B.; Bates, R. G. Activity coefficients in aqueous mixtures of hydrochloric acid with "Tris" hydrochloride or t-butylammonium chloride at 25 °C. *J. Chem. Eng. Data* **1975**, *20*, 397–398.
- (28) Joint Committee for Guides in Metrology. Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement; BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML; 120 p. DOI: 10.59161/JCGM100-2008E.



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