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Buffer Standards for the Physiological pH of *N*-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]glycine (TRICINE) from $T = (278.15$ to $328.15)$ K

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Abstract

The pH values of two buffer solutions without NaCl and seven buffer solutions with added NaCl, having ionic strengths ($I = 0.16 \text{ mol}\cdot\text{kg}^{-1}$) similar to those of physiological fluids, have been evaluated at 12 temperatures from $T = (278.15$ to $328.15)$ K by way of the extended form of the Debye-Hückel equation of the Bates-Guggenheim convention. The residual liquid junction potentials (δE_j) between the buffer solutions of TRICINE and saturated KCl solution of the calomel electrode at $T = (298.15$ and $310.15)$ K have been estimated by measurement with a flowing junction cell. For the buffer solutions with the molality of TRICINE (m_1) = $0.06 \text{ mol}\cdot\text{kg}^{-1}$, NaTRICINE (m_2) = $0.02 \text{ mol}\cdot\text{kg}^{-1}$, and NaCl (m_3) = $0.14 \text{ mol}\cdot\text{kg}^{-1}$, the pH values at 310.15 K obtained from the extended Debye-Hückel equation and the inclusion of the liquid junction correction are 7.342 and 7.342, respectively. These are in excellent agreement. The zwitterionic buffer TRICINE is recommended as a secondary pH standard in the region for clinical application.

Keywords

Buffers; TRICINE; Ionic Strength; Emf; Zwitterions

1. Introduction

Roy *et al.* [1] has reported the pK_2 values of *N*-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]glycine (TRICINE) at temperatures from $T = (278.15$ to $328.15)$ K, including 310.15 K. Various buffer substances recommended by Good *et al.* [2, 3] have proven very useful for the measurement of the pH of blood and the control of pH in the region close to that of physiological solutions. The structure of TRICINE is as follows:

For a routine calibration of the pH meter assembly, zwitterionic physiological pH standards are in need within the framework set-up by the NBS/NIST [4]. The phosphate buffer has been widely used as a physiological pH standard, but it is not an ideal primary pH standard buffer because of various limitations [4].

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Roy *et al.* [5] has published the pK_2 and pH values of the biological buffer [bis[(2-hydroxyethyl)amino]acetic acid (BICINE). This buffer has been recommended as a pH standard for use with in physiological applications. Feng and coworkers [6] have published the values of pK_2 and pH of the zwitterionic buffer *N*-(2-hydroxyethyl)piperazine-*N*-2-ethanesulfonic acid (HEPES). The HEPES buffer has been certified by the National Institute of Standards and Technology (NIST) as a primary reference standard. Bates *et al.* [7] recommended the buffer solution 0.06 *m* TRICINE + 0.02 *m* NaTRICINEate for use as a pH standard at $T = (298.15 \text{ and } 310.15) \text{ K}$.

In order to provide very accurate values of pH, we have undertaken a comprehensive study for the following compositions: (a) TRICINE (0.08 mol·kg⁻¹) + NaTRICINE (0.02 mol·kg⁻¹), $I = 0.02 \text{ mol·kg}^{-1}$, (b) TRICINE (0.09 mol·kg⁻¹) + NaTRICINE (0.03 mol·kg⁻¹), $I = 0.03 \text{ mol·kg}^{-1}$, (c) TRICINE (0.03 mol·kg⁻¹) + NaTRICINE (0.01 mol·kg⁻¹) + NaCl (0.15 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (d) TRICINE (0.03 mol·kg⁻¹) + NaTRICINE (0.03 mol·kg⁻¹) + NaCl (0.13 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (e) TRICINE (0.08 mol·kg⁻¹) + NaTRICINE (0.08 mol·kg⁻¹) + NaCl (0.08 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (f) TRICINE (0.05 mol·kg⁻¹) + NaTRICINE (0.05 mol·kg⁻¹) + NaCl (0.11 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (g) TRICINE (0.09 mol·kg⁻¹) + NaTRICINE (0.03 mol·kg⁻¹) + NaCl (0.13 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (h) TRICINE (0.06 mol·kg⁻¹) + NaTRICINE (0.02 mol·kg⁻¹) + NaCl (0.14 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$, (i) TRICINE (0.08 mol·kg⁻¹) + NaTRICINE (0.02 mol·kg⁻¹) + NaCl (0.14 mol·kg⁻¹), $I = 0.16 \text{ mol·kg}^{-1}$

2. Experimental

TRICINE was purchased from Sigma Chemical Co. (St. Louis, Missouri). It was subjected to recrystallization from 75% ethanol-water and assayed by titration with a carbonate-free standard solution of NaOH. The analyses of the unpurified and purified TRICINE averaged 99.72% and 99.98% pure, respectively. The substance TRICINE, NaCl (ACS reagent grade dried at $T = 383.15 \text{ K}$), CO₂-free doubly distilled water, and a standard solution of NaOH were used to prepare NaTRICINEate. Air buoyancy corrections were made for all masses using a vacuum correction factor of 1.00106 for dilute buffer solutions.

The preparation of the hydrogen electrodes, thermal electrolytic type silver-silver chloride electrodes, the design of the all-glass cells, control of the temperature, use of digital voltmeter, and other experimental set-ups have been reported previously [8, 9].

The cells investigated were the following:

where the double line in cells (B) and (C) indicates the liquid junction.

The residual liquid junction potential is given by $\delta E_j = E_{j(s)} - E_{j(x)}$, where $E_{j(s)}$ and $E_{j(x)}$ indicate the liquid junction potentials for the standard physiological phosphate solutions and the experimental buffer solutions of TRICINE, respectively. From cell (B), these values were obtained using the following equation [4, 6, 8]:

$$E_{j(s)} = E_{(s)} + E_{SCE}^{\circ} - k \text{pH}(s) \quad (1)$$

In equation (1) $E_{SCE}^{\circ} = -0.2415$ V (standard potential of the saturated calomel electrode), $k = 0.059156$ V, for the physiological phosphate buffer solution, $\text{pH}(s) = 7.415$ [4, 6, 8] at $T = 298.15$ K; $\text{pH}(s) = 7.395$ [4, 6, 8] at $T = 310.15$ K, $k = 0.061538$ V and $E_{SCE}^{\circ} = -0.2335$ V at 310.15 K. We have attempted to estimate values of the liquid junction potential for four out of nine buffer solutions. The difference in δE_j between the phosphate standard and each experimental buffer solution is an important factor when different standards are selected to obtain the operational pH for an unknown medium. This error can be estimated by the operational definition of pH using equation (2).

$$\text{pH}(x) = \text{pH}(s) + \frac{E_x - E_s + \delta E_j}{k} \quad (2)$$

where the subscript “x” refers to the unknown buffer TRICINE + NaTRICINE. If $\delta E_j = 0$, then equation (2) takes the form:

$$\text{pH}(x) = \text{pH}(s) + \frac{E_x - E_s}{k} \quad (3)$$

3. Methods and Results

The pressure corrected cell potential data for cell (A) containing two buffer solutions with varying chloride ion concentration in the ionic strength range $I = 0.025$ to $0.05 \text{ mol}\cdot\text{kg}^{-1}$, and seven buffer solutions with NaCl at $I = 0.16 \text{ mol}\cdot\text{kg}^{-1}$ are listed in table 1. The uncertainty of duplicate cells, on average, lies within (0.02 ± 0.01) mV in the temperature range $T = (278.15 \text{ to } 328.15)$ K.

Conventional $\text{p}a_{\text{H}}$ values have been evaluated by the method of Bates *et al.* [7, 10–11] and other investigators [12–13] for two buffer solutions without NaCl and seven buffer solutions in the presence of NaCl.

The calculation of $\text{p}a_{\text{H}}$ values for two buffer solutions without NaCl and seven buffer solutions in the presence of Cl^- were made in the temperature range $T = (278.15 \text{ to } 328.15)$ K using the cell potential (E) listed in Table 1, as well as the molality of the chloride ion. The acidity function [7, 9] is given by:

$$\text{p}(a_{\text{H}}\gamma_{\text{Cl}}) = \frac{E - E^{\circ}}{k} + \log_{10} m_{\text{Cl}} \quad (4)$$

where k is the Nernst slope, and E° is the standard potential of the silver-silver chloride electrode listed in table 1.

Values of the acidity function $\text{p}(a_{\text{H}}\gamma_{\text{Cl}})$ for Cl^- free buffer solutions were derived at each temperature and were plotted as a function of m_{Cl^-} . Straight lines with small slopes were obtained. The values of the intercepts, $\text{p}(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$ are entered in Table 2 for two buffer solutions without the presence of NaCl. The acidity function, $\text{p}(a_{\text{H}}\gamma_{\text{Cl}})$, for seven buffer solutions are listed in Tables 2 and 3 from $T = (278.15 \text{ to } 328.15)$ K, including 310.15 K. The uncertainty introduced in this type of graphical extrapolation is usually less than 0.002. The equation for the calculation of $\text{p}a_{\text{H}}$ is given below:

$$p a_{\text{H}} = p(a_{\text{H}} \gamma_{\text{Cl}})^{\circ} + \log_{10} \gamma_{\text{Cl}}^{\circ} \quad (5)$$

where the single-ion activity coefficient, $\gamma_{\text{Cl}}^{\circ}$, cannot be measured experimentally. Thus, a non-thermodynamic convention [7, 8] is normally adopted for the estimation of the ion activity coefficient of a single species, chloride. The pH values obtained from the liquid junction cell are indicated by the “operational” pH, whereas the “conventional” pH calculated from equation (5) is designated as $p a_{\text{H}}$.

The convention is not subject to any proof but is reasonable for the purpose of assigning standard pH values. The equation (6) of a ‘pH convention’ [7, 11], based on an extended form of the Debye-Hückel equation, has been widely used. In the assignment of $p a_{\text{H}}$ values and the establishment of NIST pH standard [4, 8], the calculation of $\log_{10} \gamma_{\text{Cl}}^{\circ}$ for two buffer solutions without chloride ion was made using equation (6):

$$\log_{10} \gamma_{\text{Cl}}^{\circ} = - \frac{A \sqrt{I}}{1 + B a^{\circ} \sqrt{I}} + C I \quad (6)$$

where I is the ionic strength of the buffer solution, A and B are the Debye-Hückel constants [4, 5, 9] and are temperature dependent, a constant value of $B a^{\circ} = 1.38 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ used for experimental temperatures, and C is an adjustable parameter which can be calculated by the following equation [5]:

$$C = C_{298.15} + \alpha \{(T/T^{\circ}) - 298.15\} + \beta \{(T/T^{\circ}) - 298.15\}^2 \quad (7)$$

where $C_{298.15} = 0.032 \text{ kg} \cdot \text{mol}^{-1}$, $\alpha = 6.2 \cdot 10^{-4} \text{ kg} \cdot \text{mol}^{-1}$, $\beta = -8.7 \cdot 10^{-6} \text{ kg} \cdot \text{mol}^{-1}$, $T^{\circ} = 1 \text{ K}$, and T is the thermodynamic temperature.

For the calculation of $p a_{\text{H}}$ using equation (4) for seven buffer solutions with chloride ion, the equation (6) is also used where $\log_{10} \gamma_{\text{Cl}}^{\circ}$ is replaced by $\log_{10} \gamma_{\text{Cl}}$. This procedure does not involve any extrapolation.

The $p a_{\text{H}}$ values of two buffer solutions of TRICINE without NaCl and seven buffer solutions with NaCl are calculated using equations (4) to (7) and are fitted as a function of the thermodynamic temperature:

$$\begin{aligned} &\text{For TRICINE (0.08 mol} \cdot \text{kg}^{-1}) + \text{NaTRICINE (0.02 mol} \cdot \text{kg}^{-1}): \\ p a_{\text{H}} &= 7.484 - 1.860 \cdot 10^{-2} \{(T/T^{\circ}) - 298.15\} + 5.95 \cdot 10^{-5} \{(T/T^{\circ}) - 298.15\}^2 \end{aligned} \quad (8)$$

$$\begin{aligned} &\text{For TRICINE (0.09 mol} \cdot \text{kg}^{-1}) + \text{NaTRICINE (0.03 mol} \cdot \text{kg}^{-1}): \\ p a_{\text{H}} &= 7.545 - 1.869 \cdot 10^{-2} \{(T/T^{\circ}) - 298.15\} + 8.68 \cdot 10^{-5} \{(T/T^{\circ}) - 298.15\}^2 \end{aligned} \quad (9)$$

where $278.15 \text{ K} \leq T \leq 328.15 \text{ K}$. The values of the acidity function $p(a_{\text{H}} \gamma_{\text{Cl}})$ for all buffer solutions were obtained from equation (4) whereas for the chloride free solution, the values of $p(a_{\text{H}} \gamma_{\text{Cl}})^{\circ}$ were calculated from the plot of $p(a_{\text{H}} \gamma_{\text{Cl}})$ against the molality of the chloride ion (a linear function). The intercept is $p(a_{\text{H}} \gamma_{\text{Cl}})^{\circ}$ at $m_{\text{Cl}} = 0$. The values of $p a_{\text{H}}$ listed in table 4 were obtained from equations (5)–(6). The standard deviations of regression are 0.0012, and 0.0018, respectively, for these two buffer solutions.

For the seven buffer solutions with an ionic strength $I = 0.16 \text{ mol} \cdot \text{kg}^{-1}$, the values of $p a_{\text{H}}$ listed in tables 4 and 5 are given by the equations:

For TRICINE (0.03 mol · kg⁻¹)+NaTRICINE (0.01 mol · kg⁻¹)+NaCl (0.15 mol · kg⁻¹):

$$p_{a_H} = 7.552 - 1.865 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.40 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (10)$$

For TRICINE (0.03 mol · kg⁻¹)+NaTRICINE (0.03 mol · kg⁻¹)+NaCl (0.13 mol · kg⁻¹):

$$p_{a_H} = 7.999 - 1.888 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.07 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (11)$$

For TRICINE (0.08 mol · kg⁻¹)+NaTRICINE (0.08 mol · kg⁻¹)+NaCl (0.08 mol · kg⁻¹):

$$p_{a_H} = 8.031 - 1.883 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.86 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (12)$$

For TRICINE (0.05 mol · kg⁻¹)+NaTRICINE (0.05 mol · kg⁻¹)+NaCl (0.11 mol · kg⁻¹):

$$p_{a_H} = 8.030 - 1.887 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.06 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (13)$$

For TRICINE (0.09 mol · kg⁻¹)+NaTRICINE (0.03 mol · kg⁻¹)+NaCl (0.13 mol · kg⁻¹):

$$p_{a_H} = 7.558 - 1.887 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.04 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (14)$$

For TRICINE (0.06 mol · kg⁻¹)+NaTRICINE (0.02 mol · kg⁻¹)+NaCl (0.14 mol · kg⁻¹):

$$p_{a_H} = 7.558 - 1.887 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.04 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (15)$$

For TRICINE (0.08 mol · kg⁻¹)+NaTRICINE (0.02 mol · kg⁻¹)+NaCl (0.14 mol · kg⁻¹):

$$p_{a_H} = 7.436 - 1.884 \cdot 10^{-2} \{(T/T^\circ) - 298.15\} + 7.21 \cdot 10^{-5} \{(T/T^\circ) - 298.15\}^2 \quad (16)$$

where T is the temperature in K. The standard deviations for regression from equations (10) to (16) are 0.0012, 0.0013, 0.0011, 0.0014, 0.0012, 0.0012 and 0.0010, respectively.

The potential difference of the cells (B) and (C) for four buffer solutions at $T = (298.15 \text{ K and } 310.15 \text{ K})$ are given in table 6. The values of the residual liquid junction potential, δE_j , listed also in table 6 were estimated by using equation (1). From the pH data at $T = (298.15 \text{ K and } 310.15 \text{ K})$ from table 6, there is excellent agreement between the calculated value obtained from the extended Debye-Hückel equation and the value obtained from the δE_j correction. The experimental method for determining the single-ion activity coefficient, $\log_{10} \gamma_{Cl}^\circ$ is not possible. Partanen and Minkinen [14] and Covington and Ferra [15] both used the Pitzer theory to estimate the single ion activity coefficient at ionic strengths higher than 0.1 mol·kg⁻¹ in the calculation of the pH standards of the phosphate buffer solutions. Camoes et al. [12] and Buck *et al.* [13] recommended the use of Pitzer formalism [16] for the estimation of γ_{Cl}^- because of the consistency of the improvements of the pH measurements. Work is under progress in this laboratory for the calculation of the single ion activity coefficient γ_{Cl} using Pitzer theory [17] for $I = 0.16 \text{ mol} \cdot \text{kg}^{-1}$. The results of pH for various buffers by applying this value of γ_{Cl} will be reported in a separate publication. The total uncertainties were estimated by combining the various sources of error: (i) assumption for the calculation of the $\log_{10} \gamma_{Cl}^\circ$; (ii) extrapolation to $p(a_H \gamma_{Cl})^\circ$ at $m_{Cl^-} = 0$ (within ± 0.001 pH unit); (iii) liquid junction potential measurement; and (iv) error in the experimental emf measurement ($\pm 0.02 \text{ mV}$). The overall uncertainty is about ± 0.009 pH unit. The operational pH values at $T = (298.15 \text{ K and } 310.15 \text{ K})$ (table 6) for four buffer solutions are recommended as pH standards for the measurement of the pH of physiological solutions.

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Highlights

- This work reports pH values of TRICINE buffer
- Liquid junction potential correct is applied
- These values will be used by clinical and biomedical scientists
- The pH values lie within 6.8 to 7.5

FIGURE 1.
N-[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]glycine (TRICINE)

TABLE 1

Electromotive force E (V) of Cell A: Pt(s); $H_2(g, p^\circ = 101.325 \text{ kPa})$ | TRICINE (m_1), NaTRICINE (m_2), NaCl (m_3) | AgCl(s), Ag(s)

$m/\text{mol}\cdot\text{kg}^{-1}$		T/K														
m_1	m_2	m_3	278.15	283.15	288.15	293.15	298.15	303.15	308.15	310.15	313.15	318.15	323.15	328.15	338.15	348.15
0.08	0.02	0.005	0.79915	0.80080	0.80236	0.80352	0.80464	0.80567	0.80636	0.80677	0.80729	0.80786	0.80842	0.80898	0.80954	0.81010
0.08	0.02	0.010	0.78265	0.78394	0.78511	0.78594	0.78670	0.78751	0.78792	0.78825	0.78855	0.78888	0.78914	0.78947	0.78979	0.79011
0.08	0.02	0.015	0.77286	0.77388	0.77479	0.77546	0.77608	0.77676	0.77694	0.77724	0.77741	0.77762	0.77776	0.77784	0.77791	0.77797
0.08	0.02	0.020	0.76593	0.76683	0.76747	0.76797	0.76840	0.76902	0.76910	0.76943	0.76949	0.76965	0.76958	0.76975	0.76981	0.76987
0.09	0.03	0.005	0.80442	0.80572	0.80716	0.80841	0.80954	0.81062	0.81163	0.81216	0.81275	0.81359	0.81431	0.81530	0.81630	0.81730
0.09	0.03	0.010	0.78838	0.78948	0.79058	0.79157	0.79243	0.79321	0.79391	0.79428	0.79466	0.79526	0.79557	0.79610	0.79663	0.79716
0.09	0.03	0.015	0.77900	0.78000	0.78085	0.78176	0.78246	0.78307	0.78358	0.78383	0.78408	0.78444	0.78459	0.78474	0.78489	0.78504
0.09	0.03	0.020	0.77260	0.77350	0.77436	0.77518	0.77569	0.77619	0.77653	0.77670	0.77684	0.77708	0.77707	0.77696	0.77685	0.77674
0.03	0.01	0.15	0.72560	0.72569	0.72583	0.72557	0.72556	0.72506	0.72460	0.72451	0.72423	0.72364	0.72308	0.72243	0.72178	0.72113
0.03	0.03	0.13	0.75394	0.75449	0.75490	0.75528	0.75551	0.75556	0.75574	0.75571	0.75563	0.75545	0.75520	0.75487	0.75454	0.75421
0.08	0.08	0.08	0.76742	0.76818	0.76889	0.76930	0.76990	0.77017	0.77061	0.77075	0.77082	0.77103	0.77115	0.77121	0.77127	0.77133
0.05	0.05	0.11	0.75961	0.76027	0.76083	0.76130	0.76162	0.76181	0.76205	0.76207	0.76201	0.76195	0.76183	0.76164	0.76145	0.76126
0.09	0.03	0.13	0.72956	0.72968	0.72972	0.72968	0.72966	0.81054	0.81141	0.72847	0.72816	0.72762	0.72697	0.72624	0.72551	0.72478
0.06	0.02	0.14	0.72763	0.72776	0.72776	0.72766	0.72750	0.79260	0.79320	0.72652	0.72622	0.72569	0.72518	0.72446	0.72373	0.72300
0.08	0.02	0.14	0.72096	0.72091	0.72077	0.72059	0.72029	0.76793	0.76826	0.71927	0.71897	0.71836	0.71764	0.71673	0.71582	0.71491
$E^\circ_{\text{Ag-AgCl}} \text{ (V)} =$			0.23416	0.23147	0.22863	0.22562	0.22244	0.21913	0.21572	0.21429	0.21214	0.20840	0.20455	0.20064	0.19673	0.19282

$p(a_H\gamma_{Cl})$ of (TRICINE + NaTRICINE) buffer solutions from (278.15 to 328.15) K, computed using equation (4), and values of $p(a_H\gamma_{Cl})^\circ$ estimated from the plot of $p(a_H\gamma_{Cl})$ at $m_{Cl} = 0$ for two Cl^- free buffer solutions

TABLE 2

T/K	$m/\text{mol}\cdot\text{kg}^{-1}$				$I = 0.02\ m$	$I = 0.03\ m$	$0.03\ m\ \text{TRICINE} + 0.01\ m\ \text{NaTRICINE} + 0.15\ m\ \text{NaCl}$	$0.03\ m\ \text{TRICINE} + 0.03\ m\ \text{NaTRICINE} + 0.13\ m\ \text{NaCl}$	$0.08\ m\ \text{TRICINE} + 0.08\ m\ \text{NaTRICINE} + 0.08\ m\ \text{NaCl}$
	$0.08\ m\ \text{TRICINE} + 0.02\ m\ \text{NaTRICINE} + 0.00\ m\ \text{NaCl}$	$0.09\ m\ \text{TRICINE} + 0.03\ m\ \text{NaTRICINE} + 0.00\ m\ \text{NaCl}$	$0.03\ m\ \text{TRICINE} + 0.01\ m\ \text{NaTRICINE} + 0.15\ m\ \text{NaCl}$	$0.03\ m\ \text{TRICINE} + 0.03\ m\ \text{NaTRICINE} + 0.13\ m\ \text{NaCl}$					
278.15	7.937	8.024	8.081	8.532	8.564				
283.15	7.834	7.912	7.973	8.424	8.456				
288.15	7.738	7.809	7.873	8.319	8.353				
293.15	7.638	7.709	7.771	8.220	8.250				
298.15	7.545	7.615	7.681	8.125	8.156				
303.15	7.453	7.524	7.587	8.032	8.064				
308.15	7.363	7.437	7.499	7.946	7.978				
310.15	7.329	7.407	7.467	7.912	7.946				
313.15	7.280	7.359	7.418	7.861	7.895				
318.15	7.197	7.280	7.338	7.780	7.816				
323.15	7.119	7.203	7.263	7.702	7.740				
328.15	7.043	7.136	7.190	7.626	7.666				

TABLE 3
 $p(a_H\gamma_{Cl})$ of (TRICINE + NaTRICINE) buffer solutions from (278.15 to 328.15) K, computed using equation (4)

$m/\text{mol}\cdot\text{kg}^{-1}$		$0.09\ m\ \text{TRICINE}$ $+ 0.03\ m\ \text{NaTRICINE}$ $+ 0.13\ m\ \text{NaCl}$		$0.06\ m\ \text{TRICINE}$ $+ 0.02\ m\ \text{NaTRICINE}$ $+ 0.14\ m\ \text{NaCl}$		$0.08\ m\ \text{TRICINE}$ $+ 0.02\ m\ \text{NaTRICINE}$ $+ 0.14\ m\ \text{NaCl}$		$0.05\ m\ \text{TRICINE}$ $+ 0.05\ m\ \text{NaTRICINE}$ $+ 0.11\ m\ \text{NaCl}$	
T/K	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$
278.15	8.090	8.088	7.967	8.562					
283.15	7.982	7.980	7.858	8.454					
288.15	7.878	7.876	7.754	8.350					
293.15	7.780	7.777	7.656	8.251					
298.15	7.688	7.684	7.562	8.156					
303.15	7.351	7.534	7.425	8.064					
308.15	7.442	7.445	7.338	7.977					
310.15	7.469	7.470	7.352	7.943					
313.15	7.419	7.420	7.303	7.891					
318.15	7.339	7.341	7.225	7.810					
323.15	7.262	7.266	7.148	7.733					
328.15	7.186	7.191	7.073	7.658					

TABLE 4
p_H of (TRICINE + NaTRICINE) buffer solutions from (278.15 to 328.15) K, computed using equations (4)–(6)

<i>m</i> /mol·kg ⁻¹					
0.08 <i>m</i> TRICINE + 0.02 <i>m</i> NaTRICINE + 0.00 <i>m</i> NaCl		0.09 <i>m</i> TRICINE + 0.03 <i>m</i> NaTRICINE + 0.00 <i>m</i> NaCl	0.03 <i>m</i> TRICINE + 0.01 <i>m</i> NaTRICINE + 0.15 <i>m</i> NaCl	0.03 <i>m</i> TRICINE + 0.03 <i>m</i> NaTRICINE + 0.13 <i>m</i> NaCl	0.08 <i>m</i> TRICINE + 0.08 <i>m</i> NaTRICINE + 0.08 <i>m</i> NaCl
<i>T</i> /K	<i>I</i> = 0.02 <i>m</i>	<i>I</i> = 0.03 <i>m</i>	<i>I</i> = 0.16 <i>m</i>	<i>I</i> = 0.16 <i>m</i>	<i>I</i> = 0.16 <i>m</i>
278.15	7.879	7.956	7.955	8.407	8.440
283.15	7.776	7.843	7.848	8.298	8.331
288.15	7.678	7.740	7.747	8.193	8.227
293.15	7.580	7.640	7.646	8.095	8.125
298.15	7.485	7.544	7.554	7.999	8.031
303.15	7.393	7.453	7.460	7.905	7.937
308.15	7.302	7.366	7.371	7.819	7.851
310.15	7.268	7.335	7.339	7.784	7.818
313.15	7.219	7.287	7.289	7.773	7.766
318.15	7.135	7.207	7.209	7.651	7.687
323.15	7.057	7.130	7.133	7.572	7.610
328.15	6.980	7.062	7.059	7.495	7.535

TABLE 5

pH of (TRICINE + NaTRICINE) buffer solutions from (278.15 to 328.15) K, computed using equations (4)–(6)

T/K	$m/\text{mol}\cdot\text{kg}^{-1}$				
	0.09 <i>m</i> TRICINE + 0.03 <i>m</i> NaTRICINE + 0.13 <i>m</i> NaCl <i>I</i> = 0.16 <i>m</i>	0.06 <i>m</i> TRICINE + 0.02 <i>m</i> NaTRICINE + 0.14 <i>m</i> NaCl <i>I</i> = 0.16 <i>m</i>	0.08 <i>m</i> TRICINE + 0.02 <i>m</i> NaTRICINE + 0.14 <i>m</i> NaCl <i>I</i> = 0.16 <i>m</i>	0.05 <i>m</i> TRICINE + 0.05 <i>m</i> NaTRICINE + 0.11 <i>m</i> NaCl <i>I</i> = 0.16 <i>m</i>	
278.15	7.965	7.962	7.841	8.437	
283.15	7.856	7.854	7.732	8.328	
288.15	7.753	7.751	7.628	8.224	
293.15	7.655	7.652	7.531	8.126	
298.15	7.562	7.557	7.435	8.029	
303.15	7.465	7.463	7.346	7.937	
308.15	7.375	7.374	7.258	7.849	
310.15	7.341	7.342	7.224	7.815	
313.15	7.391	7.291	7.175	7.763	
318.15	7.210	7.211	7.095	7.681	
323.15	7.131	7.136	7.018	7.603	
328.15	7.055	7.060	6.941	7.526	

TABLE 6
Emf of Cell B and pH values with δE_j correction at (298.15 and 310.15) K for TRICINE buffer

m_1	m_2	m_3	I	E_s/V		$\delta E_j/mV$		Without ^c δE_j corr		With ^d δE_j corr		Extended ^e D-H eqn.		Without ^c δE_j corr		With ^d δE_j corr		Extended ^e D-H eqn.	
				298.15 K	310.15 K	298.15 K	310.15 K	298.15 K		310.15 K		298.15 K		310.15 K		298.15 K		310.15 K	
0.09	0.03	0.00	0.03	0.69003	0.68740	0.3	0.4	7.538	7.538	7.543	7.544	7.329	7.334	7.329	7.334	7.329	7.334	7.335	7.335
0.08	0.02	0.14	0.16	0.68180	0.67861	2.1	2.3	7.399	7.399	7.434	7.435	7.188	7.223	7.188	7.223	7.188	7.223	7.224	7.224
0.09	0.03	0.13	0.16	0.68926	0.68591	2.1	2.2	7.526	7.526	7.561	7.562	7.305	7.340	7.305	7.340	7.305	7.340	7.341	7.341
0.06	0.02	0.14	0.16	0.68902	0.68599	2.1	2.2	7.522	7.522	7.556	7.557	7.307	7.342	7.307	7.342	7.307	7.342	7.342	7.342
Emf of Cell C ^a				E_s/V		fE_j/mV													
0.008695 <i>m</i> KH ₂ PO ₄ + 0.03043 <i>m</i> Na ₂ HPO ₄				0.68275	0.69147	2.6	2.9												

^aPublished data [4, 6, 8] for physiological phosphate buffer solutions; units of *m*, mol·kg⁻¹

^bThe residual liquid junction potential, $\delta E_j = E_j(s) - E_j(x)$, which can be calculated from equation (1) and the values of tables 4 – 6. The pH of the primary standard phosphate buffer is 7.415 and 7.395 at *T* = (298.15 and 310.15) K, respectively.

^cValues obtained from equation (3) and E_x and E_s data from this table

^dObtained from equation (2) using values of E_x , E_s , and δE_j from this table, and $k = 0.059156$ V at 298.15 K and 310.15 K, respectively

^eObtained from extended Debye-Hückel (DH) equation of the Bates-Guggenheim convention, data listed in tables 4–5

^f E_j is the liquid junction potential in mV.