Standards for pH Measurements of Bis-[(2-Hydroxyethyl)amino]acetic Acid (BICINE) from (278.15 to 328.15) K

Rabindra N. Roy*, Lakshmi N. Roy, Blake M. Bodendorfer, Zachary M. Downs, Alexis L. Jenkins and Isaac B. Henson

Hoffman Department of Chemistry, Drury University, 900 N. Benton Ave., Springfield, Missouri 65802, USA

Abstract: The second dissociation constant, pK_2, and related thermodynamic data for BICINE have been previously determined and reported from temperatures (278.15 to 328.15) K. For the present study, three buffer solutions without NaCl, and five with NaCl yielding an ionic strength (I = 0.16 mol·kg^{-1}) similar to that of blood plasma were prepared. These buffer solutions have been evaluated in the temperature range of (278.15 to 328.15) K using the extended form of the Debye-Hückel equation. The Bates-Guggenheim convention is only valid when $I \leq$ 0.1 mol·kg^{-1}. Values of the residual liquid junction potential (δE_j) between the BICINE solutions and the saturated KCl calomel electrode have been estimated at (298.15 and 310.15) K. Two BICINE buffer solutions are recommended as primary standard reference solutions for pH measurements of biological fluids.

Keywords: Buffer, Zwitterionic, BICINE, pH, Emf.

1. INTRODUCTION

Good *et al*. [1, 2] have recommended a set of zwitterionic amino acid buffers for the investigation of physiological solutions across a broad pH range.The second dissociation constant (pK_2) of the zwitterionic buffer BICINE has recently been published [3]. Standard pH values of six buffer solutions of BICINE and NaBICINE without NaCl in the ionic strength range I = 0.02 to 0.08 mol·kg^{-1} and four buffer solutions in isotonic saline media of I = 0.16 mol·kg^{-1} with NaCl from (278.15 to 328.15) K have been reported earlier from this laboratory [3]. The pH values at these temperatures particularly at (298.15 and 310.15) K in a wide variety of buffer solutions differing in buffer ratios and specific concentrations of BICINE and NaBICINE are highly significant for biomedical research and other clinical media. In previously published research, the buffer ratios of BICINE and NaBICINE without the presence of Cl^- are 1:1; whereas, for buffer solutions containing Cl^- with I = 0.16 mol·kg^{-1} they primarily are 1:1, 2:1, and 4:1. But there is a gap of pH data for some important concentrations and buffer ratios. The purpose, meaning and justification of this present investigation are clearly stated below.

In order to establish a 'universal' pH scale for pH measurements of blood plasma and other clinical samples, there is a strong need for reliable pH values of the same buffer, but different buffer concentrations and buffer ratios so that the pH values would lie within the physiological region of pH 6 – 8. Thus the investigation of BICINE buffer of some additional and entirely new buffer ratios and concentrations are essential for filling this missing gap in the establishment of a self-consistent pH scale for physiological application. Thus the authors have conducted this study with a view to providing accurate pH data for eight (three without NaCl and five with NaCl) completely new buffer ratios and buffer concentrations of BICINE and NaBICINE. The results are highly satisfactory. Now the combined reliable pH results of ten buffer solutions from previous publications [3] and eight buffer solutions from the present study would complete the missing gap and significantly advance the pH database for the establishment of a 'universal' pH scale.

The zwitterionic buffer HEPBS [4] has been recommended as a secondary standard in the pH range 7 to 8 for clinical research. The goal of the current investigation is to provide reliable and accurate pH values for the N- substituted amino acid buffer BICINE, the structure of which is given in Fig. (**1**).

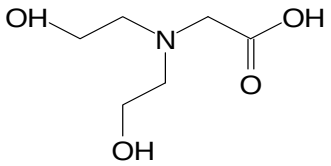

Fig. (1). [bis(2-hydroxyethyl)amino]acetic acid (BICINE).

BICINE, as well as other zwitterionic buffers, may be used as pH standard physiological buffers for biomedical research, protein chemistry, and clinical fluids. The currently used NIST certified physiological phosphate primary standard buffer has recorded pH values of 7.415 and 7.395 at (298.15 and 310.15) K, respectively [5, 6]. This phosphate buffer consists of 0.008695 mol·kg^{-1} KH_2PO_4 and 0.03043

*Address correspondence to this author at the Hoffman Department of Chemistry, Drury University, 900 N. Benton Ave., Springfield, Missouri 65802, USA; Tel: 417-873-7247; Fax: 417-873-7856;
E-mail: rroy@drury.edu

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$mol \cdot kg^{-1}$ Na_2HPO_4. There are problems associated with the widely used phosphate buffer. Some of these disadvantages have been previously explained [4, 7, 8]. The potential for complex formation with cations, such as Mg^{+2} and Ca^{+2}, does exist with use of phosphate buffer. However, the likeliness of such an occurrence for BICINE buffer has been minimized with a high NaCl concentration giving an isotonic saline solution of $I = 0.16$ $mol \cdot kg^{-1}$. The physiological buffer BICINE is highly compatible with blood and other biological media. Based on experiments [13], this buffer has negligible interference with Ca^{+2}, Mg^{+2}, etc. of blood ingredients.

Wu and associates [7, 8] have published pH and pK_2 values for *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid, HEPES; and MOPSO. Roy *et al*. [9] reported pK_2 and pH values of N-substituted aminopropane sulfonic acid DIPSO buffer. These solutions are useful for pH control in the physiological region close to that of blood serum.

The following compositions were examined for the determination of pH(s) values:(a) BICINE (0.02) + NaBICINE (0.02), (b) BICINE (0.04) + NaBICINE (0.08), (c) BICINE (0.06) + NaBICINE (0.06), (d) BICINE (0.02) + NaBICINE (0.02) + NaCl (0.14), (e) BICINE (0.04) + NaBICINE(0.04) + NaCl (0.12), (f) BICINE (0.05) + NaBICINE (0.05) + NaCl (0.11), (g) BICINE (0.06) + NaBICINE (0.06) + NaCl (0.10), (h) BICINE (0.09) +NaBICINE (0.03) + NaCl (0.13).

2. EXPERIMENTAL

The BICINE was obtained from Sigma Chemical Company. After recrystallization two times from 75% ethanol, an assay of 99.96% with a standard deviation of 0.04% was obtained by titration of BICINE with the standard NaOH solution. The detailed procedure has been previously reported in the literature [10]. Buffer solutions from (a) to (h), as mentioned above, were prepared from mass methods by weighing solid BICINE buffer, ACS reagent grade and recrystallized NaCl, a standard NaOH solution (for the preparation of NaBICINE), and carefully calculated amounts of double distilled CO_2-free water. Buoyancy corrections were made for all masses used in buffer solution preparation.

The cell design, preparation procedures of the hydrogen electrode using chloroplatinic acid, hydrogen gas purification, silver-silver chloride electrode of the thermal electrolytic type, solution preparation, voltmeter and other experimental details have been described previously [9, 11,12].

3. METHODS AND RESULTS

The emf (electromotive force) values needed for the pH(s) calculations are given in Tables **1** and **2** for the following cell (A) containing three solutions without NaCl and five solutions with NaCl to give them an ionic strength of $I = 0.16$ $mol \cdot kg^{-1}$. The emf values have been corrected to a hydrogen pressure of 101.325 kPa. At T =298.15 K the uncertainties of emf, on the average, lie within 0.02 mV in all experimental temperatures.

The method of Bates [5, 10] has been used to evaluate the conventional standard pH values for buffer solutions (a) to (h) as was done previously [12, 13, 14]. The following cell (A) is used for the collection of cell potential data:

Pt(*s*), H_2(*g*), 101.325 kPa | BICINE(m_1) + NaBICINE(m_2) + NaCl(m_3) | AgCl(*s*), Ag(*s*) (A)

where the molalities of the respective species are indicated inside the bracket.

The cell (B) is the flowing junction cell. It was used for the evaluation of the liquid junction potential at the contact point between the buffer solution and the heavier, saturated KCl solution shown with a double vertical line below:

Pt(*s*), H_2(*g*), 101.325 kPa | BICINE(m_1) + NaBICINE(m_2) + NaCl(m_3) || KCl(satd), Hg_2Cl_2(*s*), Hg(*l*) (B)

Table 1. Cell Potential of Cell A (in Volts): Pt(s); H_2(g), 101.325 kPa | BICINE (m_1), NaBICINE (m_2), NaCl (m_3) | AgCl(s), Ag(s)

m_1	m_2	m_3	*T*/K											
$mol \cdot kg^{-1}$			278.15	283.15 K	288.15	293.15	298.15	303.15	308.15	310.15	313.15	318.15	323.15	328.15
0.02	0.04	0.005	0.83782	0.84079	0.84330	0.84598	0.84855	0.85098	0.85355	0.85469	0.85630	0.85863	0.86107	0.86339
0.02	0.04	0.010	0.82183	0.82467	0.82692	0.82931	0.83163	0.83383	0.83625	0.83743	0.83869	0.84079	0.84278	0.84466
0.02	0.04	0.015	0.81254	0.81528	0.81744	0.81960	0.82185	0.82388	0.82626	0.82752	0.82850	0.83050	0.83215	0.83368
0.02	0.04	0.020	0.80636	0.80905	0.81095	0.81315	0.81543	0.81735	0.81970	0.82093	0.82178	0.82366	0.82513	0.82636
0.04	0.08	0.005	0.83546	0.83844	0.84115	0.84370	0.84629	0.84867	0.85096	0.85174	0.85304	0.85492	0.85673	0.85904
0.04	0.08	0.010	0.82056	0.82349	0.82583	0.82821	0.83056	0.83273	0.83498	0.83569	0.83693	0.82858	0.84033	0.84344
0.04	0.08	0.015	0.81215	0.81486	0.81683	0.81914	0.82140	0.82349	0.82577	0.82644	0.82786	0.82944	0.83100	0.83509
0.04	0.08	0.020	0.80643	0.80918	0.81120	0.81348	0.81570	0.81752	0.81994	0.82078	0.82202	0.82354	0.82537	0.83035
0.06	0.06	0.005	0.82756	0.83068	0.83355	0.83623	0.83882	0.84122	0.84345	0.84408	0.84544	0.84726	0.84877	0.85011
0.06	0.06	0.010	0.81166	0.81442	0.81698	0.81928	0.82158	0.82377	0.82573	0.82619	0.82748	0.82905	0.83042	0.83143
0.06	0.06	0.015	0.80230	0.80490	0.80725	0.80929	0.81148	0.81351	0.81532	0.81568	0.81694	0.81844	0.81971	0.82046
0.06	0.06	0.020	0.79604	0.79848	0.80074	0.80247	0.80469	0.80663	0.80838	0.80848	0.80991	0.81139	0.81263	0.81315

Table 2. Cell Potential of Cell A (in Volts): Pt(s); H_2(g), 101.325 kPa | BICINE (m_1), NaBICINE (m_2), NaCl (m_3) | AgCl(s), Ag(s)

m_1	m_2	m_3	*T*/K											
mol·kg^{-1}			278.15	283.15 K	288.15	293.15	298.15	303.15	308.15	310.15	313.15	318.15	323.15	328.15
0.02	0.02	0.14	0.74810	0.74997	0.75154	0.75257	0.75360	0.75461	0.75539	0.75560	0.75616	0.75665	0.75706	0.75738
0.04	0.04	0.12	0.75110	0.75298	0.75453	0.75583	0.75691	0.75797	0.75877	0.75903	0.75952	0.76017	0.76070	0.76106
0.05	0.05	0.11	0.75290	0.75465	0.75616	0.75745	0.75869	0.75978	0.76061	0.76093	0.76139	0.76209	0.76269	0.76305
0.06	0.06	0.10	0.75491	0.75660	0.75813	0.75943	0.76084	0.76197	0.76280	0.76316	0.76357	0.76438	0.76503	0.76543
0.09	0.03	0.13	0.73404	0.73535	0.73653	0.73754	0.73816	0.73870	0.73913	0.738990	.73944	0.73967	0.73968	0.73972

where the symbols "*s*," "*l*," and "*g*" imply the solid, liquid, and gaseous states.

In routine laboratory pH measurements, a glass electrode of the pH meter commonly replaces the hydrogen electrode. For cell (B), the values of the standard electrode potential, denoted as E°_{SCE}, of the saturated calomel electrode were taken as -0.2415 and -0.2335 V at (298.15 and 310.15) K [14, 15], respectively.

For cell (C), the phosphate salts were universally used NIST standard reference solutions. The cell diagram for cell (C) is as follows:

Pt(*s*), H_2(*g*), 101.325 kPa | KH_2PO_4(m_1)+ Na_2HPO_4(m_2)|| KCl(satd), Hg_2Cl_2(*s*), Hg(*l*) (C)

where m_1 = 0.008695, and m_2 = Na_2HPO_4. The values of the liquid junction potential, E_j, for the phosphate buffer and the buffer solutions were obtained using the flowing junction method [8]. The δE_j values of the standard buffer solution for cell (B) were calculated using the following equation:

$$\delta E_j = E + E^{\circ}_{SCE} - k\,\mathrm{pH} \quad (1)$$

where the values of k = 0.059156, pH = 7.415 at T = 298.15 K; k = 0.061538 and pH = 7.395 at T = 310.15 K were obtained from the literature [12]. The pH(s) values are that of the standard phosphate buffer solution and the pH(x) for BICINE buffer solutions. The relationship between pH(x) and pH(s) is as follows:

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

To calculate the pH values for all buffer solutions under investigation, calculations were made to determine the acidity function, denoted as p($a_H\gamma_{Cl}$), in the temperature range (278.15 to 328.15) K. These calculations [10-13, 16-18] were made using the emf (E) values listed in Tables **1** and **2**, the molality of the chloride ion, and the standard electrode potential of the silver-silver chloride electrode (E°). The equation to calculate the quantity p($a_H\gamma_{Cl}$) is shown below:

$$p(a_H\gamma_{Cl}) = \frac{E - E^{\circ}}{k} + \log m_{Cl^-} \quad (3)$$

where "k" is the Nernst slope.

When plotting p($a_H\gamma_{Cl}$) vs. m_{Cl^-}, linear line with a small slope was obtained to determine the intercept on the y-axis to give a p($a_H\gamma_{Cl}$)° value at m_{Cl^-}= 0. These p($a_H\gamma_{Cl}$)° values for the chloride-free buffer solutions are listed in Table **3**. The p($a_H\gamma_{Cl}$) values for the buffer solutions containing Cl^- are entered in Table **4** from (278.15 to 328.15) K.

The pH(s) values for solutions without liquid junction in the absence ofNaCl were determined using the following equation:

$$pH(s) = p(a_H\gamma_{Cl})^{\circ} + \log\gamma^{o}_{Cl} \quad (4)$$

where the single-ion activity coefficient, γ^{o}_{Cl}, cannot be experimentally measured. For the calculation of γ°_{Cl}, the "pH convention" commonly known as the Bates-Guggenheim convention [5], is expressed by the equation:

$$\log\gamma^{\circ}_{Cl} = -\frac{A\sqrt{I}}{1+1.5\sqrt{I}} \quad (5)$$

The International Union of Pure and Applied Chemistry, IUPAC, has recommended the use of this convention, but Eq. 5 is assumed to be valid for systems where I is no more than 0.1 mol·kg^{-1}. For I greater than 0.1 mol·kg^{-1}, there is no single widely accepted convention. A superior choice for solutions with I greater than 0.1 mol·kg^{-1} may need to include a linear-dependent "*CI*" term shown in Eq. 6 with an ion size parameter as well as be temperature dependent.

An extended Debye-Hückel equation [7, 9] has been selected to be the more logical approach to calculate $\log\gamma^{o}_{Cl}$ when I is greater than 0.1 mol·kg^{-1} for all of the buffer solutions containing Cl^-.

$$\log\gamma^{\circ}_{Cl} = -\frac{A\sqrt{I}}{1+Ba^{\circ}\sqrt{I}} + CI \quad (6)$$

where "*I*" is the ionic strength of the buffer solution, "*A*" and "*B*" are slope parameters known as the Debye-Hückel constants, and "*C*" is an adjustable parameter defined by Eq. 7. The following empirical equation is used for the calculation of the adjustable parameter "*C*" and was obtained from a curve-fitting method [7, 9]:

$$C = C_{298.15} + (6.2\ 10^{-4})(T - 298.15) - (8.7 \cdot 10^{-6})(T - 298.15)^2 \quad (7)$$

where $C_{298.15}$= 0.032 kg·mol^{-1} at 298.15 K and "*T*" is the temperature in Kelvin.

Table 3. p($a_H\gamma_{Cl}$)° of (BICINE+ NaBICINE) Buffer Solutions from (278.15 to 328.15) K, Obtained by Extrapolation for Chloride-Free Solutions[a] Using Eq. 3

	0.02 *m* BICINE	**0.04 *m* BICINE**	**0.06 *m* BICINE**
	+ 0.04 *m*NaBICINE+ 0.08 *m*NaBICINE+ 0.06 *m*NaBICINE		
***T*/K**	***I* = 0.04 *m***	***I* = 0.08 *m***	***I* = 0.06 *m***
278.15	8.627	8.568	8.442
283.15	8.533	8.476	8.356
288.15	8.439	8.386	8.271
293.15	8.353	8.297	8.190
298.15	8.270	8.216	8.111
303.15	8.191	8.137	8.034
308.15	8.116	8.057	7.958
310.15	8.089	8.024	7.926
313.15	8.052	7.979	7.883
318.15	7.985	7.905	7.810
323.15	7.926	7.833	7.735
328.15	7.868	7.758	7.664

[a]m = 1 mol·kg^{-1}

Table 4. p($a_H\gamma_{Cl}$) of (BICINE+ NaBICINE) Buffer Solutions from 5 to 55°C, Computed Using Eq. 4

m_1	m_2	m_3	***T*/K**											
mol·kg^{-1}			**278.15**	**283.15**	**K 288.15**	**293.15**	**298.15**	**303.15**	**308.15**	**310.15**	**313.15**	**318.15**	**323.15**	**328.15**
0.02	0.02	0.14	8.458	8.375	8.292	8.206	8.125	8.049	7.973	7.942	7.902	7.831	7.763	7.697
0.04	0.04	0.12	8.446	8.362	8.278	8.195	8.114	8.038	7.961	7.931	7.889	7.820	7.753	7.687
0.05	0.05	0.11	8.441	8.354	8.268	8.185	8.106	8.030	7.953	7.924	7.881	7.813	7.746	7.679
0.06	0.06	0.10	8.436	8.347	8.261	8.178	8.101	8.025	7.948	7.919	7.875	7.807	7.741	7.674
0.09	0.03	0.13	8.171	8.083	7.997	7.915	7.831	7.752	7.674	7.640	7.600	7.530	7.460	7.394

The pH(s) values listed in Table **5** for the BICINE buffer solutions without the presence of Cl^- were calculated using the following equations with their respective solution compositions:

BICINE (0.02) + NaBICINE (0.02):

$$pH(s) = 8.191 + (1.62\cdot10^{-2})(T - 298.15) - (9.0\cdot10^{-5})(T - 298.15)^2 \quad (8)$$

BICINE (0.04) + NaBICINE (0.08):

$$pH(s) = 8.116 + (1.67\cdot10^{-2})(T - 298.15) - (4.3\cdot10^{-5})(T - 298.15)^2 \quad (9)$$

BICINE (0.06) + NaBICINE (0.06):

$$pH(s) = 8.020 + (1.59\cdot10^{-2})(T - 298.15) - (3.0\cdot10^{-5})(T - 298.15)^2 \quad (10)$$

for the temperature range of (278.15 to 328.15) K. The standard deviations of regression for the pH(s) of the chloride-free buffer solutions are 0.0017, 0.0020, and 0.0013, respectively.

For the buffer solutions containing NaCl, with an isotonic saline media ionic strength of I = 0.16 mol·kg^{-1}, the pH(s) values were also calculated using Eqs. 3 to 7.The acidity function data p($a_H\gamma_{Cl}$) for buffer solutions containing NaCl are listed in Table **4**. The values of the pH(s) for these solutions entered in Table **6** are expressed by use of the following equations:

BICINE (0.02) + NaBICINE (0.02) + NaCl (0.14):

$$pH(s) = 8.000 - (1.59\cdot10^{-2})(T - 298.15) - (4.60\cdot10^{-5})(T - 298.15)^2 \quad (11)$$

BICINE (0.04) + NaBICINE (0.04) + NaCl (0.12):

$$pH(s) = 7.988 - (1.58\cdot10^{-2})(T - 298.15) - (4.59\cdot10^{-5})(T - 298.15)^2 \quad (12)$$

BICINE (0.05) + NaBICINE (0.05) + NaCl (0.11):

Table 5. pH(s) of (BICINE + NaBICINE)Buffer Solutions from (278.15 to 328.15) K, Computed Using Eqs. 4, 5, 6, 7[a]

	0.02 m BICINE	0.04 m BICINE	0.06 m BICINE
	+ 0.04 mNaBICINE	+ 0.08 mNaBICINE	+ 0.06 mNaBICINE
T/K	I = 0.04 m	I = 0.08 m	I = 0.06 m
278.15	8.557	8.468	8.352
283.15	8.464	8.376	8.266
288.15	8.369	8.286	8.181
293.15	8.284	8.197	8.100
298.15	8.201	8.114	8.020
303.15	8.121	8.035	7.942
308.15	8.048	7.955	7.865
310.15	8.022	7.922	7.833
313.15	7.983	7.876	7.790
318.15	7.915	7.802	7.715
323.15	7.853	7.728	7.640
328.15	7.792	7.652	7.568

[a] m = 1 mol·kg^{-1}

Table 6. pH(s) of (BICINE + NaBICINE)Buffer Solutions from (278.15 to 328.15) K,Computed Using Eqs. 4, 5, 6 ,7

m_1	m_2	m_3	T/K											
mol·kg^{-1}			278.15	283.15 K288.15293.15298.15				303.15	308.15	310.15	313.15	318.15	323.15	328.15
0.02	0.02	0.14	8.333	8.250	8.166	8.081	7.998	7.922	7.845	7.815	7.773	7.702	7.633	7.566
0.04	0.04	0.12	8.320	8.236	8.152	8.070	7.987	7.911	7.833	7.803	7.760	7.691	7.623	7.555
0.05	0.05	0.11	8.315	8.228	8.143	8.060	7.980	7.903	7.826	7.796	7.753	7.683	7.616	7.548
0.06	0.06	0.10	8.310	8.222	8.136	8.053	7.975	7.898	7.820	7.791	7.746	7.678	7.611	7.543
0.09	0.03	0.13	8.046	7.957	7.872	7.790	7.705	7.625	7.547	7.518	7.472	7.401	7.330	7.262

$$pH(s) = 7.980 - (1.58\cdot10^{-2})(T - 298.15) - (4.85\cdot10^{-5})(T - 298.15)^2 \quad (13)$$

BICINE (0.06) + NaBICINE (0.06) + NaCl (0.10):

$$pH(s) = 7.974 - (1.58\cdot10^{-2})(T - 298.15) - (4.93\cdot10^{-5})(T - 298.15)^2 \quad (14)$$

BICINE (0.09) + NaBICINE (0.03) + NaCl (0.13):

$$pH(s) = 7.705 - (1.61\cdot10^{-2})(T - 298.15) - (4.59\cdot10^{-5})(T - 298.15)^2 \quad (15)$$

The observed standard deviations of regression from Eqs.11 – 15 are 0.0018, 0.0013, 0.0008, 0.0013, and 0.0012, respectively.

4. CONCLUSIONS

The emf values of cells (B) and (C) at (298.15 and 310.15) K are given in Table **7**. The operational pH values at these two temperatures were evaluated from cells (B) and (C) by means of the flowing junction cell [7, 9]. The values of δE_j were obtained using Eq. 1and are also listed in Table **7**. The summation of the standard uncertainties for the pH(s) values was accounted for by combining multiple known sources of error: (i) values of $p(a_H\gamma_{Cl})^\circ$ for Cl^- free solutions are within ± 0.001 pH unit, (ii) assumption for the calculation of $\log \gamma^o_{Cl}$ using Eq.6 leads to an error of ± 0.002 pH unit; (iii) emf measurement is within ± 0.001 pH unit, and (iv) estimation of δE_j values yield an error of 0.003 pH unit. Thus, the overall error is ± 0.007 pH unit for buffer solutions with and without the presence of Cl^-, respectively. For BICINE, m_1 = 0.04, m_2 = 0.04, and m_3 = 0.12; excellent agreement between the calculated values with the use of the extended Debye-Hückel equation and values with the liquid junction correction at 310 K is 7.803 and 7.803, respectively. Two buffer solutions of BICINE have pH values in the narrow range 7.7 to 8.0 and are recommended as useful primary pH standards for calibrating glass electrodes of the pH meter. The authors are working for the determination of pH values of various buffer solutions using Pitzer ionic interaction the-

Table 7. Emf of Cell B and pH Values with δEjCorrection at (298.15 and 310.15) K for BICINE Buffer

m_1	m_2	m_3	I	E/V		δE_j[b]/mV		With-out[c] δE_jcorr	With[d] δE-$_j$corr	Extended[c] D-H eqn.	Without[c] δE_jcorr	With[d] δE-$_j$corr	Extend-ed[c] D-H eqn.
				298.15 K	310.15 K	298.15 K	310.15 K	298.15 K			310.15 K		
0.04	0.04	0.12	0.16	0.68180	0.67861	2.2	2.3	7.949	7.986	7.987	7.766	7.803	7.803
0.05	0.05	0.11	0.16	0.68926	0.68591	2.2	2.3	7.944	7.980	7.980	7.760	7.795	7.796
Emf of Cell C[a]													
0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4		0.68275	0.69147	2.6	2.9								

[a]Corrected to a hydrogen pressure of 101.325 kPa for physiological phosphate buffer solutions (primary reference standard buffer) at (298.15 and 310.15) K [7].

[b]$\delta E_j = E + E^{\circ}_{SCE} - k$ pH from Eq. 1 is the Emf from Table 7, k = Nernst slope with values 0.059156 at T = 298.15 K, and 0.061538 at T = 310.15 K; the pH of the primary reference standard phosphate buffer is 7.415 and 7.395 at (298.15 and 310.15) K, respectively; E°_{SCE} = electrode potential of the saturated calomel electrode = -0.2415 and -0.2335 at (298.15 and 310.15)K [14,15], respectively; units of m, mol·kg^{-1}.

[c]Values obtained from Eq. 2 where $\delta E_j = 0$ and Table 7

[d]Obtained from Eq. 2 and Table 7

[e]Obtained from extended Debye-Hückel (DH) equation of the Bates-Guggenheim convention

ory [19-20] for the calculation of the single ion activity coefficient, γ_{Cl}.

CONFLICTS OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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DISCLOSURE

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REFERENCES

[1] Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M. Hydrogen ion buffers for biological research. *Biochemistry.,* **1966**, *5*, 467-477.

[2] Ferguson, W. J.; Braunschweiger, K. I.; Braunschweiger, W. R.; Smith, J. R.; McCormick, J. J.; Wasmann, C. C.; Jarvis, N. P.; Bell, D. H.; Good, N. E. Hydrogen ion buffers for biological research. *Anal. Biochem*., **1980**, *104*, 300 -310.

[3] Roy, L. N.; Roy, R. N.; Denton, C. E.; LeNoue, S. R.; Roy, C. N.; Ashkenazi, S.; Williams, T. B.; Church, D. R.; Fuge, M. S.; Sreepada, K. S. Second dissociation constant of bis-[(2-hydroxyethyl)amino]acetic acid (BICINE) and pH of its buffer solutions from 5 - 55° C. *J. Solution Chem*., **2006**, *35*, 605-624.

[4] Roy, L. N.; Roy, R. N.; Allen, K. A.; Mehrhoff, C. J.; Henson, I. B.; Stegner, J. M.; Downs, Z. M. Buffer standards for the physiological pH of *N*-(2-hydroxyethyl)piperazine-*N*'-4-butanesulfonic acid (HEPBS) from 5 to 55 °C. *The Open Electrochemistry Journal.*, **2012**, *4*, 13-19.

[5] Bower, V. E.; Paabo, M.; Bates, R. G. A standard for the measurement of the pH of blood and other physiological media. *J. Res. Natl. Bur. Stand*., **1961**, *65A*, 267-270.

[6] Durst, R. A.; Staples, B. R. Tris/Tris HC1: Standard buffer for use in the physiological pH range. *Clin. Chem*., **1972**, *18*, 206-208.

[7] Feng, D.; Koch, W. F.; Wu, Y. C. Second dissociation constant and pH of *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid from 0 to 50 °C. *Anal. Chem*., **1989**, *61*, 1400-1405.

[8] Wu, Y. C., Berezansky, P. A., Feng, D., Koch, W. F. Second dissociation constant of 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid and pH of its buffer solutions. *Anal. Chem*., **1993**, *65*, 1084-1087.

[9] Roy, L. N.; Roy, R. N.; LeNoue, S. R.; Denton, C. E.; Fuge, M. S.; Dunseth, C. D.; Roy, C. N.; Hayden, S. R.; Wollen, J. T.; Sreepada, K. Buffer standards for the physiological pH of the zwitterionic compound, DIPSO from 5 to 55°C. *J. Solution Chem*., **2009,** *38*, 459-469.

[10] Bates, R. G., Vega, C. A., White, D. R. Jr. Standards for pH measurements in isotonic saline media of ionic strength I = 0.16. *Anal. Chem*., **1978**, *50*, 1295-1300.

[11] Bates, R. G. *Determination of pH*, 3rd ed.; Wiley: New York, 1973.

[12] Roy, R. N.; Roy, L. N.; Denton, C. E.; LeNoue, S. R.; Ashkenazi, S.; Fuge, M. S.; Dunseth, C. D.; Durden, J. L.; Roy, C. N.; Bwashi, A.; Wollen, J. T.; DeArmon, S. J. Buffer standards for the physiological pH of 3-[(1,1-dimethyl-2-hydroxymethyl)amino]-2-hydroxypropanesulfonic acid (AMPSO) from (278.15 to 328.15) K. *J. Chem. Eng. Data*, **2009,** *54*, 425- 435.

[13] Roy, L. N.; Roy, R. N.; Denton, C. E.; LeNoue, S. R.; Roy, C. N.; Ashkenazi, S.; Williams, T. B.; Church, D. R.; Fuge, M. S.; Sreepada, K. S. Second dissociation constant of bis-[(2-hydroxyethyl)amino]acetic acid (BICINE) and pH of its buffer solutions from 5 - 55° C. *J. Solution Chem*., **2006**, *35*, 605-624.

[14] Roy, R. N.; Roy, L. N.; Ashkenazi, S.; Wollen, J. T.; Dunseth, C. D.; Fuge, M. S.; Roy, C. N.; Hughes, H. M.; Morris, B. T.; Cline, K. L. Buffer standards for pH measurement of N-(2-hydroxyethyl)piperazine-N'-2-ethanesulfonic acid (HEPES) for I=0.16 mol·kg^{-1} from 5 to 55°C. *J. Solution Chem.*, **2009,** *38*, 449-458.

[15] Latimer, W. M. *Oxidation Potentials*, 2nded.; Prentice-Hall: New York, 1952.

[16] Vega, C. A.; Bates, R. G.Buffers for the physiological pH range: Thermodynamic constants of four substituted aminoethanesulfonic acids from 5 to 50 °C. *Anal. Chem*., **1976,** *48*, 1293-1296.

[17] Bates, R. G., Roy, R. N., Robinson, R. A. Buffer standards of tris(hydroxymethyl) methylglycine ("Tricine") for the physiological range pH 7.2 to 8.5. *Anal. Chem*., **1973**, 45, 1663-1666.

[18] Bates, R. G., Guggenheim, E. A. Report on the standardization of pH and related terminology. *Pure Appl. Chem*., **1960**, *1*, 163-168.

[19] Pitzer, K. S., Mayorga, G. J. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem*., **1973**, *77*, 2300-2310.

[20] Covington, A. K., Ferra, M. I. A. A Pitzer mixed electrolyte solution theory approach to assignment of pH to standard buffer solutions. *J. Solution Chem*., **1994**, *23*, 1-10.

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