JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Buffer Standards for the Biological pH of the Amino Acid *N*-[2-Hydroxyethyl]piperazine-*N*′-[3-propanesulfonic acid], HEPPS, From (278.15 to 328.15) K

Lakshmi N. Roy, Rabindra N. Roy,* Joshua T. Wollen, Meagan A. Harmon, Jessica M. Stegner, Ankita A. Shah, and Isaac B. Henson

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

ABSTRACT: For the HEPPS buffer under investigation, there are seven buffer solutions without NaCl and eight buffer solutions that contain Cl^- and have an ionic strength (I = 0.16 mol·kg^{-1}) that is similar to that of blood plasma. These buffer solutions have been evaluated in the temperature range of (278.15 to 328.15) K using the extended Debye−Hückel equation and the Bates−Guggenheim convention. The previously determined E_j values have been used to determine the operational pH values of HEPPS buffer solutions at (298.15 and 310.15) K. These are recommended as secondary standard reference solutions for pH measurements in saline media with an isotonic ionic strength of I = 0.16 mol·kg^{-1}.

INTRODUCTION

The zwitterionic amino acid buffer solutions recommended by Good et al.[1,2] are useful for the purpose of blood pH measurement in the physiological range of pH (7 to 8). The authors have reported the pH values of 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid (MOPSO)[3] from (278.15 to 328.15) K, including 310.15 K. The zwitterionic buffer *N*-[2-hydroxyethyl]piperazine-*N*′-[3-propanesulfonic acid] (HEPPS)[4] and the pH of its buffer solutions in a limited range of concentration from (278.15 to 328.15) K have been reported. Regarding the current investigation, the authors' goal is to provide reliable pH values in the concentration range I = (0.04 to 0.16) mol·kg^{-1} for the ampholyte HEPPS, which is depicted by the following structure: This zwitterionic buffer as suggested by Good and co-workers[1,2] may be used as biochemical buffers for clinical media (Figure 1). The currently used National Institute of Standards/National Bureau of Standards (NIST/NBS) 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]

Some of the disadvantages concerning the phosphate buffer are (i) precipitation of phosphates with some polyvalent cations in the blood, such as the constituents Mg^{2+} and Ca^{2+}, and (ii) the phosphate buffer's temperature coefficient (−0.0028 pH unit·K^{-1}) does not accurately approximate that of whole blood (−0.015 pH unit·K^{-1}).[6] The zwitterionic buffer compound HEPPS is not expected to yield such adverse effects.

Wu and associates[7] have published pK_2 and pH values for *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid (HEPES). Wu et al.[8] have also studied MOPSO using two point pH calibration measurements as well. Roy et al.[9] determined pK_2 and pH values of 3-(*N*-morpholino)propanesulfonic acid (MOPS) in the temperature range of (278.15 to 328.15) K. By using pH values of standard buffer solutions with the compositions 0.08 mol·kg^{-1} MOPS + 0.08 mol·kg^{-1} NaMOPS + 0.08 mol·kg^{-1} NaCl with I = 0.16 mol·g^{-1}, the commonly used glass-electrode pH meter assembly can be calibrated.

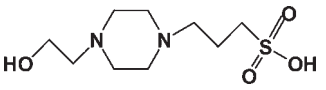

Figure 1. *N*-[2-Hydroxyethyl]piperazine-*N*′-[3-propanesulfonic acid] (HEPPS).

Seven buffer solutions without NaCl in the concentration range I = (0.04 to 0.1) mol·kg^{-1} and eight buffer solutions with NaCl at an ionic strength of I = 0.16 mol·kg^{-1} were examined in this study. All experimental results were interpreted using the extended form of the Debye−Hückel equation.

EXPERIMENTAL SECTION

The HEPPS was obtained from Research Organics (Cleveland, Ohio). Further crystallization was used for purification. The analyses of the assay gave the HEPPS buffer to be 99.96 % pure. Buffer solutions (a) to (r) were prepared by massing the HEPPS buffer, ACS reagent grade NaCl, a standard NaOH solution, and carefully calculated amounts of CO_2-free doubly distilled water. Buoyancy corrections were made for all masses used in solution preparation.

In previous publications, the cell design, preparation of hydrogen electrodes, hydrogen gas purification, silver−silver chloride electrodes (of the thermal, electrolytic type),[11] and buffer solution preparation have been described.[1,12] Details about the equipment (including model numbers), temperature control, and experimental techniques have also been previously reported.[12]

METHODS AND RESULTS

For cell A, the values of the cell potential required for the pH(s) calculations are given in Tables 1 and 2. Cell A contains

Received: June 23, 2011
Accepted: October 4, 2011
Published: October 20, 2011

ACS Publications © 2011 American Chemical Society

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

m_1	m_2	m_3	T/K											
mol·kg^{-1}			278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	310.15 K	313.15 K	318.15 K	323.15 K	328.15 K
0.02	0.04	0.005	0.83439	0.83876	0.84292	0.84677	0.85063	0.85397	0.85711	0.85845	0.86027	0.86325	0.86592	0.86825
0.02	0.04	0.010	0.81800	0.82195	0.82593	0.82960	0.83334	0.83602	0.83885	0.84029	0.84186	0.84461	0.84703	0.84911
0.02	0.04	0.015	0.80868	0.81247	0.81628	0.81986	0.82356	0.82588	0.82838	0.82973	0.83132	0.83403	0.83604	0.83787
0.02	0.04	0.020	0.80201	0.80571	0.80937	0.81291	0.81667	0.81853	0.82112	0.82218	0.82369	0.82651	0.82820	0.83018
0.02	0.08	0.005	0.85283	0.85737	0.86220	0.86635	0.87035	0.87430	0.87786	0.87934	0.88138	0.88455	0.88762	0.89002
0.02	0.08	0.010	0.83704	0.84091	0.84531	0.84942	0.85318	0.85673	0.86016	0.86150	0.86325	0.86611	0.86894	0.87128
0.02	0.08	0.015	0.82803	0.83145	0.83562	0.83956	0.84310	0.84692	0.85007	0.85141	0.85311	0.85583	0.85841	0.86070
0.02	0.08	0.020	0.82175	0.82480	0.82883	0.83290	0.83613	0.83988	0.84298	0.84419	0.84582	0.84857	0.85087	0.85318
0.04	0.02	0.005	0.80102	0.80469	0.80804	0.81129	0.81442	0.81731	0.82005	0.82118	0.82268	0.82503	0.82739	0.82928
0.04	0.02	0.010	0.78457	0.78790	0.79100	0.79398	0.79679	0.79940	0.80184	0.80284	0.80406	0.80608	0.80801	0.80962
0.04	0.02	0.015	0.77483	0.77798	0.78092	0.78370	0.78628	0.78880	0.79108	0.79199	0.79302	0.79479	0.79643	0.79786
0.04	0.02	0.020	0.76802	0.77111	0.77395	0.77653	0.77908	0.78141	0.78348	0.78432	0.78517	0.78685	0.78830	0.78961
0.04	0.08	0.005	0.83513	0.83913	0.84295	0.00000	0.85030	0.85367	0.85701	0.85783	0.85967	0.86243	0.86494	0.86741
0.04	0.08	0.010	0.81802	0.82166	0.82520	0.82930	0.83241	0.83549	0.83853	0.83924	0.84087	0.84334	0.84559	0.84749
0.04	0.08	0.015	0.80777	0.81134	0.81463	0.81892	0.82181	0.82478	0.82753	0.82819	0.82972	0.83205	0.83408	0.83589
0.04	0.08	0.020	0.80046	0.80400	0.80690	0.81140	0.81422	0.81709	0.81956	0.82028	0.82174	0.82392	0.82578	0.82771
0.03	0.09	0.005	0.84641	0.85077	0.85491	0.85887	0.86258	0.86609	0.86905	0.87076	0.87257	0.87541	0.87786	0.88035
0.03	0.09	0.010	0.83039	0.83457	0.83842	0.84213	0.84566	0.84893	0.85113	0.85322	0.85489	0.85755	0.85983	0.86211
0.03	0.09	0.015	0.82123	0.82520	0.82888	0.83237	0.83592	0.83907	0.84063	0.84314	0.84474	0.84733	0.84958	0.85178
0.03	0.09	0.020	0.81493	0.81885	0.82241	0.82587	0.82936	0.83249	0.83347	0.83642	0.83805	0.84055	0.84275	0.84506
0.06	0.03	0.005	0.79922	0.80337	0.80686	0.80997	0.81266	0.81558	0.81819	0.81928	0.82078	0.82289	0.82491	0.82664
0.06	0.03	0.010	0.78286	0.78706	0.79028	0.79314	0.79540	0.79805	0.80057	0.80168	0.80302	0.80492	0.80674	0.80826
0.06	0.03	0.015	0.77321	0.77759	0.78070	0.78344	0.78536	0.78795	0.79033	0.79152	0.79278	0.79452	0.79627	0.79768
0.06	0.03	0.020	0.76652	0.77106	0.77408	0.77667	0.77851	0.78110	0.78343	0.78472	0.78582	0.78755	0.78921	0.79056
0.08	0.02	0.005	0.78470	0.78807	0.79128	0.79424	0.79704	0.79977	0.80219	0.80311	0.80439	0.80641	0.80825	0.80989
0.08	0.02	0.010	0.76794	0.77100	0.77392	0.77652	0.77907	0.78141	0.78353	0.78433	0.78543	0.78713	0.78869	0.79005
0.08	0.02	0.015	0.75794	0.76078	0.76341	0.76573	0.76826	0.77039	0.77233	0.77305	0.77406	0.77558	0.77696	0.77816
0.08	0.02	0.020	0.75067	0.75335	0.75593	0.75815	0.76050	0.76235	0.76419	0.76486	0.76576	0.76717	0.76842	0.76950

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

m_1	m_2	m_3	T/K											
mol·kg^{-1}			278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	310.15 K	313.15 K	318.15 K	323.15 K	328.15 K
0.02	0.02	0.14	0.75305	0.75266	0.75221	0.75197	0.75221	0.75254	0.75347	0.75379	0.75469	0.75587	0.75759	0.75981
0.02	0.04	0.12	0.75841	0.75821	0.75774	0.75780	0.75797	0.75831	0.75902	0.75948	0.76004	0.76134	0.76259	0.76467
0.04	0.08	0.08	0.77053	0.77023	0.76985	0.76974	0.77023	0.77057	0.77152	0.77212	0.77282	0.77444	0.77628	0.77856
0.04	0.04	0.12	0.75804	0.75785	0.75747	0.75752	0.75774	0.75794	0.75883	0.75908	0.75960	0.76089	0.76239	0.76449
0.04	0.02	0.14	0.72485	0.72716	0.72921	0.73110	0.73278	0.73418	0.73553	0.73605	0.71738	0.73769	0.73840	0.73898
0.08	0.02	0.14	0.70798	0.70989	0.71161	0.71311	0.71447	0.71555	0.71655	0.71699	0.73800	0.71807	0.71836	0.71875
0.06	0.03	0.13	0.72606	0.72849	0.73059	0.73239	0.73396	0.73562	0.73702	0.73734	0.72804	0.73917	0.73994	0.74050
0.09	0.03	0.13	0.71764	0.71975	0.72158	0.72328	0.72484	0.72604	0.72723	0.72751	0.77289	0.72877	0.72949	0.73015

seven solutions without Cl^- and eleven solutions with Cl^- to make the solution an isotonic saline solution with an ionic strength of I = 0.16 mol·kg^{-1}. The cell potential values have been corrected to a hydrogen pressure of 101.325 kPa. At the experimental temperature range, the uncertainty in the cell potential measurement was within 0.02 mV on the average.

pH of the HEPPS Buffer. The Bates et al.[8,9,12−14] method has been used to evaluate the conventional standard pH values for all buffer solutions. For accurate calculations of eighteen buffer solutions, the following Harned-type of cell A is used for the collection of cell voltage data:

$$\mathrm{Pt(s), H_2(g), 101.325\ kPa|HEPPS}(m_1) + \mathrm{NaHEPPS}(m_2) + \mathrm{NaCl}(m_3)|\mathrm{AgCl(s), Ag(s)} \quad \text{(A)}$$

where m_1, m_2, and m_3 denote the molalities of the respective species at 1 atm =101.325 kPa in SI units.

dx.doi.org/10.1021/je200629y |J. Chem. Eng. Data 2011, 56, 4126–4132

Table 3. $p(a_H\gamma_{Cl})^\circ$ of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K Obtained by Extrapolation for Chloride-Free Solutions[a]

T	0.02 m HEPPS + 0.04 m NaHEPPS	0.02 m HEPPS + 0.08 m NaHEPPS	0.04 m HEPPS + 0.02 m NaHEPPS	0.04 m HEPPS + 0.08 m NaHEPPS	0.03 m HEPPS + 0.09 m NaHEPPS	0.06 m HEPPS + 0.03 m NaHEPPS	0.08 m HEPPS + 0.02 m NaHEPPS
K	I = 0.04 m	I = 0.08 m	I = 0.02 m	I = 0.08 m	I = 0.09 m	I = 0.03 m	I = 0.02 m
278.15	8.569	8.897	7.970	8.597	8.782	7.935	7.681
283.15	8.503	8.833	7.901	8.521	8.711	7.870	7.613
288.15	8.438	8.775	7.832	8.453	8.642	7.804	7.547
293.15	8.371	8.707	7.768	8.383	8.575	7.736	7.483
298.15	8.309	8.645	7.705	8.315	8.507	7.668	7.419
303.15	8.248	8.581	7.643	8.250	8.441	7.605	7.361
308.15	8.184	8.519	7.583	8.192	8.378	7.542	7.299
310.15	8.163	8.497	7.561	8.160	8.353	7.517	7.275
313.15	8.126	8.490	7.527	8.124	8.313	7.482	7.239
318.15	8.066	8.399	7.469	8.063	8.249	7.420	7.180
323.15	8.010	8.343	7.416	8.002	8.183	7.360	7.123
328.15	7.947	8.276	7.357	7.941	8.119	7.299	7.064

[a] m = 1 mol·kg^{-1}.

Table 4. $p(a_H\gamma_{Cl})$ of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K, Computed Using eq 3[a]

T	0.02 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.02 m HEPPS + 0.04 m NaHEPPS + 0.12 m NaCl	0.04 m HEPPS + 0.08 m NaHEPPS + 0.08 m NaCl	0.04 m HEPPS + 0.04 m NaHEPPS + 0.12 m NaCl
K	I = 0.16 m	I = 0.16 m	I = 0.16 m	I = 0.16 m
278.15	8.458	8.578	8.622	8.572
283.15	8.423	8.455	8.493	8.449
288.15	8.304	8.334	8.369	8.329
293.15	8.195	8.229	8.258	8.224
298.15	8.101	8.132	8.163	8.128
303.15	8.014	8.043	8.071	8.037
308.15	7.941	7.965	7.994	7.962
310.15	7.913	7.938	7.968	7.932
313.15	7.878	7.897	7.927	7.890
318.15	7.819	7.839	7.870	7.831
323.15	7.771	7.783	7.820	7.779
328.15	7.734	7.742	7.779	7.739

[a] m = 1 mol·kg^{-1}.

The evaluation of the liquid junction potential was made using cell B:

$$\mathrm{Pt(s), H_2(g), 101.325\ kPa|HEPPS}(m_1) + \mathrm{NaHEPPS}(m_2) + \mathrm{NaCl}(m_3)\|\mathrm{KCl(satd), Hg_2Cl_2(s), Hg(l)} \quad \text{(B)}$$

where the abbreviations "s", "l", and "g" denote the solid, liquid, and gaseous states, respectively. The values of the standard electrode potential,[15] E°_{SCE}, of the saturated calomel electrode were taken as (−0.2415 and −0.2335) V at (298.15 and 310.15) K, respectively.

The cell diagram for cell C is as follows:

$$\mathrm{Pt(s), H_2(g), 101.325\ kPa|KH_2PO_4 + Na_2HPO_4\|KCl(satd), Hg_2Cl_2(s), Hg(l)} \quad \text{(C)}$$

Table 5. $p(a_H\gamma_{Cl})$ of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K, Computed Using eqs 3, 4, 5, and 6[a]

T	0.04 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.08 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.06 m HEPPS + 0.03 m HEPPS + 0.13 m NaCl	0.09 m HEPPS + 0.03 m HEPPS + 0.13 m NaCl
K	I = 0.16 m	I = 0.16 m	I = 0.16 m	I = 0.16 m
278.15	8.035	7.732	8.027	7.874
283.15	7.967	7.662	7.961	7.805
288.15	7.899	7.594	7.894	7.736
293.15	7.834	7.527	7.826	7.670
298.15	7.771	7.463	7.761	7.606
303.15	7.707	7.399	7.701	7.542
308.15	7.646	7.315	7.613	7.545
313.15	7.587	7.278	7.577	7.417
318.15	7.528	7.220	7.522	7.357
323.15	7.470	7.160	7.464	7.301
328.15	7.412	7.104	7.405	7.246

[a] m = 1 mol·kg^{-1}.

where the phosphate salts are NBS/NIST primary standard physiological buffer solution.

The E_j values were obtained by using the flowing junction cell[7,9,14] and were calculated from the following equation:

$$E_j = E + E^\circ_{SCE} - k\mathrm{pH} \quad (1)$$

where k = 0.059156 and pH 7.415 at (298.15) K and k = 0.061538 and pH 7.395 at (310.15) K. The pH values are that of the standard phosphate buffer solution. The values of pH(x), can be calculated from the equation:

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

where "x" refers to the unknown buffer (in this case, a solution of HEPPS + NaHEPPS), "s" is the NBS/NIST standard buffer

dx.doi.org/10.1021/je200629y |J. Chem. Eng. Data 2011, 56, 4126–4132

Table 6. pH(s) of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K, Computed Using eqs 4, 5, 6, and 7[a]

T	0.02 m HEPPS + 0.04 m NaHEPPS	0.02 m HEPPS + 0.08 m NaHEPPS	0.04 m HEPPS + 0.02 m NaHEPPS	0.04 m HEPPS + 0.08 m NaHEPPS	0.03 m HEPPS + 0.09 m NaHEPPS	0.06 m HEPPS + 0.03 m NaHEPPS	0.08 m HEPPS + 0.02 m NaHEPPS
K	I = 0.04 m	I = 0.08 m	I = 0.02 m	I = 0.08 m	I = 0.09 m	I = 0.03 m	I = 0.02 m
278.15	8.492	8.798	7.912	8.497	8.678	7.866	7.623
283.15	8.425	8.733	7.842	8.421	8.607	7.801	7.555
288.15	8.360	8.671	7.773	8.353	8.538	7.734	7.488
293.15	8.294	8.607	7.709	8.283	8.471	7.667	7.424
298.15	8.230	8.544	7.645	8.214	8.402	7.601	7.359
303.15	8.168	8.479	7.583	8.149	8.335	7.535	7.301
308.15	8.104	8.416	7.522	8.084	8.272	7.471	7.239
310.15	8.083	8.394	7.500	8.057	8.246	7.446	7.215
313.15	8.046	8.357	7.466	8.020	8.206	7.410	7.178
318.15	8.985	8.295	7.408	7.959	8.141	7.348	7.119
323.15	8.929	8.234	7.354	7.897	8.074	7.287	7.060
328.15	8.865	8.170	6.295	7.835	8.009	7.225	7.001

[a] m = 1 mol·kg^{-1}.

Table 7. pH(s) of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K, Computed Using eqs 4, 5, 6, and 7[a]

T	0.02 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.02 m HEPPS + 0.04 m NaHEPPS + 0.12 m NaCl	0.04 m HEPPS + 0.08 m NaHEPPS + 0.08 m NaCl	0.04 m HEPPS + 0.04 m NaHEPPS + 0.12 m NaCl
K	I = 0.16 m	I = 0.16 m	I = 0.16 m	I = 0.16 m
278.15	8.423	8.453	8.496	8.446
283.15	8.298	8.329	8.367	8.323
288.15	8.178	8.208	8.244	8.203
293.15	8.070	8.104	8.133	8.099
298.15	7.975	8.005	8.036	8.001
303.15	7.887	7.916	7.944	7.910
308.15	7.814	7.838	7.866	7.834
310.15	7.785	7.811	7.840	7.804
313.15	7.750	7.769	7.799	7.762
318.15	7.690	7.709	7.741	7.702
323.15	7.641	7.652	7.690	7.649
328.15	7.603	7.611	7.648	7.608

[a] m = 1 mol·kg^{-1}.

solution of known pH, and $\delta E_j = E_{j(s)} - E_{j(x)}$. If $\delta E_j = 0$, the values of pH(x) will be without liquid junction.

Using cell A, the values of the cell potential (E), m_1, m_2, and m_3, and the standard electrode potential of the Ag−AgCl electrode ($E\circ$) are listed in Tables 1 and 2. In order to calculate pH(s), the values of the acidity function, $p(a_H\gamma_{Cl})$, are required. For this, the following equation[11,12] is used:

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

where "k" is the Nernst slope.

From linear regression analysis[16] by plotting $p(a_H\gamma_{Cl})$ against the molality of the chloride ion, the value of $p(a_H\gamma_{Cl})\circ$ value at $m_{Cl^-} = 0$ is obtained. These $p(a_H\gamma_{Cl})\circ$ values for the seven 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 Tables 4 and 5 from (278.15 to 328.15) K.

Conventional pH(s) values for NaCl free buffer solutions without liquid junction and were determined using the ensuing equation:

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

where the single-ion activity coefficient, γ°_{Cl}, cannot be experimentally measured. The pH values obtained from the liquid junction cell are indicated by pH whereas the "conventional" pH calculated from eq 5 is designated as pH(s). The Bates−Guggenheim convention[17] is expressed by

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

The International Union of Pure and Applied Chemistry has recommended this convention. Equation 5 is assumed to be true for concentrations at $I \le 0.1$ mol·kg^{-1}. For $I > 0.1$ mol·kg^{-1}, there is no widely used convention.

Because of this need, a pH convention[7,9] based on an extended version of the Debye−Hückel equation[7] has been selected to be the more logical approach to calculate $\log \gamma^\circ_{Cl}$ for all of the buffer solutions with and without NaCl. This equation is shown below:

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

where "I" is the ionic strength of the buffer solution, "A" and "B" are known as the Debye−Hückel constants, and "C" is an adjustable parameter. $Ba\circ$ was assumed to be 1.38 kg$^{1/2}$·mol$^{-1/2}$ for all of the experimental temperatures. The following empirical equation is used to calculate the adjustable parameter "C" by using a curve-fitting method:[7,9]

$$C = C_{298.15} + (6.2\cdot10^{-4})(T - 298.15) - (8.7\cdot10^{-6})(T - 298.15)^2 \quad (7)$$

where $C_{298.15}$ = 0.032 kg·mol^{-1} at (298.15) K[7] and T is the absolute temperature.

dx.doi.org/10.1021/je200629y |J. Chem. Eng. Data 2011, 56, 4126–4132

Table 8. pH(s) of HEPPS + NaHEPPS Buffer Solutions From (278.15 to 328.15) K, Computed Using eqs 4, 5, 6, and 7[a]

T	0.04 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.08 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.06 m HEPPS + 0.03 m HEPPS + 0.13 m NaCl	0.09 m HEPPS + 0.03 m HEPPS + 0.13 m NaCl
K	I = 0.16 m	I = 0.16 m	I = 0.16 m	I = 0.16 m
278.15	7.910	7.606	7.901	7.749
283.15	7.841	7.536	7.835	7.680
288.15	7.774	7.468	7.768	7.610
293.15	7.709	7.402	7.701	7.545
298.15	7.644	7.337	7.634	7.480
303.15	7.580	7.272	7.574	7.415
308.15	7.518	7.210	7.512	7.352
310.15	7.495	7.187	7.486	7.326
313.15	7.459	7.149	7.449	7.289
318.15	7.399	7.091	7.391	7.228
323.15	7.340	7.029	7.334	7.171
328.15	7.281	6.972	7.274	7.115

[a] m = 1 mol·kg^{-1}.

Table 9. Cell Voltage of Cell B for HEPPS Buffer

m_1	m_2	m_3	E/V	
mol·kg^{-1}			298.15 K	310.15 K
0.06	0.03	0.00	0.65785	0.69663
0.02	0.02	0.14	0.71354	0.71313
0.02	0.04	0.12	0.71546	0.71473

cell voltage of cell C[a]		
	E/V	
cell C	298.15 K	310.15 K
0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4	0.68275	0.69147

[a] Corrected to a hydrogen pressure of 101.325 kPa for physiological phosphate buffer solutions (primary reference standard buffer) at (298.18 to 328.15) K.

The pH(s) values listed in Table 6 for the seven HEPPS buffer solutions without the Cl^- were calculated using the following equations with the range of molalities m_1 and m_2 in the unit of mol·kg^{-1}:

$$\mathrm{pH(s)} = 8.231 + (-1.27\cdot10^{-2})(T-298.15) + (1.84\cdot10^{-5})(T-298.15)^2, \quad m_1 = 0.02,\ m_2 = 0.04 \tag{8}$$

$$\mathrm{pH(s)} = 8.543 + (-1.26\cdot10^{-2})(T-298.15) + (6.17\cdot10^{-6})(T-298.15)^2, \quad m_1 = 0.02,\ m_2 = 0.08 \tag{9}$$

$$\mathrm{pH(s)} = 7.646 + (-1.26\cdot10^{-2})(T-298.15) + (3.26\cdot10^{-5})(T-298.15)^2, \quad m_1 = 0.04,\ m_2 = 0.02 \tag{10}$$

Table 10. Values of the Liquid Junction Potentials for HEPPS Buffer at (298.15 and 310.15) K

system	E_j^a/mV	
	298.15 K	310.15 K
physiological phosphate (0.008695 m KH_2PO_4 + 0.03043 m NaCl)	2.6	2.9
0.06 m HEPPS + 0.03 m NaHEPPS + 0.00 m NaCl	2.2	2.5
0.02 m HEPPS + 0.02 m NaHEPPS + 0.14 m NaCl	0.3	0.6
0.02 m HEPPS + 0.04 m NaHEPPS + 0.12 m NaCl	0.4	0.6

[a] $E_j = E + E^\circ_{SCE} - k$ pH from eq 1 is the emf from Table 9, k = Nernst slope with values 0.059156 at 298.15 K, and 0.061538 at 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; 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}.

$$\mathrm{pH(s)} = 8.215 + (-1.35\cdot10^{-2})(T-298.15) + (2.75\cdot10^{-5})(T-298.15)^2, \quad m_1 = 0.04,\ m_2 = 0.08 \tag{11}$$

$$\mathrm{pH(s)} = 8.404 + (-1.34\cdot10^{-2})(T-298.15) + (1.07\cdot10^{-5})(T-298.15)^2, \quad m_1 = 0.03,\ m_2 = 0.09 \tag{12}$$

$$\mathrm{pH(s)} = 7.601 + (-1.30\cdot10^{-2})(T-298.15) + (1.72\cdot10^{-5})(T-298.15)^2, \quad m_1 = 0.06,\ m_2 = 0.03 \tag{13}$$

$$\mathrm{pH(s)} = 7.362 + (-1.26\cdot10^{-2})(T-298.15) + (2.04\cdot10^{-5})(T-298.15)^2,\ m_1 = 0.08,\ m_2 = 0.02 \tag{14}$$

for the temperature range of (278.15 to 328.15) K. The standard deviations are 0.0017, 0.0012, 0.0017, 0.0013, 0.0016, 0.0014, and 0.0013, respectively.

For the eight buffer solutions containing Cl^-, with an isotonic saline media ionic strength of I = 0.16 mol·kg^{-1}, the pH(s) values were also calculated using eqs 3, 4, 6, and 7. The values of pH(s) are expressed by the following equations:

$$\mathrm{pH(s)} = 7.976 + (-1.83\cdot10^{-2})(T-298.15) + (1.98\cdot10^{-4})(T-298.15)^2 \tag{15}$$

$$\mathrm{pH(s)} = 8.001 + (-1.86\cdot10^{-2})(T-298.15) + (1.84\cdot10^{-4})(T-298.15)^2 \tag{16}$$

$$\mathrm{pH(s)} = 8.006 + (-1.87\cdot10^{-2})(T-298.15) + (1.83\cdot10^{-4})(T-298.15)^2 \tag{17}$$

dx.doi.org/10.1021/je200629y |J. Chem. Eng. Data 2011, 56, 4126–4132

Table 11. Values of pH at (298.15 and 310.15) K for HEPPS Buffer Solutions

cell B				T = 298.15 K			T = 310.15 K		
m_1	m_2	m_3		without[a]	with[b]		without[a]	with[b]	
mol·kg^{-1}			I	E_j corr	E_j corr	calc[c]	E_j corr	E_j corr	calc[c]
0.06	0.03	0.00	0.03	6.994	7.001	7.001	7.479	7.485	7.486
0.02	0.02	0.14	0.16	7.935	7.974	7.975	7.747	7.784	7.785
0.02	0.04	0.14	0.16	7.968	8.005	8.005	7.773	7.810	7.811

[a] Values obtained from eq 3 and data from Table 9. [b] Obtained from eq 2 and E_j from Table 10. [c] Obtained from Tables 6, 7, and 8.

$$\mathrm{pH(s)} = 8.036 + (-1.89\cdot10^{-2})(T-298.15) + (2.03\cdot10^{-4})(T-298.15)^2 \quad (18)$$

$$\mathrm{pH(s)} = 7.644 + (-1.28\cdot10^{-2})(T-298.15) + (2.31\cdot10^{-5})(T-298.15)^2 \quad (19)$$

$$\mathrm{pH(s)} = 7.337 + (-1.29\cdot10^{-2})(T-298.15) + (2.54\cdot10^{-5})(T-298.15)^2 \quad (20)$$

$$\mathrm{pH(s)} = 7.636 + (-1.28\cdot10^{-2})(T-298.15) + (2.50\cdot10^{-5})(T-298.15)^2 \quad (21)$$

$$\mathrm{pH(s)} = 7.478 + (-1.30\cdot10^{-2})(T-298.15) + (2.76\cdot10^{-5})(T-298.15)^2 \quad (22)$$

The observed standard deviations of regression from eqs 15−22 are 0.0021, 0.0013, 0.0020, 0.0021, 0.0009, 0.0009, 0.0014, and 0.0012, respectively.

The cell potential values of cells B and C at (298.15 and 310.15) K are given in Table 9. The values of E_j listed in Table 10 were obtained using eq 1. The total uncertainty for the pH(s) values was accounted for by combining various known sources of error: (i) extrapolation of the $p(a_H\gamma_{Cl})\circ$ plot for Cl^- free solutions, (ii) assumption for the calculation of $\log\gamma^{\circ}_{Cl}$ using eq 7, and (iii) the error in the experimental measurement from the multimeter (an error of ± 0.02 mV). This gives an overall error of ±0.01 and ±0.005 pH unit for buffer solutions with and without the presence of Cl^-, respectively. The values of eq 2 does affect the operational pH values listed in Table 11 at (298.15 and 310.15) K. For example at 310 K, the pH value with liquid junction correction for the buffer composition of m_1 = 0.02 mol·kg^{-1}, m_2 = 0.02 mol·kg^{-1}, and m_3 = 0.14 mol·kg^{-1} is 7.485 which is close to the pH of blood serum (7.407). These buffers are recommended as secondary pH standards for calibrating electrodes for pH measuring assembly in the physiological range.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rroy@drury.edu. Fax: 417-873-7856.

Funding Sources

The authors are grateful for funding from the National Institutes of Health (AREA), under the Grant 2-R15 GM 066866-03 and the diversity supplemental Grant 3-R15 GM 066866-03 S1.

ACKNOWLEDGMENT

The authors would also like to thank Rosalia Alcoser and Anna Yendes for their dedication and hard work.

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. L.; Braunschweiger, W. R.; Smith, J. R.; McCormick, J. J.; Wasman, 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.; Fuge, M. S.; Wollen, J. T.; Stegner, J. M.; Allen, K. A.; Harmon, M. A. Buffer Standards for the Biochemical pH of 3-(*N*-Morpholino)-2-hydroxypropanesulfonic Acid from (278.15 to 328.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1860–1864.

(4) Roy, L. N.; Roy, R. N.; Wollen, J. T.; Bwashi, A.; Stegner, J. M.; Downs, Z. M.; Mehrhoff, C. J.; Bodendorfer, B. M.; Allen, K. A.; Harmon, M. A.; Henson, I. B. 3-[4-(2-Hydroxyethyl)-1-piperazinyl]-propanesulfonic Acid (HEPPS) and the pH of Its Buffer Solutions from (278.15 to 328.15) K. *J. Chem. Eng. Data* **2010**, *55*, 1327–1332.

(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**, *A 65*, 267–270.

(6) Durst, R. A.; Staples, B. R. Tris/Tris HCl: 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, R. N.; Mrad, D. R.; Lord, P. A.; Carlsten, J. A.; Good, W. S.; Allsup, P.; Roy, L. N.; Kuhler, K. M.; Koch, W. F.; Wu, Y. C. Thermodynamics of the Second Dissociation Constant and Standards for pH of 3-(*N*-morpholino)propanesulfonic Acid (MOPS) From 5 to 55 ∘C. *J. Solution Chem.* **1998**, *27*, 73–87.

(10) Bates, R. G.; Vega, C. A.; White, D. R. Standards for the 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*, 2nd ed.; Wiley: New York, 1973; Chapter 10.

(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 from (278.15 to 328.15) K. *J. Chem. Eng. Data*. **2009**, *54*, 428−435, part of the special "Robin H. Stokes Festschrift" issue.

(13) Roy, R. N.; Roy, L. N.; Denton, C. E.; LeNoue, S. R.; Roy, C. N.; Ashkenazi, S.; Williams, T. R.; Church, D. R.; Fuge, M. S.; Sreepada, K. N. Second Dissociation Constant of Bis[(2-hydroxyethyl)amino]acetic Acid

(BICINE) and pH of Its Buffer Solutions from 5 to 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*, 2nd ed.; Prentice-Hall: New York, 1952.

(16) 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.

(17) Bates, R. G.; Guggenheim, E. A. Report on the Standardization of pH and Related Terminology. *Pure Appl. Chem.* **1960**, *1*, 163–168.