Buffer Standards for the Physiological pH of 3-[(1,1-Dimethyl-2-hydroxymethyl)amino]-2-hydroxypropanesulfonic Acid from (278.15 to 328.15) K†

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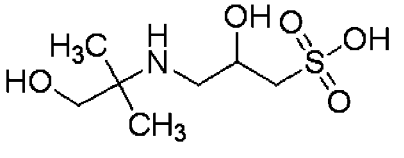
The values of the second dissociation constant, pK_2, and related thermodynamic quantities of 3-[(1,1-dimethyl-2-hydroxymethyl)amino]-2-hydroxypropanesulfonic acid (AMPSO) have already been reported in previous investigations at 12 temperatures over the temperature range (278.15 to 328.15) K, including 310.15 K (*J. Solution Chem.* **1997**, *26*, 309−317). This paper reports the results for the pH of nine buffer solutions free of the chloride ion with compositions: (a) AMPSO (0.04 mol·kg^{-1}) + NaAMPSO (0.04 mol·kg^{-1}); (b) AMPSO (0.05 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}); (c) AMPSO (0.05 mol·kg^{-1}) + NaAMPSO (0.05 mol·kg^{-1}); (d) AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}); (e) AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.02 mol·kg^{-1}); (f) AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.03 mol·kg^{-1}); (g) AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}); (h) AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.02 mol·kg^{-1}); and (i) AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.08 mol·kg^{-1}). The remaining 13 buffer solutions (j to v) have saline media of the ionic strength $I = 0.16$ mol·kg^{-1}, matching closely to that of the physiological sample. Conventional pa$_H$ values, designated as pH(s), for all nine buffer solutions (a to i) without the chloride ion and thirteen buffer solutions with the chloride ion (j to v) at $I = 0.16$ mol·kg^{-1} from (278.15 to 328.15) K have been calculated. The operational pH values for six buffer solutions at (298.15 and 310.15) K have been determined based on the difference in the values of the liquid junction potentials between the blood phosphate standard and the experimental buffer solutions. Five of these buffers are recommended as standards for the physiological pH range 7.5 to 8.5.

Introduction

In biomedical, biological, and clinical laboratories, knowledge of the pH of blood and physiological fluids is of importance. Previously, we have reported the pK_2 values of 3-[(1,1-dimethyl-2-hydroxymethyl)amino]-2-hydroxypropanesulfonic acid (AMPSO)[1] at temperatures from (278.15 to 328.15) K including 310.15 K. This zwitterionic buffer system has been recommended by Good and co-workers[2,3] for use as a physiological buffer. The structure of the AMPSO is as follows:



3-[(1,1-dimethyl-2-hydroxymethyl)amino]-2-hydroxypropanesulfonic acid

AMPSO

Standardization for calibrating electrodes of the pH meter assembly at a point close to the pH of blood (that is, 7.407) can be obtained within the framework of the former National Bureau of Standards (NBS) by using physiological phosphate pH buffer as a primary standard.[4] The phosphate buffer has been widely used as a physiological pH standard, but it is not an ideal primary pH standard buffer for physiological use at an ionic strength, $I = 0.16$ mol·kg^{-1}. The disadvantages[5] are as follows: (i) phosphates act as inhibitors to enzymatic processes, (ii) phosphate precipitates occur with some polyvalent cations, such as Mg^{2+} and Ca^{2+}, present in the blood, and (iii) the temperature coefficient of the phosphate buffer is −0.0028 pH unit·K^{-1} as compared to that of whole blood (−0.015 pH unit·K^{-1}) and plasma (0.01 pH unit·K^{-1}).[5]

Good and his associates[2,3] provided 25 primarily new biological buffers which are mostly compatible with common physiological media. They outlined suitable criteria for the evaluation of these materials. Roy et al.[6] have published the pK_2 and pH values of the biological buffer bis[(2-hydroxyyethyl)amino]acetic acid (BICINE) and the values of pH for the zwitterionic buffer *N*-[tris(hydroxymethyl)methyl-3-amino]propanesulfonic acid (TAPS).[7] Both of these buffers have been recommended as pH standards in the range of physiological applications. Feng and co-workers[8] 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.[8] The values of pK_2 and pH for 3-(*N*-morpholino)propanesulfonic acid (MOPS)[9] and 3-(*N*-morpholino)-2-hydroxypropanesulfonic acid (MOPSO)[10] have been reported. The pH of these solutions closely matches that of the common clinical media. In 1973, Bates et al.[11] recommended a pH standard for a buffer solution of 0.06 *m* tricine + 0.02 *m* sodium tricinate. Goldberg et al.[12] reported the results of the thermodynamic quantities of about

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68 physiological buffers. The comprehensive review article indicated that no results of pH are available in the literature for AMPSO.

We now propose to investigate AMPSO to provide very accurate and reproducible pH values in the range of physiological application. The following buffer compositions on the molality scale are given:

(a) AMPSO (0.04 $mol \cdot kg^{-1}$) + NaAMPSO (0.04 $mol \cdot kg^{-1}$), $I = 0.04\ mol \cdot kg^{-1}$

(b) AMPSO (0.05 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$), $I = 0.01\ mol \cdot kg^{-1}$

(c) AMPSO (0.05 $mol \cdot kg^{-1}$) + NaAMPSO (0.05 $mol \cdot kg^{-1}$), $I = 0.05\ mol \cdot kg^{-1}$

(d) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$), $I = 0.01\ mol \cdot kg^{-1}$

(e) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.02 $mol \cdot kg^{-1}$), $I = 0.02\ mol \cdot kg^{-1}$

(f) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.03 $mol \cdot kg^{-1}$), $I = 0.03\ mol \cdot kg^{-1}$

(g) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$), $I = 0.01\ mol \cdot kg^{-1}$

(h) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.02 $mol \cdot kg^{-1}$), $I = 0.02\ mol \cdot kg^{-1}$

(i) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.08 $mol \cdot kg^{-1}$), $I = 0.08\ mol \cdot kg^{-1}$

(j) AMPSO (0.05 $mol \cdot kg^{-1}$) + NaAMPSO (0.05 $mol \cdot kg^{-1}$) + NaCl (0.11 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$ (isotonic saline media).

(k) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.08 $mol \cdot kg^{-1}$) + NaCl (0.08 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(l) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.02 $mol \cdot kg^{-1}$) + NaCl (0.14 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(m) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.02 $mol \cdot kg^{-1}$) + NaCl (0.14 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(n) AMPSO (0.02 $mol \cdot kg^{-1}$) + NaAMPSO (0.04 $mol \cdot kg^{-1}$) + NaCl (0.12 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(o) AMPSO (0.02 $mol \cdot kg^{-1}$) + NaAMPSO (0.02 $mol \cdot kg^{-1}$) + NaCl (0.14 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(p) AMPSO (0.03 $mol \cdot kg^{-1}$) + NaAMPSO (0.03 $mol \cdot kg^{-1}$) + NaCl (0.13 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(q) AMPSO (0.05 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$) + NaCl (0.15 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(r) AMPSO (0.09 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$) + NaCl (0.15 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(s) AMPSO (0.08 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$) + NaCl (0.15 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(t) AMPSO (0.04 $mol \cdot kg^{-1}$) + NaAMPSO (0.04 $mol \cdot kg^{-1}$) + NaCl (0.12 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(u) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.03 $mol \cdot kg^{-1}$) + NaCl (0.13 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

(v) AMPSO (0.06 $mol \cdot kg^{-1}$) + NaAMPSO (0.01 $mol \cdot kg^{-1}$) + NaCl (0.15 $mol \cdot kg^{-1}$), $I = 0.16\ mol \cdot kg^{-1}$

The detailed procedure for the preparation of these buffer solutions for AMPSO is described in the Experimental Section.

Experimental

AMPSO was purchased from Sigma Chemical Co. (St. Louis, Missouri). The details of the purification by further crystallization as well as the determination of the assay have been reported in an earlier paper.[1] In the present study, the analyses of the unpurified and purified AMPSO averaged (99.71 and 99.88) % pure, respectively. A standard solution of NaOH was used to assay both materials and showed that the AMPSO was 0.9975 ± 0.0003. All mass measurements were made with a mass factor uncertainty of 0.02 %, substance AMPSO, NaCl (ACS reagent grade dried at 383.15 K), a standard solution of NaOH to prepare NaAMPSO, and finally calculated amounts of CO_2-free doubly distilled water. Air buoyancy corrections were applied for all masses used.

The preparation of the hydrogen electrodes and the silver−silver chloride electrodes of the thermal electrolytic type,[13] the design of the all-glass cells, the purification of the hydrogen gas, and preparation of the solutions, control of temperature, and use of digital voltmeter have been reported previously.[1,9] A correction for the residual liquid-junction potential is required if accurate pH values are to be achieved. Thus, the cells studied were the following

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

where m_1, m_2, and m_3 indicate molalities of the respective species, and 101.325 kPa is the pressure of hydrogen in SI units. The flowing junction cell (B) was used for the evaluation of the liquid junction potential at the contact between the buffer solution and the heavier saturated KCl solution of the calomel electrode shown with a double vertical line.

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

where the abbreviations (s), (l), and (g) denote solid, liquid, and gaseous state, respectively.

For cell (C), the phosphate salts were NIST standard reference materials with the composition [KH_2PO_4 (0.008695 $mol \cdot kg^{-1}$) + Na_2HPO_4 (0.03043 $mol \cdot kg^{-1}$)], and its solutions are recommended for pH measurements in physiological solutions.

$$\text{Pt(s); } H_2\text{(g), 101.325 kPa}|\text{phosphate buffer}\|\text{KCl(satd)}|Hg_2Cl_2\text{(s), Hg(l)} \quad \text{(C)}$$

The values of the liquid junction potential, E_j, for the physiological phosphate solutions and other experimental buffer solutions of AMPSO from cell (B) were obtained[8,9] using the following equation[9]

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

where $E^{\circ}_{SCE} = -0.2415$ V, $k = 0.059156$, and pH = 7.415 (physiological phosphate buffer solution) at 298.15 K; $E^{\circ}_{SCE} = -0.2335$, $k = 0.061538$, and pH = 7.395 at 310.15 K. We have attempted to calculate values of the liquid junction potential for six buffer solutions out of 19 buffer solutions. The difference in E_j between the phosphate standard and each experimental buffer solution is an important factor when different standards are selected to obtain the values of the operational pH for an unknown medium. This error can be estimated by the operational definition of pH, indicated as pH(x), by

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

where the subscript "x" refers to the unknown buffer AMPSO + NaAMPSO; s is the reference solution (NIST physiological phosphate buffer) of known pH; and $\delta E_j = E_{j(s)} - E_{j(x)}$. If $\delta E_j = 0$, then eq 2 takes the form

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

Methods and Results

The cell potential data for cell (A) containing nine buffer solutions without the presence of a chloride ion, and thirteen

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

$\text{mol}\cdot\text{kg}^{-1}$								T/K					
m_1	m_2	m_3	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
0.04	0.04	0.005	0.89389	0.89499	0.89622	0.89709	0.89796	0.89877	0.89933	0.89944	0.89961	0.89985	0.90004	0.90012
0.04	0.04	0.010	0.87761	0.87869	0.87969	0.88039	0.88093	0.88141	0.88175	0.88181	0.88190	0.88201	0.88162	0.88167
0.04	0.04	0.015	0.86849	0.86969	0.87054	0.87110	0.87149	0.87187	0.87204	0.87213	0.87216	0.87199	0.87166	0.87138
0.04	0.04	0.020	0.86201	0.86337	0.86414	0.86456	0.86492	0.86516	0.86508	0.86519	0.86511	0.86484	0.86450	0.86400
0.05	0.01	0.005	0.85453	0.85495	0.85573	0.85614	0.85664	0.85681	0.85692	0.85703	0.85700	0.85690	0.85669	0.85648
0.05	0.01	0.010	0.83849	0.83873	0.83905	0.83917	0.83926	0.83908	0.83877	0.83875	0.83856	0.83807	0.83751	0.83704
0.05	0.01	0.015	0.82917	0.82934	0.82934	0.82933	0.82917	0.82880	0.82835	0.82827	0.82789	0.82724	0.82645	0.82570
0.05	0.01	0.020	0.82283	0.82302	0.82291	0.82266	0.82230	0.82178	0.82118	0.82102	0.82057	0.81974	0.81878	0.81792
0.05	0.05	0.005	0.89494	0.89605	0.89706	0.89800	0.89903	0.89947	0.90012	0.90013	0.90027	0.90052	0.90067	0.90068
0.05	0.05	0.010	0.87951	0.88049	0.88124	0.88201	0.88252	0.88292	0.88340	0.88346	0.88343	0.88358	0.88338	0.88320
0.05	0.05	0.015	0.87087	0.87171	0.87244	0.87303	0.87359	0.87355	0.87406	0.87418	0.87406	0.87414	0.87382	0.87355
0.05	0.05	0.020	0.86539	0.86584	0.86642	0.86707	0.86744	0.86744	0.86780	0.86807	0.86786	0.86785	0.86749	0.86721
0.06	0.01	0.005	0.84822	0.84880	0.84911	0.84930	0.84930	0.84916	0.84923	0.84902	0.84892	0.84842	0.84783	0.84720
0.06	0.01	0.010	0.83235	0.83262	0.83263	0.83256	0.83230	0.83184	0.83162	0.83127	0.83097	0.83019	0.82941	0.82817
0.06	0.01	0.015	0.82337	0.82345	0.82338	0.82338	0.82269	0.82208	0.82173	0.82125	0.82085	0.81992	0.81868	0.81727
0.06	0.01	0.020	0.81742	0.81736	0.81720	0.81693	0.81632	0.81559	0.81507	0.81460	0.81409	0.81311	0.81156	0.81000
0.06	0.02	0.005	0.86928	0.87013	0.87087	0.87137	0.87181	0.87212	0.87232	0.87241	0.87248	0.87248	0.87229	0.87195
0.06	0.02	0.010	0.85320	0.85378	0.85420	0.85438	0.85461	0.85469	0.85457	0.85456	0.85437	0.85415	0.85363	0.85303
0.06	0.02	0.015	0.84391	0.84434	0.84462	0.84450	0.84470	0.84461	0.84432	0.84421	0.84389	0.84351	0.84285	0.84208
0.06	0.02	0.020	0.83729	0.83765	0.83779	0.83749	0.83772	0.83748	0.83703	0.83699	0.83643	0.83599	0.83519	0.83430
0.06	0.03	0.005	0.87792	0.87918	0.88010	0.88078	0.88152	0.88199	0.88248	0.88265	0.88280	0.88264	0.88262	0.88239
0.06	0.03	0.010	0.86124	0.86213	0.86285	0.86328	0.86357	0.86379	0.86395	0.86400	0.86399	0.86362	0.86333	0.86272
0.06	0.03	0.015	0.85127	0.85175	0.85213	0.85231	0.85268	0.85274	0.85266	0.85265	0.85256	0.85220	0.85183	0.85129
0.06	0.03	0.020	0.84430	0.84456	0.84488	0.84497	0.84510	0.84512	0.84489	0.84483	0.84467	0.84432	0.84381	0.84310
0.08	0.01	0.005	0.84096	0.84210	0.84217	0.84239	0.84239	0.84217	0.84191	0.84182	0.84143	0.84092	0.84087	0.83957
0.08	0.01	0.010	0.82481	0.82600	0.82590	0.82555	0.82556	0.82503	0.82447	0.82427	0.82376	0.82289	0.82307	0.82118
0.08	0.01	0.015	0.81537	0.81671	0.81649	0.81618	0.81587	0.81516	0.81440	0.81413	0.81364	0.81268	0.81296	0.81061
0.08	0.01	0.020	0.80887	0.81056	0.81030	0.80972	0.80935	0.80864	0.80775	0.80745	0.80701	0.80597	0.80645	0.80370
0.08	0.02	0.005	0.86246	0.86346	0.86414	0.86475	0.86513	0.86527	0.86541	0.86549	0.86549	0.86527	0.86516	0.86482
0.08	0.02	0.010	0.84572	0.84641	0.84673	0.84702	0.84707	0.84689	0.84669	0.84672	0.84649	0.84603	0.84561	0.84489
0.08	0.02	0.015	0.83590	0.83639	0.83653	0.83655	0.83645	0.83600	0.83573	0.83569	0.83538	0.83467	0.83408	0.83324
0.08	0.02	0.020	0.82903	0.82937	0.82931	0.82925	0.82895	0.82839	0.82786	0.82783	0.82743	0.82668	0.82595	0.82490
0.08	0.08	0.005	0.89598	0.89747	0.89874	0.89978	0.90060	0.90165	0.90224	0.90224	0.90241	0.90284	0.90284	0.90253
0.08	0.08	0.010	0.88016	0.88118	0.88218	0.88291	0.88319	0.88396	0.88425	0.88431	0.88419	0.88432	0.88409	0.88370
0.08	0.08	0.015	0.87099	0.87171	0.87256	0.87318	0.87313	0.87385	0.87405	0.87393	0.87395	0.87402	0.87361	0.87330
0.08	0.08	0.020	0.86470	0.86535	0.86596	0.86638	0.86597	0.86699	0.86700	0.86698	0.86681	0.86678	0.86633	0.86583
								$E°$/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

Table 2. Cell Potential of Cell A (in Volts): Pt(s); H_2(g), 101.325 kPa | AMPSO (m_1), NaAMPSO (m_2), NaCl (m_3) | AgCl(s), Ag(s)[a]

$\text{mol}\cdot\text{kg}^{-1}$								E/V					
m_1	m_2	m_3	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	318.15K	323.15 K	328.15 K
0.05	0.05	0.11	0.82376	0.82381	0.82375	0.82349	0.82306	0.82266	0.82175	0.82159	0.82110	0.82015	0.81913	0.81788
0.08	0.08	0.08	0.83150	0.83166	0.83169	0.83160	0.83133	0.83105	0.83036	0.83015	0.82969	0.82895	0.82803	0.82702
0.08	0.02	0.14	0.78258	0.78228	0.78134	0.78038	0.77967	0.77842	0.77696	0.77614	0.77536	0.77349	0.77168	0.77005
0.06	0.02	0.14	0.79167	0.79119	0.79057	0.78979	0.78856	0.78769	0.78612	0.78550	0.78458	0.78285	0.78118	0.77942
0.02	0.04	0.12	0.84408	0.84450	0.84483	0.84515	0.84505	0.84497	0.84474	0.84460	0.84429	0.84357	0.84324	0.84236
0.02	0.02	0.14	0.81809	0.81813	0.81802	0.81734	0.81663	0.81591	0.81489	0.81453	0.81399	0.81291	0.81171	0.81054
0.03	0.03	0.13	0.82076	0.82085	0.82086	0.82007	0.81944	0.81861	0.81770	0.81730	0.81657	0.81558	0.81442	0.81306
0.05	0.01	0.15	0.77824	0.77755	0.77679	0.77535	0.77411	0.77267	0.77114	0.77050	0.76921	0.76773	0.76585	0.76400
0.09	0.01	0.15	0.76470	0.76377	0.76264	0.76105	0.75964	0.75801	0.75628	0.75557	0.75408	0.75246	0.75039	0.74815
0.08	0.01	0.15	0.76635	0.76551	0.76451	0.76338	0.76132	0.75983	0.75808	0.75727	0.75587	0.75421	0.75208	0.74985
0.04	0.04	0.12	0.82173	0.82194	0.82198	0.82203	0.82060	0.81997	0.81920	0.81884	0.81810	0.81733	0.81637	0.81512
0.06	0.03	0.13	0.80169	0.80144	0.80104	0.80052	0.79894	0.79801	0.79722	0.79670	0.79572	0.79470	0.79345	0.79184
0.06	0.01	0.15	0.77317	0.77241	0.77150	0.77049	0.76850	0.76708	0.76549	0.76481	0.76339	0.76191	0.75998	0.75788

[a] $m = 1\ \text{mol}\cdot\text{kg}^{-1}$.

buffer solutions in which NaCl had been added to make $I = 0.16\ \text{mol}\cdot\text{kg}^{-1}$, have been corrected to a hydrogen pressure of 101.325 kPa. The values of the cell potential at 298.15 K are the average of two or three readings (at the beginning, in the middle, and sometimes at the end of the temperature run). Duplicate cells usually gave readings on the average within (0.02 ± 0.01) mV in the temperature range (278.15 to 328.15) K. All these results are listed in Tables 1 and 2, respectively.

pH of AMPSO Buffer. Conventional pa_H values have been evaluated by the method of Bates et al.[11,14−17] for nine buffer solutions without NaCl and thirteen buffer solutions in the presence of NaCl. The complete buffer compositions (a to v) are listed in the Introduction section.

To calculate pa_H values for nine buffer solutions without NaCl, calculations of the values of the acidity function $p(a_H\gamma_{Cl})°$ in the absence of Cl^- and $p(a_H\gamma_{Cl})$ for all thirteen buffer solutions in the presence of Cl^- were made in the temperature range (278.15 to 328.15) K, from the cell potential (E) listed in Tables 1 and 2, the molality of the chloride ion, and $E°$. The standard potentials of the silver−silver chloride electrode are listed at the bottom of Table 1. The expression for the acidity function[11,13] is given by

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

where k is the Nernst slope.

Values of the acidity function $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ were derived at each temperature for each buffer solution and were plotted as a function of m_{Cl^-}, and straight lines of small slopes were obtained. The values of the intercepts, $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{\circ}$, for nine buffer solutions without the presence of NaCl listed above from (a) to (j), were calculated using eq 5, and are given in Table 3. The acidity function $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ for thirteen buffers (k to v) listed above are entered in Tables 4, 5, and 6 from (278.15 to 328.15) K. The uncertainty (mean deviation) introduced in this type of graphical extrapolation is usually less than 0.002 from the lines drawn. Conventional $\mathrm{pa_H}$ values for the solution without the presence of the chloride ion were calculated by the following expression

$$\mathrm{pa_H} = p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{\circ} + \log_{10} \gamma^{\circ}_{\mathrm{Cl}} \tag{5}$$

where the single-ion activity coefficient, $\gamma^{\circ}_{\mathrm{Cl}}$, cannot be measured experimentally. A nonthermodynamic convention[4,9] for the estimation of $\gamma^{\circ}_{\mathrm{Cl}}$ has been adopted for the calculation of $\mathrm{pa_H}$ by eq 5. The pH values obtained from the liquid junction cell

Table 3. $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{\circ}$ **of (AMPSO + NaAMPSO) Buffer Solutions from (278.15 to 328.15) K Obtained by Extrapolation for Chloride-Free Solution**[a]

	0.04 m AMPSO + 0.04 m NaAMPSO	0.05 m AMPSO + 0.01 m NaAMPSO	0.05 m AMPSO + 0.05 m NaAMPSO	0.06 m AMPSO + 0.01 m NaAMPSO	0.06 m AMPSO + 0.02 m NaAMPSO	0.06 m AMPSO + 0.03 m NaAMPSO	0.08 m AMPSO + 0.01 m NaAMPSO	0.08 m AMPSO + 0.02 m NaAMPSO	0.08 m AMPSO + 0.08 m NaAMPSO
T (K)	$I = 0.04\ m$	$I = 0.01\ m$	$I = 0.05\ m$	$I = 0.01\ m$	$I = 0.02\ m$	$I = 0.03\ m$	$I = 0.01\ m$	$I = 0.02\ m$	$I = 0.08\ m$
278.15	9.644	8.931	9.650	8.810	9.201	9.365	8.688	9.081	9.680
283.15	9.495	8.786	9.508	8.672	9.060	9.232	8.555	8.946	9.544
288.15	9.361	8.658	9.369	8.536	8.925	9.099	8.416	8.813	9.411
293.15	9.229	8.530	9.237	8.405	8.796	8.968	8.288	8.686	9.281
298.15	9.103	8.412	9.113	8.280	8.668	8.844	8.165	8.563	9.158
303.15	8.983	8.294	8.988	8.158	8.548	8.722	8.043	8.441	9.037
308.15	8.866	8.179	8.870	8.045	8.431	8.608	7.927	8.325	8.918
310.15	8.817	8.137	8.819	7.998	8.386	8.564	7.882	8.281	8.868
313.15	8.748	8.072	8.749	7.933	8.321	8.496	7.811	8.214	8.798
318.15	8.638	7.967	8.637	7.822	8.212	8.381	7.702	8.104	8.688
323.15	8.529	7.865	8.529	7.720	8.106	8.275	7.602	8.002	8.578
328.15	8.427	7.768	8.423	7.618	8.003	8.169	7.496	7.900	8.466

[a] $m = 1\ \mathrm{mol \cdot kg^{-1}}$.

Table 4. $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ **of (AMPSO + NaAMPSO) Buffer Solutions from (278.15 to 328.15) K Computed Using Equation 4**[a]

	0.05 m AMPSO + 0.05 m NaAMPSO + 0.11 m NaCl	0.08 m AMPSO + 0.08 m NaAMPSO + 0.08 m NaCl	0.08 m AMPSO + 0.02 m NaAMPSO + 0.14 m NaCl	0.06 m AMPSO + 0.02 m NaAMPSO + 0.14 m NaCl	0.02 m AMPSO + 0.04 m NaAMPSO + 0.12 m NaCl
T (K)	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$
278.15	9.725	9.727	9.083	9.248	10.131
283.15	9.585	9.586	8.950	9.109	9.991
288.15	9.450	9.451	8.813	8.975	9.857
293.15	9.320	9.321	8.684	8.846	9.730
298.15	9.194	9.196	8.566	8.716	9.604
303.15	9.075	9.076	8.444	8.600	9.484
308.15	8.953	8.956	8.326	8.475	9.367
310.15	8.910	8.911	8.276	8.428	9.322
313.15	8.842	8.842	8.211	8.359	9.253
318.15	8.732	8.733	8.098	8.246	9.141
323.15	8.627	8.627	7.991	8.139	9.040
328.15	8.521	8.523	7.892	8.035	8.935

[a] $m = 1\ \mathrm{mol \cdot kg^{-1}}$.

Table 5. $p(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$ **of (AMPSO + NaAMPSO) Buffer Solutions from (278.15 to 328.15) K Computed Using Equation 4**[a]

	0.02 m AMPSO + 0.02 m NaAMPSO + 0.14 m NaCl	0.03 m AMPSO + 0.03 m NaAMPSO + 0.13 m NaCl	0.05 m AMPSO + 0.01 m NaAMPSO + 0.15 m NaCl	0.09 m AMPSO + 0.01 m NaAMPSO + 0.15 m NaCl
T (K)	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$
278.15	9.727	9.743	9.035	8.789
283.15	9.588	9.605	8.896	8.651
288.15	9.455	9.472	8.764	8.516
293.15	9.319	9.334	8.627	8.381
298.15	9.190	9.206	8.502	8.257
303.15	9.068	9.080	8.379	8.135
308.15	8.946	8.960	8.260	8.017
310.15	8.900	8.913	8.215	7.972
313.15	8.833	8.842	8.142	7.898
318.15	8.722	8.733	8.037	7.795
323.15	8.616	8.626	7.930	7.689
328.15	8.513	8.520	7.828	7.585

[a] $m = 1\ \mathrm{mol \cdot kg^{-1}}$.

Table 6. $p(a_H\gamma_{Cl})$ of (AMPSO + NaAMPSO) Buffer Solutions from (278.15 to 328.15) K Computed Using Equation 4[a]

	0.08 *m* AMPSO + 0.01 *m* NaAMPSO + 0.15 *m* NaCl	0.04 *m* AMPSO + 0.04 *m* NaAMPSO + 0.12 *m* NaCl	0.06 *m* AMPSO + 0.03 *m* NaAMPSO + 0.13 *m* NaCl	0.06 *m* AMPSO + 0.01 *m* NaAMPSO + 0.15 *m* NaCl
T (K)	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$	$I = 0.16\ m$
278.15	8.819	9.726	9.397	8.943
283.15	8.682	9.589	9.259	8.805
288.15	8.549	9.457	9.126	8.671
293.15	8.421	9.333	8.998	8.544
298.15	8.285	9.191	8.859	8.407
303.15	8.165	9.068	8.738	8.286
308.15	8.047	8.949	8.625	8.168
310.15	8.000	8.903	8.578	8.122
313.15	7.927	8.832	8.506	8.048
318.15	7.823	8.725	8.402	7.944
323.15	7.715	8.621	8.299	7.839
328.15	7.611	8.517	8.194	7.734

[a] $m = 1\ \text{mol}\cdot\text{kg}^{-1}$.

Table 7. pa_H of AMPSO + NaAMPSO Buffer Solutions from (278.15 to 328.15) K Computed Using Equations 4, 5, 6, and 7[a]

	0.04 *m* AMPSO + 0.04 *m* NaAMPSO	0.05 *m* AMPSO + 0.01 *m* NaAMPSO	0.05 *m* AMPSO + 0.05 *m* NaAMPSO	0.06 *m* AMPSO + 0.01*m* NaAMPSO	0.06 *m* AMPSO + 0.02 *m* NaAMPSO	0.06 *m* AMPSO + 0.03 *m* NaAMPSO	0.08 *m* AMPSO + 0.01 *m* NaAMPSO	0.08 *m* AMPSO + 0.02 *m* NaAMPSO	0.08 *m* AMPSO + 0.08 *m* NaAMPSO
T (K)	$I = 0.04\ m$	$I = 0.01\ m$	$I = 0.05\ m$	$I = 0.01\ m$	$I = 0.02\ m$	$I = 0.03\ m$	$I = 0.01\ m$	$I = 0.02\ m$	$I = 0.08\ m$
278.15	9.567	8.888	9.566	8.767	9.142	9.296	8.644	9.023	9.581
283.15	9.418	8.742	9.424	8.629	9.001	9.163	8.511	8.888	9.444
288.15	9.283	8.614	9.285	8.492	8.866	9.029	8.372	8.754	9.311
293.15	9.151	8.486	9.152	8.361	8.737	8.899	8.244	8.627	9.181
298.15	9.024	8.368	9.028	8.235	8.608	8.774	8.120	8.503	9.056
303.15	8.903	8.249	8.902	8.113	8.487	8.652	8.000	8.381	8.935
308.15	8.786	8.134	8.783	8.000	8.370	8.537	7.881	8.265	8.815
310.15	8.737	8.091	8.731	7.953	8.325	8.492	7.837	8.220	8.766
313.15	8.667	8.026	8.661	7.887	8.259	8.424	7.765	8.153	8.694
318.15	8.557	7.920	8.549	7.776	8.151	8.308	7.656	8.043	8.584
323.15	8.447	7.819	8.440	7.674	8.044	8.201	7.556	7.940	8.473
328.15	8.345	7.721	8.333	7.571	7.940	8.095	7.449	7.837	8.360

[a] $m = 1\ \text{mol}\cdot\text{kg}^{-1}$.

Table 8. pa_H Values for AMPSO (m_1) + NaAMPSO (m_2) + NaCl (m_3) Buffer Solutions from (278.15 to 328.15) K Computed Using Equations 4, 5, 6, and 7

$\text{mol}\cdot\text{kg}^{-1}$			*T*/K											
m_1	m_2	m_3	278.15K	283.15K	288.15K	293.15K	298.15K	303.15K	308.15K	310.15K	313.15K	318.15K	323.15K	328.15K
								pa_H						
0.05	0.05	0.11	9.599	9.459	9.325	9.195	9.068	8.948	8.826	8.782	8.714	8.603	8.496	8.390
0.08	0.08	0.08	9.601	9.461	9.325	9.196	9.069	8.949	8.828	8.783	8.714	8.604	8.497	8.392
0.08	0.02	0.14	8.958	8.825	8.688	8.559	8.439	8.318	8.198	8.148	8.082	7.969	7.861	7.760
0.06	0.02	0.14	9.123	8.983	8.849	8.721	8.589	8.472	8.348	8.300	8.231	8.117	8.009	7.904
0.02	0.04	0.12	10.005	9.865	9.731	9.605	9.477	9.357	9.239	9.194	9.125	9.012	8.910	8.804
0.02	0.02	0.14	9.601	9.463	9.329	9.194	9.064	8.941	8.818	8.772	8.704	8.593	8.485	8.382
0.03	0.03	0.13	9.617	9.479	9.347	9.209	9.079	8.954	8.832	8.785	8.714	8.603	8.495	8.388
0.05	0.01	0.15	8.909	8.771	8.638	8.502	8.375	8.252	8.133	8.087	8.013	7.907	7.800	7.697
0.09	0.01	0.15	8.664	8.525	8.391	8.256	8.130	8.008	7.889	7.844	7.770	7.665	7.559	7.454
0.08	0.01	0.15	8.694	8.556	8.423	8.296	8.159	8.038	7.919	7.872	7.799	7.693	7.585	7.780
0.04	0.04	0.12	9.600	9.464	9.332	9.208	9.064	8.941	8.822	8.775	8.703	8.596	8.491	8.385
0.06	0.03	0.13	9.272	9.134	9.000	8.872	8.733	8.611	8.497	8.450	8.378	8.272	8.168	8.063
0.06	0.01	0.15	8.817	8.679	8.546	8.419	8.280	8.159	8.040	7.994	7.920	7.815	7.708	7.603

are referred by the "operational" pH, whereas the "conventional" pH calculated from eq 5 is designated as pa_H.

The convention is reasonable but is not subject to any proof. The eq 6 of a "pH convention",[4] based on an extended Debye−Hückel equation, has been widely used. In the assignment of pa_H values and in the establishment of NIST pH standard,[8,10,14−18] the calculation of $\log_{10}\gamma_{Cl}^{\circ}$ for all of the buffer−chloride solutions was made by using the following equation

$$\log_{10}\gamma_{Cl}^{\circ} = -\frac{A\sqrt{I}}{1 + Ba^{\circ}\sqrt{I}} + CI \tag{6}$$

where *I* is the ionic strength of the buffer solution; *A* and *B* are the Debye−Hückel constants;[6,7,13] hydrolysis of the buffer species is negligible; *C* is an adjustable parameter; and *Ba*° was taken to be 1.38 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$ at all temperatures.[9] In the Bates−Guggenheim convention,[4] the value of *Ba*° was assigned to be 1.5 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$, and $C = 0$ for ionic strength $I \le 0.1\ \text{mol}\cdot\text{kg}^{-1}$. The following equation is used for the calculation of the parameter *C*[8,9]

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

where $C_{298.15} = 0.032\ \text{kg}\cdot\text{mol}^{-1}$ at 298.15 K and *T* is the absolute temperature.[8]

The values of pa_H are listed in Tables 7 and 8, respectively, for nine buffer solutions of AMPSO without NaCl and thirteen

Table 9. Cell Voltage of Cell B for AMPSO Buffer

mol·kg^{-1}			E/V	
m_1	m_2	m_3	298.15 K	310.15 K
0.06	0.01	0.00	0.73067	0.72553
0.08	0.01	0.00	0.72392	0.71846
0.08	0.08	0.08	0.77784	0.77458
0.06	0.03	0.13	0.75847	0.75402
0.08	0.02	0.14	0.74108	0.73538
0.08	0.01	0.15	0.72457	0.71833

Cell Voltage of Cell C[a]

Cell C	E/V	
0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4	T = 298.15 K 0.68275	T = 310.15 K 0.69144

[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.

Table 10. Values of the Liquid Junction Potentials for AMPSO Buffer at (298.15 and 310.15) K Computed Using Equation 1

	E^a_j/mV	
system	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 AMPSO + 0.01 m NaAMPSO + 0.00 m NaCl	2.1	2.7
0.08 m AMPSO + 0.0 1 m NaAMPSO + 0.00 m NaCl	2.1	2.7
0.08 m AMPSO + 0.0 8 m NaAMPSO + 0.08 m NaCl	0.5	0.7
0.06 m AMPSO + 0.0 3 m NaAMPSO + 0.13 m NaCl	0.4	0.7
0.08 m AMPSO + 0.02 m NaAMPSO + 0.14 m NaCl	0.3	0.6
0.08 m AMPSO + 0.0 1 m NaAMPSO + 0.15 m NaCl	0.4	0.6

[a] $E_j = E + E^\circ_{\mathrm{SCE}}$-$\kappa$pH from eq 1; E is the cell voltage from Table 9; k = Nernst slope with values 0.059156 units at 298.15 K, and 0.061538 units 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, respectively; E°_{SCE} = standard electrode potential of the saturated calomel electrode = −0.2415 V and −0.2335 V at (298.15 and 310.15) K, respectively.

buffer solutions with NaCl. These are calculated using eqs 4 to 7 and are expressed as a function of temperature.

For AMPSO (0.04 mol·kg^{-1}) + NaAMPSO (0.04 mol·kg^{-1}):

$$\mathrm{pa_H} = 9.026 - 2.5145 \cdot 10^{-2}(T - 298.15) + 8.28 \cdot 10^{-5}(T - 298.15)^2 \quad (8)$$

For AMPSO (0.05 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.366 - 2.4068 \cdot 10^{-2}(T - 298.15) + 8.72 \cdot 10^{-5}(T - 298.15)^2 \quad (9)$$

For AMPSO (0.05 mol·kg^{-1}) + NaAMPSO (0.05 mol·kg^{-1}):

$$\mathrm{pa_H} = 9.026 - 2.5366 \cdot 10^{-2}(T - 298.15) + 7.68 \cdot 10^{-5}(T - 298.15)^2 \quad (10)$$

For AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.236 - 2.4741 \cdot 10^{-2}(T - 298.15) + 8.75 \cdot 10^{-5}(T - 298.15)^2 \quad (11)$$

For AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.02 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.610 - 2.4817 \cdot 10^{-2}(T - 298.15) + 8.54 \cdot 10^{-5}(T - 298.15)^2 \quad (12)$$

For AMPSO (0.06 mol·kg^{-1}) + NaAMPSO (0.03 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.776 - 2.4675 \cdot 10^{-2}(T - 298.15) + 6.74 \cdot 10^{-5}(T - 298.15)^2 \quad (13)$$

For AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.01 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.119 - 2.4681 \cdot 10^{-2}(T - 298.15) + 7.92 \cdot 10^{-5}(T - 298.15)^2 \quad (14)$$

For AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.02 mol·kg^{-1}):

$$\mathrm{pa_H} = 8.502 - 2.4437 \cdot 10^{-2}(T - 298.15) + 7.51 \cdot 10^{-5}(T - 298.15)^2 \quad (15)$$

For AMPSO (0.08 mol·kg^{-1}) + NaAMPSO (0.08 mol·kg^{-1}):

$$\mathrm{pa_H} = 9.057 - 2.4925 \cdot 10^{-2}(T - 298.15) + 5.94 \cdot 10^{-5}(T - 298.15)^2 \quad (16)$$

where 278.15 K ≤ T ≤ 328.15 K. The standard deviations of regression for the $\mathrm{pa_H}$ of the nine chloride-free buffer solutions are 0.0028, 0.0027, 0.0018, 0.0015, 0.0017, 0.0022, 0.0022, 0.0011, and 0.0019, respectively.

For 13 buffer solutions containing NaCl at an indicated ionic strength I = 0.16 mol·kg^{-1}, the values of $\mathrm{pa_H}$ listed in Table 8 are expressed by the following equations.

Table 11. Values of pH at (298.15 and 310.15) K for AMPSO Buffer Solutions Using Data for E_j Corrections from Table *10*

Cell B				T = 298.15 K			T = 310.15 K		
mol·kg^{-1}				pH					
m_1	m_2	m_3	I	without[a] E_j corr	with[b] E_j corr	calc[c]	without[a] E_j corr	with[b] E_j corr	calc[c]
0.06	0.01	0.00	0.01	8.225	8.233	8.235	7.949	7.952	7.953
0.08	0.01	0.00	0.01	8.111	8.119	8.120	7.834	7.837	7.837
0.08	0.08	0.08	0.16	9.034	9.068	9.069	8.746	8.782	8.783
0.06	0.03	0.13	0.16	8.695	8.732	8.733	8.412	8.448	8.450
0.08	0.02	0.14	0.16	8.401	8.438	8.439	8.109	8.146	8.148
0.08	0.01	0.15	0.16	8.122	8.159	8.159	7.832	7.869	7.872

[a] pH = 7.415 + [(E/V − 0.68275)/0.059156] at 298.15 K, and pH = 7.395 + [(E/V − 0.69144)/0.061538] at 310.15 K; the EMF values (Table 9) are 0.68275 V and 0.69144 V at (298.15 and 310.15) K for the physiological phosphate buffer standard solution. [b] Values obtained from eq 2 and E_j data of Table 10. [c] Obtained from Tables 7 and 8.

For AMPSO (0.05 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.05 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.11 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 9.069 - 2.4897\cdot 10^{-2}(T - 298.15) + 7.75\cdot 10^{-5}(T - 298.15)^2 \quad (17)$$

For AMPSO (0.08 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.08 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.08 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 9.070 - 2.4911\cdot 10^{-2}(T - 298.15) + 7.38\cdot 10^{-5}(T - 298.15)^2 \quad (18)$$

For AMPSO (0.08 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.02 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.14 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.436 - 2.4691\cdot 10^{-2}(T - 298.15) + 6.94\cdot 10^{-5}(T - 298.15)^2 \quad (19)$$

For AMPSO (0.06 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.02 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.14 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.592 - 2.5093\cdot 10^{-2}(T - 298.15) + 7.15\cdot 10^{-5}(T - 298.15)^2 \quad (20)$$

For AMPSO (0.02 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.04 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.12 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.592 - 2.5093\cdot 10^{-2}(T - 298.15) + 7.15\cdot 10^{-5}(T - 298.15)^2 \quad (21)$$

For AMPSO (0.02 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.02 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.14 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 9.065 - 2.5276\cdot 10^{-2}(T - 298.15) + 8.33\cdot 10^{-5}(T - 298.15)^2 \quad (22)$$

For AMPSO (0.03 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.03 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.13 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 9.079 - 2.5438\cdot 10^{-2}(T - 298.15) + 8.02\cdot 10^{-5}(T - 298.15)^2 \quad (23)$$

For AMPSO (0.05 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.01 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.15 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.32 - 2.5111\cdot 10^{-2}(T - 298.15) + 8.32\cdot 10^{-5}(T - 298.15)^2 \quad (24)$$

For AMPSO (0.09 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.01 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.15 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.131 - 2.5017\cdot 10^{-2}(T - 298.15) + 8.3\cdot 10^{-5}(T - 298.15)^2 \quad (25)$$

For AMPSO (0.08 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.01 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.15 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.161 - 2.5105\cdot 10^{-2}(T - 298.15) + 8.01\cdot 10^{-5}(T - 298.15)^2 \quad (26)$$

For AMPSO (0.04 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.04 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.12 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 9.065 - 2.5201\cdot 10^{-2}(T - 298.15) + 8.5\cdot 10^{-5}(T - 298.15)^2 \quad (27)$$

For AMPSO (0.06 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.03 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.13 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.736 - 2.5070\cdot 10^{-2}(T - 298.15) + 8.89\cdot 10^{-5}(T - 298.15)^2 \quad (28)$$

For AMPSO (0.06 $\text{mol}\cdot\text{kg}^{-1}$) + NaAMPSO (0.01 $\text{mol}\cdot\text{kg}^{-1}$) + NaCl (0.15 $\text{mol}\cdot\text{kg}^{-1}$):

$$\text{pa}_\text{H} = 8.282 - 2.5137\cdot 10^{-2}(T - 298.15) + 8.47\cdot 10^{-5}(T - 298.15)^2 \quad (29)$$

where T is the temperature in K. The standard deviations for regression of the "observed" results from eqs 17 to 29 are 0.0015, 0.0012, 0.0024, 0.0017, 0.0017, 0.0017, 0.0022, 0.0018, 0.0019, 0.0022, 0.0026, 0.0028, and 0.0024, respectively.

The potential difference of the cells (B) and (C) at (298.15 and 310.15) K are given in Table 9. By means of the flowing junction cell, the values of E_j listed in Table 10 were estimated by using eq 1. As evident from the pH data at (298.15 and 310.15) K from Table 11, there is a wide variation in pH (as high as ± 0.04 pH units). There is no known experimental method for accurately determining the single-ion activity coefficient, $\log_{10} \gamma^\circ_\text{Cl}$. Partanen and Minkkinen,[19] as well as Covington and Ferra,[20] used the Pitzer theory approach for the estimation of the single ion activity coefficient at ionic strengths higher than 0.1 $\text{mol}\cdot\text{kg}^{-1}$ in the calculation of the pH standards of the phosphate buffer solutions. In separate publications from this laboratory, the pa_H values of the standard buffer solutions will be reported by using Pitzer formalism for an ionic strength $I = 0.16\ \text{mol}\cdot\text{kg}^{-1}$ at (298.15 and 310.15) K. The calculation of $\log_{10} \gamma_\text{Cl}$ leads to uncertainty in the pa_H values. A second source is the error in the liquid junction potential measurement. However, the calculated pH values and the values obtained from the E_j corrections are in very good agreement (within ± 0.003). The total uncertainties were estimated by combining the various sources of error: (i) assumption for the calculation of the $\log_{10} \gamma^\circ_\text{Cl}$ (± 0.004 pH unit), (ii) extrapolation to $p(a_\text{H}\gamma_\text{Cl})^\circ$ at $m_\text{Cl} = 0$ (within ± 0.001 pH unit), (iii) liquid junction potential measurement using the flow junction cell, (iv) error in the experimental emf measurement (± 0.02 mV), and (v) standard potential of the Ag−AgCl electrode. Thus, the overall uncertainty is about ± 0.009 pH unit. The operational pH values at (298.15 and 310.15) K (Table 11) for six buffer solutions having the compositions (with and without the presence of NaCl) are recommended as pH standards for the measurement of the pH of blood and other physiological fluids.

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