(24) Dvorak, K.; Boublik, T. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1249.
(25) Boublik, T.; Benson, G. C. *Can. J. Chem.* **1969**, *47*, 539.
(26) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(27) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(28) Johnson, A. I.; Furter, W. F. *Can. J. Chem. Eng.* **1965**, *43*, 356.
(29) Chu, J. C. *Distillation Equilibrium Data*; Van Nostrand Reinhold: New York, 1950.
(30) Murti, P.; Van Winkle, M. *Ind. Eng. Chem.* **1958**, *50*, 72DS.
(31) Sada, E.; Morisue, T.; Yamaji, H. *Can. J. Chem. Eng.* **1975**, *53*, 350.

Received for review July 8, 1988. Revised December 20, 1989. Accepted May 15, 1990.

Dissociation Constants of Primary Phosphate Ion for pH Control in 20 and 50 Mass % 1-Propanol/Water Solvents from 37 to −10 °C

Carmen A. Vega* and Maria José Crespo

Department of Chemistry, University of Puerto Rico, Mayaguez, Puerto Rico 00708

Earlier work leading to the standard potential of the Ag/AgCl electrode in 20 and 50 mass % 1-propanol/water solvents at temperatures ranging from 37 to −10 °C has been extended to study the dissociation constants of the primary phosphate ion ($H_2PO_4^-$) in the same media at this temperature range. Cells without liquid junction, Pt;H_2(g, 1 atm)|KH_2PO_4, Na_2HPO_4, NaCl|AgCl;Ag, were used to determine the dissociation constants of $H_2PO_4^-$ in these 1-propanol/water media. Buffer solutions composed of KH_2PO_4 and Na_2HPO_4 were prepared in the molality scale (*m*) and are recommended as standards for pH measurements.

Introduction

The standard potential for the Ag/AgCl electrode in 20 and 50 mass % 1-propanol/water solvents from a wide range of temperatures has been used to study phosphate buffer solutions in the same media at temperatures ranging from 37 to −10 °C. Cells without liquid junction

Pt;H_2(g, 1 atm)|KH_2PO_4,Na_2HPO_4,NaCl|AgCl;Ag

were used to determine the dissociation constants of $H_2PO_4^-$ (second acid dissociation constants of H_3PO_4) in 20 and 50 mass % 1-propanol/water media. Over the same temperature range, the thermodynamic quantities for the dissociation process can be derived easily.

The standard potential for the Ag/AgCl electrode in 1-propanol/water solvents has been determined by several authors (*1*-*4*). The values used in this investigation were those of Elsemonghy and Fonda (*4*). Some of the needed values were extrapolated or interpolated when necessary. The E_m values used are tabulated in Table I. The measurements were made (± 0.05 mV) with a Fluke Model 8000A potentiometer. The temperature measurements were made in a thermostated bath to ±0.05 °C precision. We have now investigated the second dissociation of H_3PO_4 in 20 and 50 mass % below 0 °C. These solutions are useful as reference standards for pH measurements and control in processes such as the separation of blood plasma protein fractions (*5*) and the stabilization of chelate complexes for different metals (*6*). A comparison of the dissociation of $H_2PO_4^-$ in water (*7*) and in different alcohol/water media (*8*, *9*) is presented in Table II.

We are concerned with providing a variety of operational pH values for solutions in alcohol/water media. The hydrogen electrode behaves satisfactorily in alcohol + water solvents, and a comparison of the emf obtained with that given by a glass electrode is often substantially uninpaired at solvent compositions below 90 mass % alcohols. A pH meter is also capable of giving reproducible emf values in alcohol/water solvents.

Experimental Section

The KH_2PO_4 and Na_2HPO_4 were NBS Standard Reference Materials 186 IC and 186 IIC; they were dried for 2 h at 120 °C. The 1-propanol was obtained from Aldrich Chemical Co., Inc. (spectral grade). Solvents were prepared by weighing the desired amount of double-distilled deionized water and adding the amount of 1-propanol to the desired mass percent composition. Then the calculated amount of KH_2PO_4, Na_2HPO_4, and NaCl was added to the desired concentration ranging from 0.1 to 0.001 ionic strength. Limited solubility in 50 mass % 1-propanol precluded the measurements of phosphate/NaCl solutions, and many of the cells misbehaved as a consequence of precipitation or freezing below room temperature. But no difficulty was experienced in obtaining equilibrium values of the emf before freezing occurred.

The preparation of electrodes and other experimental details were the same as in earlier work (*10*). Cells displayed good stability and the final emf at 25 °C, obtained after the measurements descending to −10 °C, usually agreed with the initial values within 0.10 mV.

Results and Discussion

The cell used for the measurements can be represented by

Pt;Hg(g, 1 atm)|KH_2PO_4 (*m*),Na_2HPO_4 (*m*),NaCl (*m*)|AgCl;Ag

where *m* is molality. The observed data, corrected to a partial pressure of hydrogen of 1 atm (101.325 kPa) as described earlier (*10*), are listed in Table III.

The mathematical relationship between the measured emf (*E*), the standard emf ($E°$), and the thermodynamic second dissociation constant of H_3PO_4 (pK_2) value was formulated as follows:

$$pK_2' = pK_2 - \beta I = \frac{(E - E°)F}{2.3026RT} + \log m + \frac{2AI^{1/2}}{1 + Ba°I^{1/2}}$$

where I is the ionic strength (for KH_2PO_4/Na_2HPO_4/NaCl(1:1:1), I is 5 *m*), and *A* and *B* are the constants of the Debye–Huckel theory, given in Table IV together with other physical constants of the mixed solvent needed for their evaluation. The ion-size parameters $a°$, which gave a satisfactory linear extrapolation,

0021-9568/90/1735-0404$02.50/0

Table I. Standard Potential ($E°$) for the AgCl/Ag Electrode in the Cell Pt|H_2 (g, P = 101.325 kPa)|HCl (m) in Water + 20 and 50 Mass % 1-Propanol|AgCl/Ag

	$E°$ at various T, V								
X, mass %	37 °C	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C	-5 °C	-10 °C
20	0.197 73	0.206 41	0.209 82	0.213 03	0.217 20	0.220 88	0.224 56	0.228 23	0.231 91
50	0.165 05	0.174 56	0.178 49	0.182 18	0.18 210	0.190 12	0.194 04	0.197 86	0.201 88

Table II. Comparison of the Dissociation of $H_2PO_4^-$ in Water and Different Alcohol/Water Media (7-9)

ϵ[a]	pK_2	solvent	X, mass %
48.67	8.08	1-propanol/water	50
48.70	8.53	ethanol/water	50
56.30	8.44	methanol/water	50
51.61	8.69	2-methoxyethanol/water	50
68.39	7.47	1-propanol/water	20
66.40	7.80	ethanol/water	20
71.12	7.30	2-methoxyethanol/water	20
78.00	7.19	pure water	100

[a] ϵ = dielectric constant of the solvent.

were in the range 4.2–5.1 Å, depending on temperature and solvent composition.

The pK_2 was determined by linear regression methods from the values of pK_2' for each solution studied. The results for pK_2 at different temperatures are summarized in Table V. The changes of pK_2 with temperature and solvent composition are shown in Figure 1.

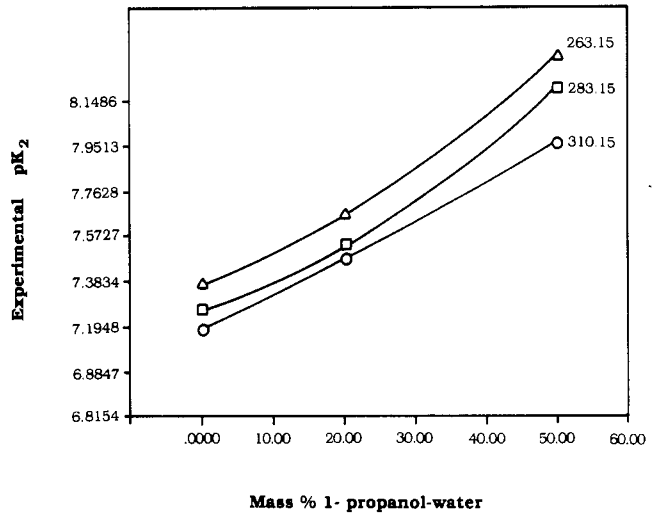

Figure 1. pK_2 values as a function of the mass percent of 1-propanol and water for the second dissociation constant of H_3PO_4.

As far as we are aware, there have been no previous attempts to provide reference solutions for the standardization of pH measurements in 1-propanol/water media at temperatures below 0 °C. The values given here should be useful. The conventional activity pH (−log a_H) values for the chloride-free

Table III. Electromotive Force Values of the Cell Pt/Hg(g, P = 101.325 kPa)|$H_2PO_4^-$ (m) in Water + 20 and 50 Mass % 1-Propanol|AgCl/Ag

	emf value					
T, K	I = 0.007 5753	I = 0.014 991	I = 0.019 867	I = 0.022 671	I = 0.024 795	I = 0.028 515
			20 Mass % 1-Propanol|AgCl/Ag			
310.15		0.805 81		0.794 70		0.789 01
298.15			0.782 82	0.784 84	0.778 17	0.777 82
293.15			0.779 13	0.780 00	2.771 95	0.771 42
288.15			0.774 19	0.770 45	0.768 21	0.766 47
283.15			0.768 73		0.761 72	0.760 40
278.15			0.763 02		0.753 35	0.754 14
273.15			0.756 87		0.748 25	
268.15			0.755 16		0.742 19	
263.15	0.717 73	0.754 28	0.742 09		0.745 74	
310.15				0.783 52	0.781 17	0.777 23
298.15			0.773 28	0.771 10	0.767 49	0.766 89
293.15		0.768 50	0.767 80	0.765 67	0.763 62	
288.15				0.760 25	0.757 91	0.756 55
283.15				0.754 42	0.751 26	0.751 32
278.15	0.758 99		0.759 83	0.748 19	0.737 14	0.745 09
273.15	0.747 74		0.749 60	0.739 76	0.735 93	0.739 84
268.15	0.741 70		0.744 51	0.733 30	0.732 54	0.734 24
263.15	0.735 55		0.741 41			0.728 77
			50 Mass % 1-Propanol|AgCl/Ag			
310.15		0.813 75		0.805 94		0.783 30
298.15		0.810 66		0.790 40		
293.15		0.804 83		0.785 26		
288.15		0.801 08		0.780 26		
283.15		0.795 58		0.774 66		
278.15		0.789 30		0.768 39		
273.15			0.776 44	0.766 20		
268.15	0.788 07	0.779 184	0.771 82	0.757 50		
263.15	0.784 58		0.774 22	0.756 74	0.755 38	
310.15	0.778 82	0.772 91		0.768 41	0.768 45	0.760 36
298.15		0.761 94	0.748 42	0.756 26	0.756 84	0.751 46
293.15	0.761 82	0.757 31		0.750 46	0.751 62	0.746 23
288.15	0.756 80	0.752 52		0.745 01	0.746 07	0.741 09
283.15	0.751 81	0.747 64		0.739 71	0.740 71	0.737 04
278.15	0.746 42	0.742 64		0.734 46	0.734 93	0.732 56
273.15		0.735 13		0.729 01		
268.15	0.734 38	0.728 69		0.722 47		
263.15		0.723 18				

Table IV. Properties of 1-Propanol/Water Solvents[a]

T, K	E°, V	d, g mL^{-1}	ϵ	A, kg mol^{-1}	B, kg mol^{-1} m^{-1}
		20 Mass % 1-Propanol/Water			
310.15	0.9604	61.38	0.6809	0.35719	67.77
298.15	0.9672	64.89	0.6669	0.3555	32.60
293.15	0.9695	66.70	0.6571	0.3541	24.09
288.15	0.9720	68.39	0.6503	0.3531	17.38
283.15	0.9748	69.82	0.6482	0.3530	12.54
278.15	0.9775	71.39	0.6448	0.3528	9.04
273.15	0.9802	72.95	0.6423	0.3527	6.20
268.15	0.9828	74.51	0.6406	0.3527	4.45
263.15	0.9855	76.07	0.6396	0.3534	2.88
		50 Mass % 1-Propanol/Water			
310.15	0.8950	43.28	1.1106	0.4106	72.49
298.15	0.9029	46.13	1.0749	0.4074	35.64
293.15	0.9054	47.42	1.0595	0.4058	25.68
288.15	0.9089	48.67	1.0476	0.4055	18.50
283.15	0.9119	49.85	1.0392	0.4042	13.335
278.15	0.9151	51.06	1.0314	0.4036	9.609
273.15	0.9182	52.28	1.0247	0.4032	6.556
268.15	0.9213	53.49	1.0197	0.4030	4.723
263.15	0.9245	54.71	1.0158	0.4029	3.051

[a] E° = potential at standard conditions; d = density; ϵ = dielectric constant; A and B are constants of the Debye–Huckel equation as a function of temperature (T).

Table V. Values of $T\mathrm{p}K_2$ for the Second Dissociation Constants of H_3PO_4 in 0, 20, and 50 Mass % 1-Propanol/Water Solvents

	$T\mathrm{p}K_2$		
T, K	0 mass %	20 mass %	50 mass %
263.15		2013.7	2188.4
268.15		2035.0	2214.8
273.15	1997.6	2066.8	2248.8
278.15	2025.4	2091.9	2275.3
283.15	2053.9	2129.1	2315.2
288.15	2083.7	2162.9	2351.6
293.15	2114.5	2197.8	2376.4
298.15	2146.0	2227.6	2410.5
303.15	2179.4		
308.15	2214.1		
310.15		2316.3	2465.8
313.15	2248.7		
318.15	2284.6		
323.15	2321.2		
328.15	2358.4		
333.15	2386.8		

phosphate buffer can be calculated from the limiting value of the acidity function $\mathrm{p}(a_H\gamma_{Cl})$ by

$$\mathrm{p}(a_H\gamma_{Cl}) = \frac{E - E^\circ}{2.3026RT} + \log m_{Cl^-}$$

At $m_{Cl} = 0$

$$\mathrm{p}a_H = \mathrm{p}(a_H\gamma_{Cl}) + \log \gamma_{Cl}$$

and

$$\mathrm{p}a_H = \mathrm{p}K_2 + \frac{3AI^{1/2}}{1 + a^\circ BI^{1/2}} + \beta I$$

The dissociation constants ($\mathrm{p}K_2$) for the primary phosphate ion ($H_2PO_4^-$) in pure water and 20 and 50 mass % 1-propanol/water are summarized in Table VI.

Conclusions

A new group of buffers with pH ranging from 7.65 to 8.32 are reported here at temperatures below 0 °C. It will be possible to buffer solutions at −5 and −10 °C with 1:1 phosphate buffer ratios and still be sure to be near the physiological pH.

Table VI. Values of $\mathrm{p}K_2$ for the Second Dissociation Constants of H_3PO_4 in Pure Water and 20 and 50 Mass % 1-Propanol/water Calculated by Using $T\mathrm{p}K_2 = A + BT + CT^2$ Equations

	$\mathrm{p}K_2$		
T, K	pure water	20 mass % 1-propanol/water	50 mass % 1-propanol/water
263.15		7.65 ± 0.09	8.32 ± 0.04
268.15		7.59 ± 0.07	8.26 ± 0.01
273.17	7.3131	7.57 ± 0.07	8.23 ± 0.04
278.15	7.2817	7.52 ± 0.06	8.18 ± 0.02
283.15	7.2537	7.52 ± 0.02	8.18 ± 0.02
288.15	7.2312	7.51 ± 0.02	8.16 ± 0.03
293.15	7.2130	7.50 ± 0.03	8.11 ± 0.03
298.15	7.1976	7.47 ± 0.03	8.08 ± 0.03
303.15	7.189		
308.15	7.185		
310.15		7.47 ± 0.02	7.95 ± 0.07
313.15	7.180		
318.15	7.180		
323.15	7.183		
328.15	7.187		
333.15	7.194		

Acknowledgment

We thank Angel L. Kaifer for his comments on the manuscript.

Glossary

A, B	Debye–Huckel constants
m	molality (mol/kg of solvent)
F	Faraday constant (96 487 C/mol)
E	potential (V)
E°	potential at standard conditions (V)
emf	electromotive force
R	gas constant
$\mathrm{p}K_2'$	second dissociation constant
I	ionic strength
β	adjustable parameter
a°	ion-size parameter
$\mathrm{p}a_H$	$-\log a_H$
γ	activity coefficient
$\mathrm{p}K_2$	thermodynamic second dissociation constant
$\mathrm{p}(a_H\gamma_{Cl})$	acidity function
mass %	mass percent

Literature Cited

(1) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *Electrochim. Acta* **1973**, *18*, 81.

(2) Roy, R. N.; Vernon, W.; Gibbons, J. J.; Bothwell, A. L. M. *J. Chem. Thermodyn.* **1971**, *3*, 883.

(3) Gentile, P. S.; Eberle, L.; Cefola, M.; Celiano, A. V. *J. Chem. Eng. Data* **1963**, *8*, 420.

(4) Elsemongy, M. M.; Fonda, A. S. *J. Chem. Thermodyn.* **1981**, *13*, 1123.

(5) Cohn, E. J.; Gurd, F. R. N.; Surgenor, D. M.; Barnes, B. A.; Brown, R. K.; Deronaux, G.; Gillespie, J. M.; Kahnt, F. W.; Lever, W. F.; Liu, C. H.; Mateiman, D.; Mouton, R. F.; Schmid, K.; Uroma, E. *J. Am. Chem. Soc.* **1950**, *72*, 465.

(6) Dadgar, A.; De Lorenzo, R. *J. Chem. Eng. Data* **1970**, *15*, 298.

(7) Bates, R. G.; Acree, S. F. *J. Res. Natl. Bur. Stand.* **1945**, *34*, 373.

(8) Paabo, M.; Robinson, R. A.; Bates, R. G. *J. Am. Chem. Soc.* **1965**, *83*, 415.

(9) Bates, R. G.; Bennetto, H. P.; Sankar, M. *Anal. Chem.* **1980**, *52*, 1598.

(10) Vega, C. A.; Butler, R. A.; Pérez, B.; Torres, C. *J. Chem. Eng. Data* **1985**, *30*, 376.

Received for review June 26, 1989. Revised January 30, 1990. Accepted June 19, 1990.