First and Second Dissociation Constants of Phosphoric Acid in 1 and 3 m Sodium Chloride Solutions from 268.15 to 318.15 K

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The acid dissociation constants of H_3PO_4 and $H_2PO_4^-$ in 1 and 3 m NaCl were determined from measurements of the electromotive force (emf) of cells without a liquid junction at intervals of 10 K from 268.15 to 318.15 K. The hydrogen gas electrode and silver–silver chloride reference electrode were used. The dissociation constants pK_1^* and pK_2^* (referred to standard states in pure NaCl solutions) were derived from the corrected emf data by a modified Harned–Ehlers method. The degree of ionization of H_3PO_4 in the solutions of the first step was large; hence, the values of m_H needed in the calculation were estimated from literature data for HCl/NaCl solutions of equal ionic strength and chloride molality. Errors introduced by approximations were eliminated by extrapolation to the limit of the pure aqueous NaCl solvent. Standard deviations of the intercepts (pK^*) at the six temperatures varied from 0.006 to 0.029. The dissociation constants in the temperature range $T = 268.15$ K to $T = 318.15$ K were fitted to equations of the form $pK^* = A/T + B + C \ln T$, the parameters of which are listed.

Introduction

Early studies, prompted by developments in solution chemistry from the laboratory of H. S. Harned, focused attention on salt effects in acid–base dissociation, especially of monoprotic acids and simple amino acids (1, 2). In recent years, the properties of electrolytes in "isotonic saline" (3) and in seawater (4) have stimulated renewed interest in this topic. Of particular concern to marine chemists are the effects of sea salts on the two dissociation steps of carbonic acid (5–7), together with the role carbonates play in the greenhouse effect and the partition of fossil fuel CO_2 between the atmosphere and the oceans (8).

Inasmuch as the distribution of carbonate among the species CO_2, HCO_3^-, and CO_3^{2-} is a function of the concentration of free hydrogen ion, an accurate index of the level of H^+ in marine systems is of primary importance. Much attention has therefore been given to a definition of pH in seawater that will lead most directly to a useful assessment of carbonate speciation (9–11). Standard reference buffer solutions of precisely assigned pH in seawater are essential for this purpose. Phosphates are a common constituent of natural waters and have important physiological functions in marine systems. Furthermore, the second dissociation range of phosphoric acid embraces the pH of normal seawater, and consequently the presence of phosphates may influence the pH and carbonate speciation.

Normal seawater has an ionic strength near 0.7, and many of its properties approximate those of a solution of NaCl, molality 0.7 mol·kg^{-1}. Consequently, Johansson and Welborg (12) and Hershey, Fernandez, and Millero (13), among others, have undertaken to determine the salt effect of NaCl on the dissociation constants of phosphoric acid in solutions of sodium chloride or in artificial seawater. In some instances, these studies have extended over a wide range of salinities at several temperatures. The method of potentiometric titration in cells with glass electrodes was generally favored, in view of its simplicity.
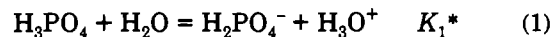
In essence, the method used in the present work, based on that devised by Harned and Ehlers (14), applied to the solvent media 1 m NaCl and 3 m NaCl instead of pure H_2O. It utilizes the hydrogen gas electrode, which is free from the salt errors that plague the glass electrode. The first and second dissociation constants of phosphoric acid were derived from measurements of the electromotive force (emf) (E) of cells without a liquid junction with silver–silver chloride reference electrodes. The cell is represented schematically as follows:

Pt;H_2 (g,101.325 kPa)|phosphate buffer,
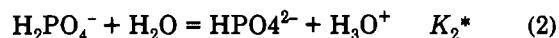
NaCl|AgCl;Ag　(A)
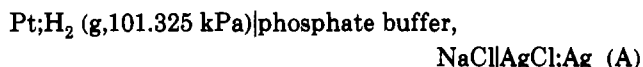
Measurements of E were made at intervals of 10 K from 268.15 to 318.15 K; they permit estimates of the enthalpy and entropy changes upon dissociation to be made.

The first dissociation is represented by

$$H_3PO_4 + H_2O = H_2PO_4^- + H_3O^+ \quad K_1^* \quad (1)$$

and the second by

$$H_2PO_4^- + H_2O = HPO_4^{2-} + H_3O^+ \quad K_2^* \quad (2)$$

The constants for these dissociation processes are properly designated K_1^* and K_2^*, respectively. They are thermodynamic equilibrium constants referred to standard states in either 1 m NaCl or 3 m NaCl.

Experimental Section

Potassium dihydrogen phosphate and disodium hydrogen phosphate were obtained as standard reference materials from the National Institute of Standards and Technology (NIST). Sodium chloride of reagent grade was used. The silver oxide used in forming the thermal-electrolytic Ag;AgCl electrodes was prepared and carefully washed as recommended by Bates (15). Chloroplatinic acid for the hydrogen electrodes was purchased from the Aldrich Chemical Co. The catalytic surface of platinum black was deposited electrolytically on the electrodes in a manner recommended elsewhere (15).

All of the cell solutions were prepared by weight. For the determination of K_1, the unit buffer ratio of H_3PO_4 to KH_2PO_4 was assured by addition of the calculated amount of a

Table 1. Standard Emf ($E°*$) of the Cell Pt(H₂)|HCl,NaCl(m_2)|AgCl;Ag from 268.15 to 318.15 K

	$E°*$/V				$E°*$/V	
T/K	m_2 = 1 mol·kg⁻¹	m_2 = 3 mol·kg⁻¹		T/K	m_2 = 1 mol·kg⁻¹	m_2 = 3 mol·kg⁻¹
268.15	0.251 35	0.234 46		298.15	0.236 88	0.219 00
278.15	0.247 07	0.229 64		308.15	0.231 25	0.213 45
288.15	0.242 30	0.224 51		318.15	0.225 05	0.207 63

Table 2. Emf (E) of the Cell Pt;H₂(g,101.325 kPa)|H₃PO₄(m_1),KH₂PO₄(m_1),Cl⁻(m_2)|AgCl;Ag from 268.15 to 318.15 K

		E/V					
m_1/(mol·kg⁻¹)	m_2/(mol·kg⁻¹)	268.15 K	278.15 K	288.15 K	298.15 K	308.15 K	318.15 K
0.017 585	0.9602	0.3652	0.3648	0.3638	0.3626	0.3617	0.3611
0.028 56	0.9323	0.3606	0.3603	0.3591	0.3578	0.3574	0.3566
0.035 22	0.9199	0.3580	0.3578	0.3569	0.3561	0.3546	0.3540
0.044 02	0.9000	0.3565	0.3563	0.3553	0.3543	0.3530	0.3528
0.057 23	0.8803	0.3542	0.3539	0.3528	0.3516	0.3502	0.3492
0.065 92	0.8599	0.3524	0.3524	0.3516	0.3502	0.3497	0.3491
0.066 05	0.8600	0.3526	0.3520	0.3511	0.3502	0.3487	0.3486
0.076 17	0.8402	0.3522	0.3513	0.3504	0.3494	0.3483	0.3477
0.094 23	0.7382	0.3513	0.3507	0.3496	0.3486	0.3486	0.3483
0.018 727	2.960	0.3174	0.3173	0.3161	0.3142	0.3110	0.3092
0.028 63	2.940	0.3132	0.3127	0.3114	0.3097	0.3073	0.3045
0.038 08	2.920	0.3095	0.3090	0.3080	0.3064	0.3030	0.3008
0.048 44	2.901				0.3031	0.3006	
0.048 44	2.900	0.3078	0.3073	0.3063	0.3037	0.3008	0.2987
0.066 60	2.860	0.3041	0.3035	0.3023	0.3001	0.2979	0.2964
0.095 11	2.800	0.3045	0.3037	0.3022	0.3002	0.2993	0.2978

Table 3. Emf (E) of the Cell Pt;H₂(g,101.325 kPa)|KH₂PO₄(m_1),Na₂HPO₄(m_1),NaCl(m_2)|AgCl;Ag from 268.15 to 318.15 K

		E/V					
m_1/(mol·kg⁻¹)	m_2/(mol·kg⁻¹)	268.15 K	278.15 K	dd288.15 K	298.15 K	308.15 K	318.15 K
0.010 036	0.9601	0.5904	0.5945	0.5978	0.6023	0.6071	0.6113
0.015 017	0.9402					0.6085	0.6126
0.019 979	0.9202	0.5939		0.6009	0.6056		
0.020 01	0.9201	0.5942	0.5963	0.6005	0.6049	0.6090	0.6122
0.030 01	0.8801	0.5935	0.5967		0.6055	0.6095	0.6144
0.030 04	0.8798	0.5933	0.5965	0.6018	0.6059	0.6107	0.6160
0.040 05	0.8401	0.5977	0.6012	0.6047	0.6087	0.6121	0.6164
0.050 05	0.7999	0.6007	0.6032	0.6067	0.6117	0.6153	0.6179
0.070 02	0.7202	0.6036	0.6059	0.6102	0.6148	0.6189	0.6239
0.100 03	0.6001	0.6104		0.6164	0.6210	0.6251	0.6295
0.015 654	2.920	0.5445	0.5445	0.5479	0.5494	0.5519	0.5545
0.023 47	2.880	0.5430	0.5430	0.5471	0.5501	0.5528	0.5541
0.039 13	2.800	0.5482	0.5482	0.5512	0.5541	0.5577	0.5541
0.042 86	2.915	0.5468	0.5492	0.5524	0.5558		
0.054 77	2.720	0.5473	0.5473	0.5513	0.5553	0.5584	0.5613
0.054 85	2.761	0.5483	0.5507	0.5543	0.5570	0.5619	0.5656
0.078 25	2.600	0.5517	0.5517	0.5551	0.5584	0.5615	0.5648
0.088 75	2.600	0.5534	0.5553	0.5584	0.5616	0.5641	0.5673
0.091 38	2.600		0.5549	0.5589	0.5625	0.5670	0.5711

standard solution of HCl to the weighed quantity of KH₂-PO₄. For the K_2 measurements, equal molal quantities of KH₂PO₄ and Na₂HPO₄ were used. Finally, the desired amount of NaCl was added.

A period of 12 h was allowed for initial equilibrium of the emf; at subsequent temperatures, 30 min sufficed. The values were corrected to a hydrogen partial pressure at 1 atm (101.325 kPa) with the aid of standard tables (15). A small correction for the lowered vapor pressure of the solutions of ionic strength 3 at 308.15 and 318.15 K was applied. Other details of the equipment and procedures may be found elsewhere (16, 17).

Methods and Results

The emf data were used to calculate an acidity function designated $p*$:

$$\frac{(E/V - E°*/V)F}{RT \ln 10} + \log(m_{Cl}/m_0) = -\log(a_H*\gamma_{Cl}*) \equiv p* \quad (3)$$

where T is the temperature in kelvins and m_0 = 1 mol·kg⁻¹. The asterisk signifies that the reference standard state is an aqueous solution of NaCl rather than water. The standard potential $E°*$ was derived from $E°$ in water (18) and the

activity coefficients of HCl (0.01 m) in NaCl solutions (19):

$$E°*/V = E°/V - 2k(\log \gamma_{0.01} - 0.0003) \quad (4)$$

where k is written for $(RT \ln 10)/F$. This equation embodies the linear "Harned rule" (20) for acid/salt mixtures. The standard potentials are summarized in Table 1, and the corrected emf data are listed in Tables 2 and 3.

Formally, both pK_1* and pK_2* are related to $p*$ by

$$pK* = p* - \log \frac{m_1 + m_H}{m_1 - m_H} + \log \frac{\gamma*_a\gamma*_{Cl}}{\gamma*_b} \quad (5)$$

where the subscripts a and b refer to the acid form and its conjugate base, respectively. Measurements at constant or nearly constant ionic strength (I) permit certain simplifications in the use of eq 5. For the determination of pK_1*, the last term of eq 5 is expected to be nearly negligible at all of the buffer molalities m_1, and for pK_2* it becomes so (by definition) in the pure NaCl solution without added phosphate. Hence, the true values of pK_1* and pK_2* can be obtained by extrapolation to m_1 = 0 of "apparent" values obtained with omission of the activity-coefficient term of eq

Table 4. pK_1^* and pK_2^* in the Range 368.15–318.15 K, Constants of Equation 7, and Enthalpy and Entropy of Dissociation at 298.15 K

	pK_1^*		pK_2^*	
T/K	1 m NaCl	3 m NaCl	1 m NaCl	3 m NaCl
268.15	1.774 ± 0.010^a	1.578 ± 0.022^a	6.349 ± 0.014^a	6.250 ± 0.019^a
278.15	1.765 ± 0.011	1.618 ± 0.022	6.252 ± 0.018	6.130 ± 0.025
288.15	1.745 ± 0.015	1.651 ± 0.018	6.202 ± 0.007	6.085 ± 0.021
298.15	1.748 ± 0.016	1.667 ± 0.019	6.157 ± 0.008	6.028 ± 0.019
308.15	1.755 ± 0.012	1.630 ± 0.023	6.118 ± 0.006	5.975 ± 0.025
318.15	1.797 ± 0.011	1.642 ± 0.019	6.089 ± 0.007	5.922 ± 0.029
A	3186.47	−3702.49	3057.74	2290.75
B	−71.5327	84.5469	−55.4475	−36.0650
C	10.9861	−12.3689	9.0114	6.0379
σ^b	0.010	0.015	0.008	0.016
$\Delta H^\circ/(\text{kJ·mol}^{-1})$	−1.70	−0.28	7.10	9.39
$\Delta S^\circ/(\text{J·K}^{-1}\text{·mol}^{-1})$	−39	−33	−94	−84

[a] Standard deviation of the intercept (pK^*). [b] σ = standard deviation of the fit.

5. The course of the extrapolation was closely linear, as might be expected from the Harned rule.

Calculation of pK_1^*

The first ionization of phosphoric acid is extensive, and the estimation of m_H (which amounted to 15–30% of m_1) can introduce a significant error in the calculation of pK_1^*. This difficulty was minimized earlier, and the determination of pK_1 in water achieved with reasonable accuracy, by use of buffer ratios $H_2PO_4^-/H_3PO_4$ as high as 6, in order to repress ionization (21). Salt enhances the strength of phosphoric acid, however, and an alternative procedure was deemed advisable in the present work. It was assumed that, at equal values of E, m_H is the same in the phosphate/chloride mixtures as in HCl/NaCl mixtures which have the same m_{Cl} and ionic strength. Electromotive-force values for HCl at constant ionic strength (I = 1 or 3) in solutions of NaCl can be derived with the aid of medium effects (γ_m) and Harned slopes (α_{12}) from the data of Harned and co-workers (19, 22):

$$E/\text{V} = E^\circ/\text{V} - k \log(m_H m_{Cl}/m_0^2) - 2k(\log \gamma_m + \alpha_{12}m_H/m_0) \quad (6)$$

The value of α_{12} varies from 0.038 at 283.15 K to 0.026 at 313.15 K and is essentially identical at I = 1 and I = 3. In our study, m_H did not exceed 0.018; hence, $\alpha_{12}m_H$ contributed less than 0.08 mV to E, and consequently the value α_{12} = 0.032 at 298.15 K was used at all temperatures. As the ionic strengths of the solutions were not exactly 1 or 3, the needed values of γ_m (the activity coefficient of HCl in pure NaCl solutions) were obtained by interpolation, with extrapolation to 268.15 K. It was estimated that the uncertainty thus introduced in E was less than 0.1 mV, or about 0.002 in pK. A computer program was written to evaluate m_H by successive approximations, utilizing eq 6. Apparent values of pK_1^* were then fitted to an equation linear in m_1. The intercepts at m_1 = 0 are the thermodynamic values of pK_1^* in NaCl solutions. They are listed in Table 4.

Calculation of pK_2^*

Inasmuch as the phosphate buffers with compositions given in Table 2 have pH values near 7, m_H is negligible compared with m_1, and "apparent" values of pK_2^* (derived with neglect of the last term of eq 5) are identical with the acidity function p^*. They were fitted by least-squares methods to equations linear in m_1. The intercepts (pK_2^*) are given in Table 4.

Discussion

The values of pK_1^* and pK_2^* at the six temperaures studied were fitted to the equation

$$pK^* = A/(T/\text{K}) + B + C \ln(T/\text{K}) \quad (7)$$

The parameters A, B, and C are given in Table 4. The uncertainties in pK^* are larger than similar data for phosphoric acid in pure water and consequently do not justify detailed analysis of the thermodynamics of the dissociation processes. Nevertheless, estimates of the standard changes of enthalpy (ΔH°) and entropy (ΔS°) at T = 298.15 K, also given in Table 4, are of interest, as is the effect of NaCl on these quantities and on pK. These are shown by the following comparison:

solvent	pK	$\Delta H^\circ/(\text{kJ·mol}^{-1})$	$\Delta S^\circ/(\text{J·K}^{-1}\text{·mol}^{-1})$
	First Dissociation (Equation 1)		
H_2O (21)	2.15	−7.65	−67
NaCl (1 m)	1.75	−1.7	−39
NaCl (3 m)	1.67	−0.3	−33
	Second Dissociation (Equation 2)		
H_2O (23)	7.20	4.13	−124
NaCl (1 m)	6.16	7.1	−94
NaCl (3 m)	6.03	9.4	−84

Hershey, Fernandez, and Millero (13) have determined pK_1^* and pK_2^* (concentration basis) by potentiometric titrations with the glass electrode in solutions of NaCl at ionic strengths from 0.5 to 6. Their results at 298.15 K for pK_1^* at I = 1 and I = 3 are, respectively, 1.79 and 1.73. For pK_2^*, the corresponding data are 6.33 and 6.19. Standard errors were estimated to be 0.04 and 0.02, respectively.

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