

Buffer Solutions of Potassium Dihydrogen Phosphate and Sodium Succinate at 25 °C

Maya Paabo, Roger G. Bates, and Robert A. Robinson

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A buffer mixture consisting of equal molalities (m) of potassium dihydrogen phosphate and sodium succinate is proposed as a useful reference point in the study of acid-base equilibria, bridging the present gap between pH 5.5 and pH 6.8. The $p(a_{H^+}\gamma_{Cl^-})$ at 25 °C has been determined by electromotive-force measurements for five buffer solutions in which m varied from 0.005 to 0.025. The conventional pa_H of each solution has been derived and found to be in good agreement with that calculated from existing data for the two equilibria concerned. The pa_H varies from 6.251 at $m=0.005$ to 6.109 at $m=0.025$. The buffer mixture has been used successfully for the determination of the dissociation constants of 2-nitro-4-chlorophenol and 2,6-dichlorophenol.

1. Introduction

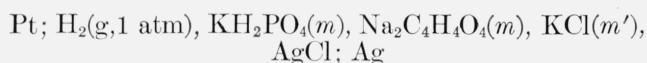
The useful application of the acidity function $-\log(a_{H^+}\gamma_{Cl^-})$ or $p(a_{H^+}\gamma_{Cl^-})$ in the accurate determination of dissociation constants or pK values has been described [1, 2].¹ In the determination of the pK of a weak acid by the spectrophotometric method, a buffer solution is needed with a value of $p(a_{H^+}\gamma_{Cl^-})$ not too far removed from the pK of the acid. For example, in the determination of the dissociation constant of p -nitrophenol at 25 °C [3], $pK=7.156$, a series of equimolar mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate of different total ionic strengths were used; their $p(a_{H^+}\gamma_{Cl^-})$ values lay between 6.912 and 7.080. For 2-chloro-4-nitrophenol, $pK=5.45$, solutions equimolar with respect to both sodium hydrogen succinate and sodium succinate were used [4]; their $p(a_{H^+}\gamma_{Cl^-})$ values lay between 5.477 and 5.553.

Neither of these buffer systems would be particularly suitable for an acid with pK about 6.2 and we have, therefore, now studied the buffer system consisting of sodium succinate and potassium dihydrogen phosphate at equal molalities (m). The $p(a_{H^+}\gamma_{Cl^-})$ values of five solutions in which m varied from 0.005 to 0.025 have been determined at 25 °C. By the application of a conventional definition of the activity coefficient of chloride ion, conventional pa_H values of these solutions have been calculated.

2. Method

The electromotive-force method by which $p(a_{H^+}\gamma_{Cl^-})$ was determined and values of pa_H assigned has been thoroughly described in earlier publications [2, 5]. It consisted of the following three steps:

1. Measurement of the emf of the following cell:



at 25 °C. Five different buffer mixtures consisting of equimolar amounts of potassium dihydrogen phosphate and sodium succinate (m varying from 0.005 to 0.025) were studied. Measurements were made with four concentrations (m') of potassium chloride, namely 0.005, 0.01, 0.015, and 0.02 molal, at each of the five buffer concentrations.

The emf was corrected to a partial pressure of 1 atm hydrogen in the usual way, and $p(a_{H^+}\gamma_{Cl^-})$ was calculated from each value of the emf (E) by the formula

$$p(a_{H^+}\gamma_{Cl^-}) = \frac{(E - E^\circ)F}{RT \ln 10} + \log m' \quad (1)$$

The standard potential (E°) was taken to be 0.22234 v at 25 °C [6], and the coefficient $F/(RT \ln 10)$ has the value 16.9047 v^{-1} at this temperature.

2. The limiting value of $p(a_{H^+}\gamma_{Cl^-})$ in the absence of potassium chloride, termed $p(a_{H^+}\gamma_{Cl^-})^\circ$, was determined for each of the five buffer solutions by plotting $p(a_{H^+}\gamma_{Cl^-})$ as a function of the molality of added potassium chloride and extrapolating to 0.

3. The conventional pa_H was computed from $p(a_{H^+}\gamma_{Cl^-})^\circ$ by the relationship.

$$pa_H = p(a_{H^+}\gamma_{Cl^-})^\circ + \log \gamma_{Cl^-} \quad (2)$$

with the use of the convention [7]

$$\log \gamma_{Cl^-} = \frac{-A\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (3)$$

where I is the ionic strength and A , the Debye-Hückel slope, has the value 0.5108 mole^{-1/2} kg^{1/2} at 25 °C.

3. Experimental Procedure

The potassium dihydrogen phosphate was NBS Standard Sample 1861b. Two different samples of sodium succinate hexahydrate, reagent grade, were used. In addition, a portion of one of the samples

¹Figures in brackets indicate the literature references at the end of this paper.

was recrystallized and dried to remove its water of hydration. There were no apparent differences among buffers made from the three samples of sodium succinate. Potassium chloride was recrystallized once from water. The conductivity of the distilled water used to prepare the solutions was no greater than $0.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

An increase of emf with time, the cause of which has not been determined, was observed. This increase was more rapid with the dilute solutions than with the more concentrated ones. It was therefore found necessary to make the emf measurements on the three most dilute buffer mixtures on the same day the solutions were prepared. However, the same values of the emf were obtained for fresh 0.02 *m* and 0.025 *m* buffer solutions on the day of preparation and one day later.

In terms of pa_H units, the 0.025 *m* buffer solution increased in pa_H by only 0.002 after standing two days and 0.012 after 12 days. However, the 0.01 *m* solution increased by 0.012 unit in 24 hr and the 0.005 *m* solution by 0.028 in the same time.

The stability of the primary and secondary phosphates in aqueous solution seems beyond question. Furthermore, no instability of buffer solutions composed of primary and secondary succinates was found in earlier work [8]. Nevertheless, it is advisable, for the greatest accuracy, to use the mixed buffers on the day of their preparation. This procedure was successful in the determination of the dissociation constants of 2-nitro-4-chlorophenol and 2,6-dichlorophenol (see below).

4. Results and Discussion

The results of the emf measurements and the calculations of $p(a_H\gamma_{Cl})$ are summarized in table 1. The average values of $p(a_H\gamma_{Cl})$ corresponding to the four molalities of potassium chloride are plotted as a function of the chloride molality in figure 1. The intercepts at $m'=0$, that is $p(a_H\gamma_{Cl})^\circ$, are given in table 2. The intercepts were determined by the method of least squares; the standard deviation of the intercept, σ_i , is given in the third column of the table. The pa_H values listed in the last column were calculated from $p(a_H\gamma_{Cl})^\circ$ together with the conventional definition of the activity coefficient of chloride ion [see eqs (2) and (3)]. The pa_H of equimolal solutions of potassium dihydrogen phosphate and sodium succinate at 25° is plotted in figure 2 as a function of the molality of each salt.

It is of interest to compare these experimental values of pa_H with the pa_H calculated from the dissociation constants for the two acid-base equilibria which fix the acidity of these buffer solutions. The dissociation constant of dihydrogen phosphate ion is given by $pK_{2P}=7.200$ at 25 °C [9], whereas that for succinate ion is expressed by $pK_{2S}=5.636$ at the same temperature [8]. From the mass law expressions for the two equilibria,

$$2 pa_H = pK_{2P} + pK_{2S} - \log \frac{m_P - m_S}{m_P = m_S} - \log \frac{\gamma_P}{\gamma_P} - \log \frac{\gamma_S}{\gamma_S} \quad (4)$$

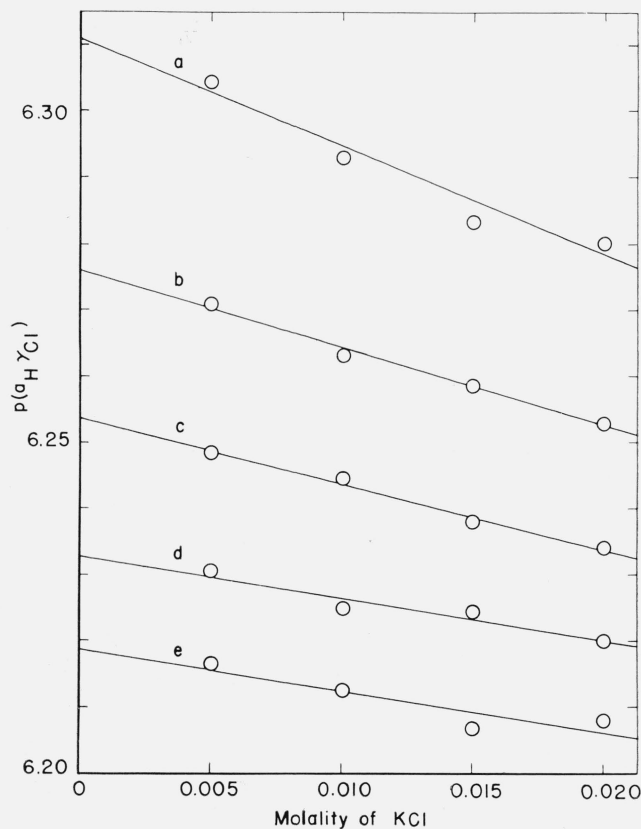


FIGURE 1. Effect of added potassium chloride on the $p(a_H\gamma_{Cl})$ for equimolal mixtures of potassium dihydrogen phosphate and sodium succinate at 25 °C.

Molality of each buffer salt: a, 0.005; b, 0.01; c, 0.015; d, 0.02; e, 0.025.

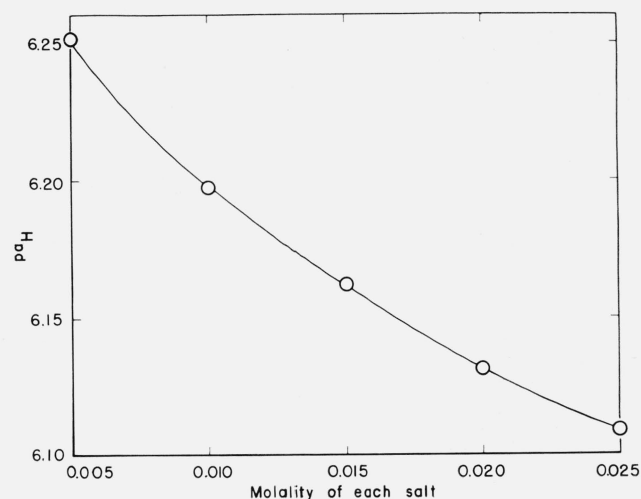


FIGURE 2. pa_H at 25 °C for equimolal mixtures of potassium dihydrogen phosphate and sodium succinate as a function of the molality of each salt.

TABLE 1. *Electromotive force of the cell Pt; H₂(g, 1 atm), KH₂PO₄(m), Na₂Suc (m'), KCl (m'), AgCl; Ag at 25 °C.*

Values of $p(a_{\text{H}}\gamma_{\text{Cl}})$

<i>m</i>	<i>m'</i>							
	0.005		0.010		0.015		0.020	
	<i>E</i>	$p(a_{\text{H}}\gamma_{\text{Cl}})$	<i>E</i>	$p(a_{\text{H}}\gamma_{\text{Cl}})$	<i>E</i>	$p(a_{\text{H}}\gamma_{\text{Cl}})$	<i>E</i>	$p(a_{\text{H}}\gamma_{\text{Cl}})$
0.025	0.72610 .72627 .72605 .72636	6.215 6.218 6.214 6.219	0.70815 .70830 .70806 .70810 .70808	6.212 6.215 6.211 6.212 6.211	0.69757 .69751 .69724 .69723	6.210 6.209 6.204 6.204	0.68990 .69013 .68999 .69026	6.205 6.209 6.206 6.211
.020	.72691 .72706 .72709	6.229 6.231 6.232	.70896 .70879 .70872 .70904	6.226 6.223 6.222 6.228	.69833 .69835 .69861	6.223 6.223 6.227	.69083 .69098 .69053	6.221 6.223 6.216
.015	.72808	6.248	.71005	6.245	.69923	6.238	.69162	6.234
.010	.72945 .72936	6.272 6.270	.71121 .71108	6.264 6.262	.70052 .70039	6.260 6.257	.69273 .69272	6.253 6.253
.005	.73136 .73140	6.304 6.304	.71298 .71296 .71279	6.294 6.294 6.291	.70191 .70193	6.283 6.283	.69430 .69439	6.279 6.281

TABLE 2. $p(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$ and pa_{H} for equimolal solutions of potassium dihydrogen phosphate and sodium succinate at 25 °C

<i>m</i>	$p(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$	σ_i	pa_{H}
0.025	6.219	0.001	6.109
.020	6.233	.001	6.131
.015	6.254	.001	6.162
.010	6.276	.001	6.197
.005	6.311	.002	6.251

where P and S refer respectively to the phosphate and succinate ions of the indicated charge.

The acid-base reaction taking place when the two buffer salts are mixed in solution may be represented by



The extent to which this reaction proceeds need not be known, for the concentration term of eq (4) has a value of unity, provided the stoichiometric molalities of potassium dihydrogen phosphate and sodium succinate were equal. Furthermore, the ionic strength (*I*) is equal to 4*m* regardless of the extent to which reaction (5) proceeds.

The last two terms of eq (4) may be estimated as follows. In the course of the investigations which led to the determination of $pK_{2\text{P}}$ and $pK_{2\text{S}}$ the quantities $\log [\gamma_{\text{P}}/(\gamma_{\text{P}} - \gamma_{\text{Cl}})]$ and $\log [\gamma_{\text{S}}/(\gamma_{\text{S}} - \gamma_{\text{Cl}})]$ in phosphate buffer solutions and succinate buffer solutions, respectively, were evaluated and found to fit the Hückel equation with ion-size parameters of 4.4 Å and 7.0 Å. If these same parameters are used to calculate the ratios of the activity coefficients of the two phosphate anions and of the two succinate anions in the mixed buffer at 25°, eq (4) then becomes

$$pa_{\text{H}} = 1/2 (pK_{2\text{P}} + pK_{2\text{S}}) - \frac{1.532 \sqrt{m}}{1 + 2.89 \sqrt{m}} - \frac{1.532 \sqrt{m}}{1 + 4.60 \sqrt{m}} \quad (6)$$

The pa_{H} values calculated by this equation are compared in table 3 with those derived directly from the emf measurements. The agreement, which is most satisfactory, lends support to the reliability of the experimental data.

TABLE 3. "Observed" and calculated values of pa_{H} for five aqueous mixtures of KH₂PO₄ and Na₂ C₄H₄O₄ at 25 °C

$m_{\text{KH}_2\text{PO}_4} = m_{\text{Na}_2\text{Suc}}$	pa_{H} (observed)	pa_{H} (calc., eq(6))
0.025	6.109	6.111
.02	6.131	6.133
.015	6.162	6.160
.01	6.197	6.194
.005	6.251	6.246

The change of pa_{H} with temperature can be calculated in a similar fashion. Inspection of eq (4) shows that the effect of temperature changes on the pa_{H} of the phosphate-succinate mixture will be a combination of the change of the mean pK with temperature and of the temperature effect on the activity coefficients. The heats of dilution of completely dissociated electrolytes are neither large nor very different in the dilute range, and it is justifiable for our purpose to replace $d \log (\gamma_{\text{P}}/\gamma_{\text{P}})/dT$ and $d \log (\gamma_{\text{S}}/\gamma_{\text{S}})/dT$ by $3 d \log \gamma_{\pm}/dT$, where γ_{\pm} is the mean ionic activity coefficient of one of the common uni-univalent strong electrolytes and *T* is the temperature in °K. From eq (4), one may therefore write

$$\frac{d}{dT} pa_{\text{H}} = \frac{1}{2} \frac{d}{dT} (pK_{2\text{P}} + pK_{2\text{S}}) - 3 \frac{d}{dT} \log \gamma_{\pm} \quad (7)$$

Data in the literature [8, 9] provide the following temperature coefficients:

$$\frac{d pK_{2\text{P}}}{dT} = 0.020912 - \frac{2073.0}{T^2} \quad (8)$$

and

$$\frac{d pK_{2\text{S}}}{dT} = 0.019153 - \frac{1679.13}{T^2} \quad (9)$$

Furthermore, it has been shown that $d \log \gamma_{\pm}/dT$ for four common strong electrolytes has the following average values at 25°: $-0.00007 \text{ deg}^{-1}$ at *I*=0.01, $-0.00012 \text{ deg}^{-1}$ at *I*=0.04, and -0.0002 deg^{-1} at *I*=0.1.

From these data it may be seen that the contribution of the changes in pK to $d pa_{\text{H}}/dT$ is $-0.00180 \text{ deg}^{-1}$ at 20 °C, $-0.00107 \text{ deg}^{-1}$ at 25 °C, and $-0.00038 \text{ deg}^{-1}$ at 30 °C. The temperature coefficient of pa_{H} at 25 °C for three of the mixed buffers is as follows:

<i>m</i>	$d pa_{\text{H}}/dT$
0.005	$-0.00086 \text{ deg}^{-1}$
.01	-0.00071
.025	-0.0004

It is clear that the phosphate-succinate mixture has

a lower p_a -temperature coefficient than either the phosphate buffer or the succinate buffer at room temperature. This is a considerable advantage when the buffer is used in spectrophotometric measurements where the temperature of the absorption cells is not well controlled.

5. Application to the Determination of Dissociation Constants

To illustrate the use of these buffer solutions in spectrophotometric work and to obtain a further check on their $p(a_H\gamma_{Cl})^\circ$ values, determinations of the dissociation constants of two substituted phenols in aqueous solution at 25 °C have been made.

In the spectrophotometric method [1, 10], the dissociation constant K of a weak uncharged acid HA,

$$K = \frac{a_H + m_A^-}{m_{HA}} \frac{\gamma_A^-}{\gamma_{HA}}, \quad (10)$$

is determined by measuring the degree of dissociation in a solution of known $p(a_H\gamma_{Cl})^\circ$ by optical methods. Substitution of α , the degree of dissociation, in eq (10) gives

$$pK = p(a_H\gamma_{Cl})^\circ - \log \frac{\alpha}{1-\alpha} - \log \frac{\gamma_A^-}{\gamma_{Cl}^\circ \gamma_{HA}}. \quad (11)$$

A small correction is made to allow for the effect of the weak acid on $p(a_H\gamma_{Cl})^\circ$ [11].

The succinate-phosphate buffer has been used to measure the dissociation constants of two substituted phenols. Details are given in tables 4 and 5. In the case of 2-nitro-4-chlorophenol (table 4), the last term of eq (11) has been neglected in arriving at pK (corr.) The average of the five pK values is 6.45₈. There is a small but regular upward trend of pK with decreasing ionic strength; this may indicate that the last term of eq (11) is not completely negligible, and extrapolation to zero ionic strength, by the method of least squares, gives pK 6.46₅. Either value is in good agreement with that obtained earlier [4].

The value now found for 2,6-dichlorophenol, 6.78₆, (table 5) is also in good agreement with 6.79₁, which has been obtained in some unpublished work, using the potassium dihydrogen phosphate-disodium hydrogen phosphate buffer.

TABLE 4. Dissociation constant of 2-nitro-4-chlorophenol in water at 25 °C

Ionic strength ^a	$p(a_H\gamma_{Cl})^\circ$	D ^b	$\log \frac{D-D_1}{D_2-D}$	pK	pK (corr.)
0.10	6.219	0.356	-0.230	6.449	6.448
.08	6.233	.359	-.223	6.456	6.455
.06	6.254	.366	-.206	6.460	6.458
.04	6.276	.374	-.187	6.463	6.460
.02	6.311	.384	-.165	6.476	6.469

$$\text{Avg. } K = 3.48 \times 10^{-7}$$

^aThe molar concentration of 2-nitro-4-chlorophenol was 4.80×10^{-5} . The buffer solutions contained equimolar disodium succinate and potassium dihydrogen phosphate.

^bThe absorption cells were 4 cm in length. D_1 , the optical density of the undissociated phenol, measured in 0.01 M HCl, was 0.062. D_2 , the optical density of the fully ionized phenol, measured in 0.01 M NaOH, was 0.855. Measurements were made at 427 mμ.

TABLE 5. Dissociation constant of 2,6-dichlorophenol in water at 25 °C

Ionic strength ^a	$p(a_H\gamma_{Cl})^\circ$	D ^b	$\log \frac{D-D_1}{D_2-D}$	pK	pK (corr.)
0.10	6.219	0.365	-0.572	6.791	6.790
.08	6.233	.376	-.556	6.789	6.787
.06	6.254	.389	-.537	6.791	6.789
.04	6.276	.409	-.509	6.785	6.782
.02	6.311	.431	-.478	6.789	6.783

$$\text{Avg. } K = 1.64 \times 10^{-7}$$

^aThe molar concentration of 2,6-dichlorophenol was 8.73×10^{-5} . The buffer solutions contained equimolar disodium succinate and potassium dihydrogen phosphate.

^bThe absorption cells were 4 cm in length. D_1 , the optical density of the undissociated phenol, measured in 0.01 M HCl, was 0. D_2 , the optical density of the fully ionized phenol, measured in 0.01 M NaOH, was 1.728. Measurements were made at 300 mμ.

6. References

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