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Formulation of dynamic buffer capacity for phytic acid

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Abstract

The general formulation of dynamic buffer capacity for polyprotic acids and bases (and polyprotic acid and base salts) has been derived. Polyprotic acids show buffer capacity over a broad range of pH values, according to their successive protonation constants. Polyprotic acids with equidistant pK_i values behave as universal buffers. The paper covers the dynamic buffer capacity for phytic acid, which posse's twelve acid groups. Phytic acid, the hexaphosphate ester of myo-inositol, has a great biological relevance, and shows antioxidant/anticancer properties.

Keywords

Acid-Base Equilibria, Buffer Capacity, Phytic Acid, Titration

1. Introduction

Phytic acid $(CHOPO(OH)_2)_6$, known as inositol hexaphosphate, IP6) is an organic acid (Fig. 1); inositol = cyclohexane-1,2,3,4,5,6-hexol [1]. As a major phosphoric component of many seeds, it is extracted mainly from rice bran. In particular, phytic acid prevents oxidative stress in seeds. Moreover, phytic acid, by virtue of its ability to chelate Fe (+2), shows antioxidant action [2-6]. Thus it is a potent inhibitor of the iron-driven formation of reactive oxygen species that adversely affect the production or storage of various forms of food. It explains why seeds belonging to many plant species are viable for a long time; in spite of the fact they contain a potentially dangerous mixture of iron, oxygen, and unsaturated fatty acids. The splitting of phytic acid, lower inositol phosphate esters and inorganic phosphate can be affected by phytase that belongs to a special class of phosphomonoesterases [7-9]. Phytic acid has also striking anticancer properties, demonstrated in both *in vivo* and *in vitro* studies [10]. Phytic acid reduces melanin spots (brightening pigmentation), shrinks dilated vessels, and acts as antioxidant. When used as facial cream, it exhibits also mild moisturizing effect.

Phytic acid is also used in analyses as an acidulant for pH adjustment [11], e.g. in capillary electrophoresis (CE [12]). Because of its twelve acidic groups, phytic acid can be used as a buffer over a wide pH range 2-11). The use of phytic acid both as a modifier and as a pH buffer results in enhanced differences between the various protein mobilities when compared with the use of monoprotic buffers; it improves e.g. resolution in protein separations [13].

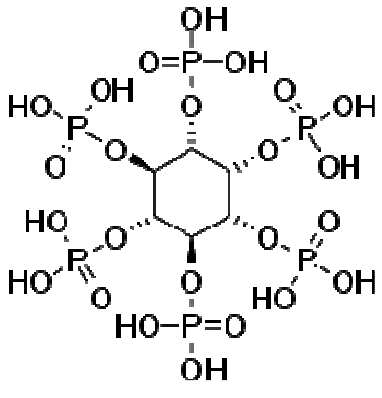


Fig. 1. *Phytic acid [14].*

2. Acid-Base Properties of Phytic Acid

The 12-protic phytic acid can be denoted briefly as $H_{12}L$. Its acid-base properties can be expressed by pKi = -logK_i (i = 1,…,12) values for successive protonation constants, K_i. An accurate knowledge of the pK_i values is essential for a thorough understanding of its reactions in solution. However, large discrepancies among these data, found in literature were stated [15,16]. The protonated species are sometimes of very similar stability. From [17] we have: pK_1 = 1.92, pK_2 = 1.92, pK_3 = 1.92, pK_4 = 2.38, pK_5 = 2.38, pK_6 = 3.16, pK_7 = 5.20, pK_8 = 6.25, pK_9 = 7.98, pK_{10} = 9.19, pK_{11} = 9.53, pK_{12} = 9.53. These pK_i values are frequently put in context with stablility constants of complexes formed by anionic species of phytic acid with different cations, see e.g. [18]

3. Formulation of Dynamic Buffer Capacity

3.1. General Notations

The dynamic buffer capacity is defined as follows [19,20]

$$\beta_V = \left|\frac{dc}{dpH}\right| \tag{1}$$

where

$$c = C \cdot \frac{V}{V_0 + V} \tag{2}$$

denotes current concentration of a reagent R in a D+T mixture obtained after addition of V mL of C mol/L solution of the reagent R (considered as titrant, T) into V_0 mL of a solution named as titrand (D). If the additivity in volumes of D and T is assumed, then the volume of D+T is V_0+V mL, at this point. In particular, the reagent R can be a strong base, MOH, a strong acid, HB, a weak polyprotic acid H_nL or its salt of $M_mH_{n-m}L$ (m = 1,…,n) or $H_{n+m}LB_m$ type [19,21]. From (1) and (2) we have

$$\beta_V = \left|\frac{dc}{dV}\cdot\frac{dV}{dpH}\right| = \frac{C\cdot V_0}{(V_0+V)^2}\cdot\left|\frac{dV}{dpH}\right| \tag{3}$$

The buffer capacity β_V is an intensive property, expressed in terms of molar concentration, i.e., intensive variable. The expressions for dV/dpH in (3) will be formulated in further parts of the paper.

For the sake of simplicity in notation, the charges of particular species $X_i^{z_i}$ can be omitted when put in square brackets, expressing molar concentration, [X_i].

Let us assume that V mL of MOH (C, mol/L) is added, as reagent R, into V_0 mL of $K_mH_{n-m}L$ (C_0, mol/L) + HB (C_{0a}, mol/L) + MOH (C_{0b}, mol/L). The concentration balances are as follows:

$$[M] = \frac{C_{0b}V_0 + CV}{V_0+V},\ [B] = \frac{C_{0a}V_0}{V_0+V},$$

$$[K] = \frac{m\cdot C_0V_0}{V_0+V},\ \sum_{i=0}^{q}[H_iL] = \frac{C_0V_0}{V_0+V} \tag{4}$$

Denoting

$$[H_iL] = K_i^H\cdot[H]^i\cdot[L] \tag{5}$$

$$b_i = K_i^H\cdot[H]^i = 10^{\log K_i^H - i\cdot pH} \tag{6}$$

$$f_i = \frac{b_i}{\sum_{j=0}^{q} b_j} \tag{7}$$

$$\alpha = [H] - [OH] = 10^{-pH} - 10^{pH-pK_W} \tag{8}$$

$$\Delta_0 = C_{0b} - C_{0a} \tag{9}$$

and applying the formula for mean number of protons attached to L^{-n} [19]

$$\begin{aligned}\bar{n} &= \frac{\sum_{i=1}^{q} i\cdot[H_iL]}{\sum_{i=0}^{q}[H_iL]} = \frac{\sum_{i=0}^{q} i\cdot K_i^H\cdot[H]^i}{\sum_{j=0}^{q} K_j^H\cdot[H]^j}\\ &= \frac{\sum_{i=0}^{q} i\cdot b_i}{\sum_{j=0}^{q} b_j} = \sum_{i=0}^{q} i\cdot f_i = \sum_{i=1}^{q} i\cdot f_i\end{aligned} \tag{10}$$

in the charge balance

$$\alpha + [M] + [K] + \sum_{i=0}^{q}(i-n)[H_iL] = 0 \tag{11}$$

we get, by turns,

$$\alpha + \frac{C_{0b}V_0 + CV}{V_0+V} - \frac{C_{0a}V_0}{V_0+V} + m\cdot\frac{C_0\cdot V_0}{V_0+V} = (n-\bar{n})\cdot\frac{C_0\cdot V_0}{V_0+V} \tag{12}$$

$$\alpha V_0 + \alpha V + \Delta_0 V_0 + CV_0 = (n-m-\bar{n})\cdot C_0\cdot V_0 \tag{13}$$

$$V = V_0\cdot\frac{(n-m-\bar{n})\cdot C_0 - \Delta_0 - \alpha}{C+\alpha} \tag{14}$$

$$\begin{aligned}V_0 + V &= V_0\cdot\frac{(n-m-\bar{n})\cdot C_0 - \Delta_0 + C}{C+\alpha}\\ &= ((n-m)\cdot C_0 - \Delta_0 + C)\cdot V_0\cdot\frac{1}{C+\alpha} - C_0\cdot V_0\cdot\frac{\bar{n}}{C+\alpha}\end{aligned} \tag{15}$$

Differentiating Eq. (15) gives

$$\frac{d(V_0+V)}{dpH}=\frac{dV}{dpH}=-((n-m)C_0-\Delta_0+C)\cdot V_0\cdot\frac{1}{(C+\alpha)^2}\cdot\frac{d\alpha}{dpH} - C_0\cdot V_0\cdot\frac{\frac{d\bar{n}}{dpH}\cdot(C+\alpha)-\bar{n}\cdot\frac{d\alpha}{dpH}}{(C+\alpha)^2} \quad (16)$$

Applying the relation

$$\frac{dz}{dpH}=\frac{dz}{d[H]}\cdot\frac{d[H]}{dpH}=-\ln 10\cdot[H]\cdot\frac{dz}{d[H]} \quad (17)$$

for z = α (Eq. (8)) and $\bar{n}$ (Eq. (10)), we get [20,21]

$\frac{d\alpha}{dpH}=-\ln 10\cdot([H]+[OH])=-\ln 10\cdot(\alpha^2+4K_W)^{1/2}$, where

$$K_W=[H][OH] \quad (18)$$

$$\frac{d\bar{n}}{dpH}=-\ln 10\cdot\sum_{j>i=0}^{q}(j-i)^2\cdot f_i f_j \quad (19)$$

and then from Eq. (17) we have

$$\frac{dV}{dpH}=\frac{V_0\cdot\ln 10}{(C+\alpha)^2}\cdot(((n-m)\cdot C_0-\Delta_0+C-C_0\cdot\bar{n})\cdot([H]+[OH])+C_0\cdot(C+\alpha)\cdot\sum_{j>i=0}^{q}(j-i)^2\cdot f_i f_j) \quad (20)$$

$$\sum_{j>i=0}^{12}(j-i)^2\cdot f_i f_j = f_0f_1+f_1f_2+f_2f_3+f_3f_4+f_4f_5+f_5f_6+f_6f_7+f_7f_8+f_8f_9+f_9f_{10}+f_{10}f_{11}+f_{11}f_{12}$$
$$+4(f_0f_2+f_1f_3+f_2f_4+f_3f_5+f_4f_6+f_5f_7+f_6f_8+f_7f_9+f_8f_{10}+f_9f_{11}+f_{10}f_{12})$$
$$+9(f_0f_3+f_1f_4+f_2f_5+f_3f_6+f_4f_7+f_5f_8+f_6f_9+f_7f_{10}+f_8f_{11}+f_9f_{12})$$
$$+16(f_0f_4+f_1f_5+f_2f_6+f_3f_7+f_4f_8+f_5f_9+f_6f_{10}+f_7f_{11}+f_8f_{12})$$
$$+25(f_0f_5+f_1f_6+f_2f_7+f_3f_8+f_4f_9+f_5f_{10}+f_6f_{11}+f_7f_{12})$$
$$+36(f_0f_6+f_1f_7+f_2f_8+f_3f_9+f_4f_{10}+f_5f_{11}+f_6f_{12}) \quad (24)$$
$$+49(f_0f_7+f_1f_8+f_2f_9+f_3f_{10}+f_4f_{11}+f_5f_{12})$$
$$+64(f_0f_8+f_1f_9+f_2f_{10}+f_3f_{11}+f_4f_{12})$$
$$+81(f_0f_9+f_1f_{10}+f_2f_{11}+f_3f_{12})$$
$$+100(f_0f_{10}+f_1f_{11}+f_2f_{12})$$
$$+121(f_0f_{11}+f_1f_{12})$$
$$+144f_0f_{12}$$

Some explanation needs the formulation of $\log K_i^H$ (i = 1,…,12) values in Equations (5) – (7) and then (24) and (25). The relations between $\log K_i^H$ and pK_i (i = 1,…,12) are as follows:

$$\log K_1{}^H = pK_{12},\ \log K_2{}^H = pK_{11}+pK_{12},\ \dots,$$

$$\log K_{12}{}^H=\sum_{i=1}^{12}pK_i \quad (25)$$

3.2. Buffer Capacity in the System Phytic Acid + NaOH

Considering the titration of V_0 mL of C_0 mol/L $H_{12}L$ with V mL of C mol/L NaOH and applying the formulae derived above, we have: M = Na, q= n=12, $C_{0b} = C_{0a} = 0$, i.e., $\Delta_0 = 0$, and then from Equations (14) and (20) we have:

$$V=V_0\cdot\frac{(12-\bar{n})\cdot C_0-\alpha}{C+\alpha} \quad (21)$$

$$\frac{dV}{dpH}=\frac{V_0\cdot\ln 10}{(C+\alpha)^2}\cdot((12\cdot C_0+C-C_0\cdot\bar{n})\cdot([H]+[OH])+C_0\cdot(C+\alpha)\cdot\sum_{j>i=0}^{12}(j-i)^2\cdot f_i f_j) \quad (22)$$

where (Eq. 10)

$$\bar{n}=\sum_{i=1}^{12}i\cdot f_i=f_1+2f_2+3f_3+4f_4+5f_5+6f_6+7f_7+8f_8+9f_9+10f_{10}+11f_{11}+12f_{12} \quad (23)$$

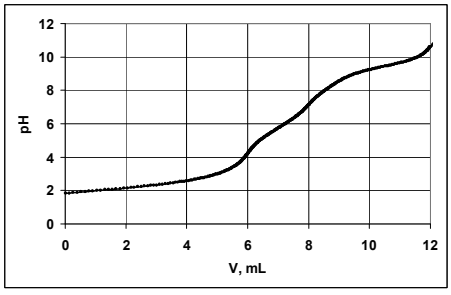
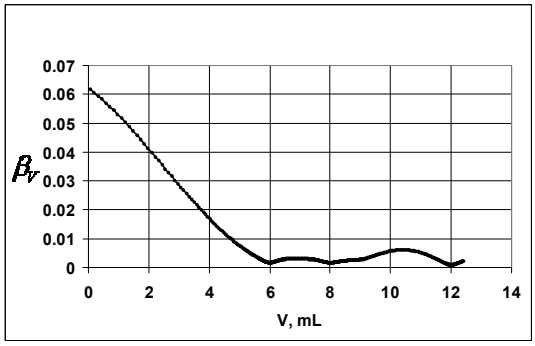
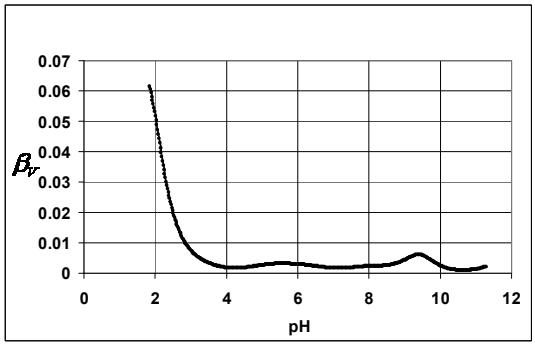


Fig. 2. *The pH titration curve; for details – see text.*

The pH titration curve, pH = pH(V), plotted for V_0 = 10 mL, C_0 = 0.01 mol/L $H_{12}L$, C = 0.1 mol/L NaOH, is presented in Fig. 2. The β_V vs. V and β_V vs. pH relationships are plotted in Figures 3a and 3b.



(3a)



(3b)

Fig. 3. *The plots for (3a) β_V vs. V and (3b) β_V vs. pH relationships; for details – see text.*

4. Final Comments

The buffer capacity β_V for any polyprotic acid or base (of polyprotic acid or base salt) may be readily derived from the concentration and charge balance equations. Phytic acid (inositol hexaphosphate) with twelve acidic groups and spacing pK_i values behaves nearly as a universal buffer. Giving the low values of the first successive protonation constants the buffer capacity of phytic acid increase rapidly from pH 4 downwards. The buffer strength is high and relatively constant between pH 4 and 10.

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