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Comparison between ortho- and meta-phosphoric acid containing phosphate potential buffering systems

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All chemical methods in aqueous media require pH measurement and adjustment. The most reliable method for pH regulation is the addition of suitable buffers. That is why the present brief study is devoted to the evaluation of the potentials for elaboration of buffer solutions by the addition of phosphoric acid to 0.066 M disodium monohydrogen orthophosphate dihydrate ($Na_2HPO_4.2H_2O$) solution. The selected acidic components were dilute solutions of either orthophosphoric (H_3PO_4) or metaphosphoric ($(HPO_3)_n$) acids. This study was performed in two consecutive stages: (i) evaluation of the resulting pH after different volume ratios between the respective acidic and alkaline components, and (ii) determination of their buffering capacity by precise instrumental titrations, assisted by a digital high-precision pH meter. The results show that both solutions can be used as reliable buffers.

Keywords: disodium monohydrogen phosphate**,** orthophosphoric acid, metaphosphoric acid, pH ranges, buffering capacity

INTRODUCTION

For decades, phosphating has been a fundamental metal finishing procedure [1, 2]. Recently, it has been applied for further enhancement of the protective properties of cerium conversion coatings (CeCC) [3–5]. In this sense, Tsanev *et al.* [6] and Andreeva *et al.* [7] have proposed phosphate sealing of CeCC layers with simultaneous calcium phosphate formation. This approach appears rather attractive since it enables potential applications for bone-like implants, as recently proposed in various review and research works [8–14]. Furthermore, the biocompatibility of calcium phosphate-based materials enables their use for controlled drug delivery [15, 16] and cancer therapy [17]. Finally, the phosphating of CeCC layers appears as an alternative approach for the synthesis of cerium phosphate materials, which have recently shown great potential for various applications, as noted by several authors [18-21].

Another important field of application of phosphates is the formation of vanadium phosphate layers for Li- and Na-ion batteries [22-25]. In this sense, the trend is focused on the modification of the chemical composition [26-28], alternative phosphate materials [29], and vanadium phosphate recycling [30]. In addition, multifunctional Ni-Co-P layers also represent a major area of scientific research activity [31-35], along with doped Ni-P layers [35-40]. In particular, Ignatova *et al.* [41, 42] paid special attention to the impact of the type [41] and content [42] of the phosphorus source on the properties of the resulting Ni-Co-P coatings.

Some authors have also emphasized the impact of pH on the formation of electroplated coatings [43] and ferrite nanoparticles [44, 45]. Consequently, there is a need to develop mixtures of phosphorus compounds with defined pH ranges and buffering capacities. In response to this necessity, the present brief study forms part of a systematic description of a variety of phosphate/borate [46, 47] mixtures, including descriptions of their pH ranges and buffering properties. Moreover, the description of the experimental procedures in the present work could

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assist other research activities aimed at elaborating suitable electrolytes for spontaneous and electrochemical formation of advanced active layers such as those described above. Consequently, the content of this paper can serve as a valuable information source for the development of advanced innovative phosphate-containing layers for corrosion protection of Mg [48], Zn [49, 50], Al [4, 51, 52], and Ti [53] alloys, as well as mild steel [54, 55].

Therefore, the aim of the present work is to evaluate the pH buffering potentials of two mixtures prepared from an alkaline phosphate and two phosphorus-containing acids. The experiments were performed using a 0.066 M solution of disodium monohydrogen phosphate and 0.050 M ortho- or meta-phosphoric acids. The respective measurements were performed using a precision pH meter.

EXPERIMENTAL

pH Range determination

A set of potential phosphate buffer systems (PBS) was obtained by mixing the initial solutions in defined volume ratios. The compositions of the initial solutions are summarized in Table 1.

Table 1. Compositions of the initial alkaline and acidic component solutions.

Buffer	Component type	Calculated concentration	Real content
PBS-1	Alkaline component	$Na_2HPO_4.2H_2O$ - 0.066 M	11.9520 g of 99.5% pure compound to 1 dm^3 solution
	Acidic component	o-H_3PO_4 - 0.050 M	3.40 ml of 85% acid
PBS-2	Alkaline component	$Na_2HPO_4.2H_2O$ - 0.066 M	11.9520 g of 99.5% pure compound to 1 dm^3 solution
	Acidic component	40-44% (HPO_3) to 50-60% Na_3PO_4	5.4560 g of industrial product to 1 dm^3 solution

*The weight of metaphosphoric acid was selected to be equal to the weight of 3.40 ml of orthophosphoric acid considering its density equal to 1.88 g/ml according to the product label.

The alkaline component with CAS No. 10028-24-7 was a product of Merck (Germany). The orthophosphoric acid with CAS No. 7664-38-2 was also provided by Merck (Germany), whereas the metaphosphoric acid (Art. No. 01-320) was delivered by Ferak-Laborat GmbH (Germany). This product is described by the producer as a mixture of HPO_3 (40–44%) and $NaPO_3$ (50–60%) with remnants of H_3PO_3 and traces of various impurities.

The pH determinations were performed using a precise HI 255 combined meter, a product of Hanna Instruments. It was equipped with a HI 1131 commercial universal glass electrode. The device was calibrated prior to each measurement set. Data acquisition was performed through five measurements under identical conditions. Each individual measurement was performed after 5 min of electrode immersion in the stirred solution at room temperature. The solutions were pre-stirred for another 5 min immediately before each measurement.

The mean pH values were acquired from the raw data for each set of five measurements for each volume ratio. The calculations were performed according to the expression below:

$$pH = pH_{av} \pm \Delta pH\,, \tag{1}$$

where: pH_{av} is the average pH value obtained from five measurements, and ΔpH is the standard deviation.

The average pH values were calculated using Equation (2):

$$pH_{av} = \sum_{i=1}^{i=n} \frac{pH_i}{n}\,, \tag{2}$$

where: pH_{av} – average pH value; pH_i – individual pH value obtained from the respective measurement (i = 1 to n); n – total number of pH measurements (in this case, n = 5).

The standard deviation was calculated using Equation (3):

$$\Delta pH_{av} = \pm\sqrt{\sum_{i=1}^{i=n} \frac{\left(pH_i - pH_{av}\right)^2}{n(n-1)}}\,, \tag{3}$$

where: all quantities are as defined in Equation (2).

For clarity, the data in Tables 2 and 3 are illustrated in Figure 2. It was plotted after defining the ratios of the solution volumes according to Equation (4):

$$VR_1 = \frac{V_1}{V_1 + V_2} \text{ or } VR_2 = \frac{V_2}{V_1 + V_2}\,, \tag{4}$$

where: VR – volume ratio of the used primary solutions; V_1 – volume of the alkaline solution composing the buffer mixture (mL); V_2 – volume of the acidic solution composing the buffer mixture (mL). Figure 2 represents the correlations between VR, calculated from the volumes in Table 2, and the pH values of the resulting buffer solutions.

Considering the importance of the raw data for this study, the values obtained from direct measurements are combined with the calculated average pH values and their standard deviations in Table 2.

Buffering capacity determination

The buffering capacity determination was performed after defining the volume ratios between the alkaline and acidic borate or phosphate solutions corresponding to buffer mixtures with pH ≈ 7. The experimental work was carried out through five-fold titrations with standardized alkaline NaOH or HCl solutions. The titrant standardizations were performed using a primary 0.05 M $(COOH)_2$ standard solution. It was obtained by dissolving 6.3334 ± 0.0001 g of $(COOH)_2.2H_2O$ (99.5%), supplied by Chim-spectar Ltd. (Bulgaria), in 1 dm^3 of distilled water in a volumetric flask. The necessity for standardization using primary standard solutions is determined by the susceptibility of NaOH to carbonation and hydration upon contact with ambient air, and by the volatility of HCl.

The buffering capacity was calculated using Equation (5) after five-fold titrations with the respective standardized alkaline and acidic solutions:

$$BC = \frac{MV_{ss}}{\Delta(pH)V_{buff}}.\frac{1}{n}, \quad (5)$$

where: BC is the buffering capacity (mol.pH^{-1}); MV_{ss} is the quantity of the added standard solution of known alkaline or acidic compound (mol). In the present case, the data for the standard solution molarity are shown in Table 5, whereas their volumes, used for titrations, are summarized in Table 6. Δ(pH) is the pH change (dimensionless). In the present case, its value is assumed to be unity. V_{buff} is the volume of the buffer solution subjected to titration (15 mL in the present case). The coefficient (1/n) corresponds to the compound whose solution is subjected to pH measurement. If the compound is alkaline, then n = number of OH^- anions per molecule. If it is acidic, then n = number of H_3O^+ (i.e., H^+ cations) moieties per molecule of the dissolved compound. In both cases, for NaOH and HCl, its value is 1/n = 1.

The titrations were performed instrumentally using the already described pH meter, until the pH value of the potential buffer solution shifted by one unit. For this purpose, 15 mL of the respective neutral potential buffer solutions were titrated with the standardized alkaline and acidic solutions described above.

RESULTS AND DISCUSSION

Results from pH range determination

Systematic research activities were performed, comprising the pH ranges and buffering capacities of the proposed potential buffers. Hence, the possible pH interval of the compositions prepared with o-H_3PO_4 is presented in Table 2 and illustrated in Figure 1.

The data show that the possible pH values of these compositions cover a large interval: from above pH ≈ 10 down to nearly pH ≈ 1.75. Moreover, neutral pH values can be reached when the alkaline compound (i.e., Na_2HPO_4) is present in prevailing amounts.

In turn, Figure 1 shows that a neutral pH can be reached only in points P_1 and P_2, both corresponding to about 62 mL of 0.05 M Na_2HPO_4 solution and the addition of orthophosphoric acid up to a total mixture volume of 100 mL.

Similar results were obtained for the second potential buffer system prepared with the addition of metaphosphoric acid. Table 3 presents results that are almost identical to those described above. Hence, the pH range extends between pH ≈ 10 and pH ≈ 2, and a neutral medium was achieved at twice the Na_2HPO_4 content.

Figure 2 also shows only two points, P_1 and P_2, which indicate that a neutral mixture can be obtained with about 59 mL of Na_2HPO_4 and 41 mL of $(HPO_3)_n$, when both solutions have approximately similar molarities.

Table 2. Added component solution volumes and resulting pH values of PBS-1 mixtures.

Component solution volumes (ml)		Volume ratios		Consecutive measurement number					Calculated mean pH values
Na_2HPO_4	o-H_3PO_4	VR_1	VR_2	pH_1	pH_2	pH_3	pH_4	pH_5	
40	0	1.000	0.000	10.050	10.049	10.046	10.042	10.039	10.045 ± 0.046
20	10	0.667	0.333	7.085	7.084	7.085	7.086	7.087	7.085 ± 0.014
20	20	0.500	0.500	6.506	6.505	6.503	6.502	6.504	6.504 ± 0.024
15	25	0.375	0.625	5.392	5.379	5.372	5.371	5.368	5.376 ± 0.179
10	20	0.333	0.667	3.630	3.618	3.607	3.608	3.609	3.614 ± 0.270
10	30	0.250	0.750	3.187	3.183	3.177	3.175	3.172	3.179 ± 0.192
5	35	0.125	0.875	2.176	2.167	2.161	2.151	2.155	2.163 ± 0.393
0	40	0.000	1.000	1.747	1.760	1.754	1.750	1.749	1.752 ± 0.263

Table 3. Added component solution volumes and resulting pH values of PBS-2 systems.

Component solution volumes (ml)		Volume ratios		Consecutive measurement number					Calculated mean pH values
Na_2HPO_4	$(HPO_3)_n$	VR_1	VR_2	pH_1	pH_2	pH_3	pH_4	pH_5	
40	0	1.000	0.000	10.050	10.049	10.046	10.042	10.039	10.045 ± 0.046
20	10	0.667	0.333	7.193	7.192	7.194	7.194	7.190	7.193 ± 0.023
20	20	0.500	0.500	6.717	6.710	6.708	6.710	6.710	6.711 ± 0.052
15	25	0.375	0.625	6.205	6.184	6.180	6.176	6.172	6.183 ± 0.208
10	20	0.333	0.667	5.985	5.996	5.995	5.990	5.989	5.991 ± 0.076
10	30	0.250	0.750	3.024	3.027	3.026	3.023	3.031	3.026 ± 0.103
5	35	0.125	0.875	2.338	2.342	2.332	2.328	2.323	2.333 ± 0.326
0	40	0.000	1.000	1.906	1.910	1.909	1.904	1.889	1.904 ± 0.447

Table 4. Results of the secondary standard solution titrations.

Buffer code	Standard for titration	Consecutive measurement number					Calculated mean values (cm^3)
		Volume 1 (cm^3)	Volume 2 (cm^3)	Volume 3 (cm^3)	Volume 4 (cm^3)	Volume 5 (cm^3)	
PBS-1	NaOH	6.60	6.65	6.65	6.75	6.65	6.66 ± 0.82
	HCl	8.65	8.55	8.60	8.60	8.55	8.59 ± 0.49
PBS-2	NaOH	6.25	6.20	6.20	6.25	6.25	6.23 ± 0.44
	HCl	8.10	8.05	8.15	8.15	8.10	8.11 ± 0.52

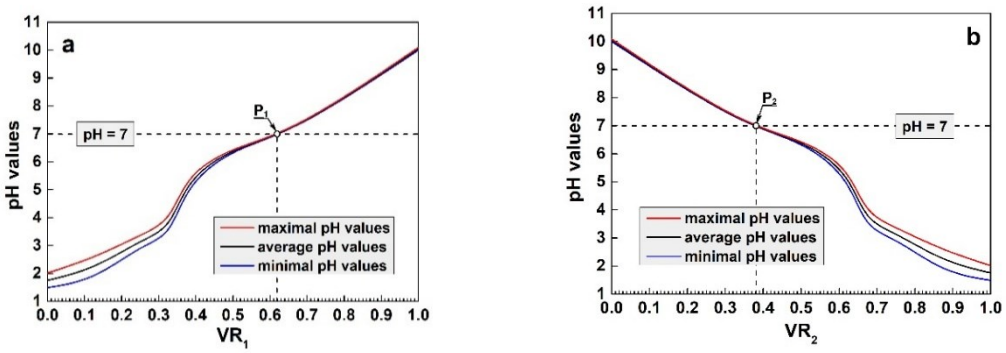

Fig. 1. Correlation between the pH value ranges for phosphate potential buffer based on o-H_3PO_4 and the primary composing solutions: (a) for VR_1 and (b) for VR_2.

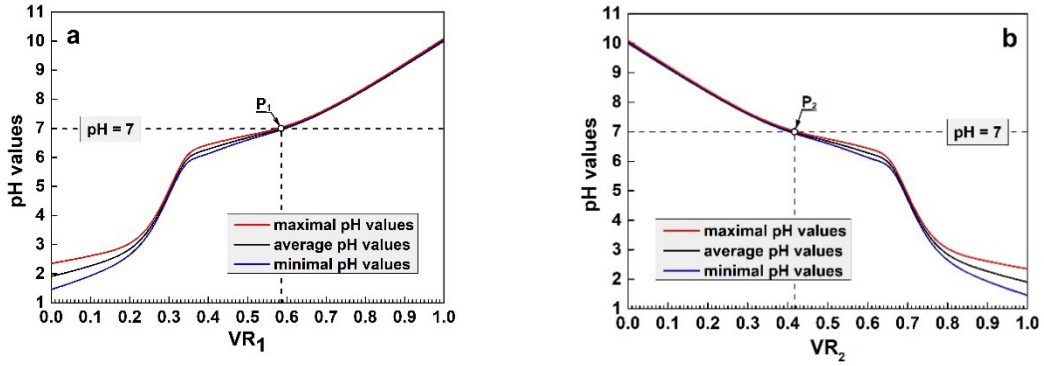

Fig. 2. Correlation between the pH value ranges for phosphate potential buffer based on $(HPO_3)_n$ and the primary composing solutions: (a) for VR_1 and (b) for VR_2.

The curves in both figures show the same trend. In the alkaline pH range, straight lines with slopes approaching unity (i.e., 45°) are observed, whereas clear curvatures (Fig. 1) or sharp bends (Fig. 2) occur in the mid-range. At the lowest pH values, below pH ≈ 4 (Fig. 1) or pH ≈ 3 (Fig. 2), the curves again exhibit a lower slope. A slight curve splitting appears

in the acidic pH range in both cases, although data reproducibility remained rather high.

Results from the buffering capacity determination

This procedure required preliminary determination of the exact concentrations of both secondary standard solutions. It was performed through their instrumental titrations with the $(COOH)_2$ primary standard solution, using the pH meter described in the experimental part. The respective titrations with 15 mL solutions of the primary standard required 30.66 ± 0.32 mL of the NaOH solution, revealing that the average NaOH concentration value is 49.156×10^{-3} M. This value was further used for the determination of the HCl concentration. It was defined by five titrations of the HCl solution with the NaOH secondary standard. Thus, the average volume of the HCl solution expended for these titrations was 14.69 ± 0.28 mL. Hence, the calculations have shown that the HCl secondary solution concentration had an average value of 50.193×10^{-3} M.

These secondary standard solutions were used for the definition of the buffering capacity (BC) of the phosphate mixtures with neutral pH. For that purpose, titrations were performed using the secondary standard solutions on 15 mL samples of PBS-1 and PBS-2, respectively. The acquired data are summarized in Table 4.

Additionally, similar titrations were performed using the *Reagecon* (UK) commercial buffer for neutral media. Hence, 7.40 mL of NaOH solution and 11.10 mL of HCl standard were expended. These values fall within the range of the data in Table 4. Consequently, both phosphate mixtures could be used as reliable buffers.

Further, the buffering capacities (BC) of the investigated phosphate mixtures were determined by applying the data described above in Equation (5). The respective results show that the titrations with the alkaline solution resulted in: $BC_{PBS\text{-}1}{}^{NaOH} = 21.83\times10^{-3}$ mol pH^{-1} for the former mixture and $BC_{PBS\text{-}2}{}^{NaOH} = 20.41\times10^{-3}$ mol pH^{-1}. In turn, the titrations with the acidic secondary standard resulted in the following BC values: $BC_{PBS\text{-}1}{}^{HCl} = 28.74\times10^{-3}$ mol pH^{-1} and $BC_{PBS\text{-}2}{}^{HCl} = 27.13\times10^{-3}$ mol pH^{-1}.

The analysis of these numerical data leads to the inference that both PBS-1 and PBS-2 systems possess comparable buffering capacity values. The reason for this is that, when dissolved in water, metaphosphoric acid converts to orthophosphoric acid due to hydration (Eq. 6):

$$HPO_3 + H_2O \rightarrow H_3PO_4 \quad (6)$$

Nevertheless, comparison of the buffering capacities of the studied systems reveals that the use of o-H_3PO_4 is preferable, since the BC of PBS-1 slightly exceeds that of PBS-2.

CONCLUSIONS

The present work deals with the determination of possible pH intervals and the assessment of the pH buffering potentials of two mixtures prepared from an alkaline phosphate and two phosphorus-containing acids. The experiments were performed using a 0.066 M solution of disodium monohydrogen phosphate and 0.050 M ortho- or metaphosphoric acids. The respective measurements were carried out using a precision pH meter.

The experiments have shown that a rather wide pH range can be achieved by varying the ratios between the initial component solutions.

In the case of the Na_2HPO_4 / o-H_3PO_4 system, neutral pH can be reached by mixing 62 mL of 0.05 M Na_2HPO_4 solution with orthophosphoric acid to obtain a 100 mL mixture.

In the latter case, a neutral mixture can be obtained by about 59 mL of Na_2HPO_4 and 41 mL of $(HPO_3)_n$, when both solutions have approximately similar (i.e., ~0.05 M) molarities.

The buffering properties of both PBS-1 and PBS-2 were compared with those of a commercial buffer and also numerically evaluated. The respective results have shown that the proposed potential buffer systems exhibit reliable buffering properties comparable to those of the commercial product. Moreover, their buffering capacities were determined, and the acquired results show that both systems can be used as buffers for the purpose of chemical synthesis of various advanced coatings and other types of materials.

In addition, further data analysis has shown that the use of o-H_3PO_4 is preferable, since the buffering capacity of PBS-1 slightly exceeds that of PBS-2, although the difference between their values is insignificant.

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