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Potential buffers based on borax, orthophosphoric and metaphosphoric acid

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The solution composition and pH are factors of key importance for the efficiency of any chemical and electrochemical surface treatment procedure. In this sense, the present brief study is an attempt to obtain stable and reliable buffer solutions through mixing of two compounds, acting as alkaline and acidic buffer components, respectively. The alkaline component was a 0.050 M solution of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$). Two potential buffer solutions were prepared by the addition of either 0.050 M orthophosphoric acid or a similar quantity of metaphosphoric acid as the acidic compound. The study was performed in two stages: (i) evaluation of the resulting pH after different volume ratios between the respective alkaline and acidic 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 behave as relatively reliable buffers.

Keywords: pH buffers, borate and phosphate compositions, pH ranges, buffering capacity

INTRODUCTION

Although phosphating is a well-known procedure [1, 2], the optimization of this process continues to be the object of intensive research activities [3, 4]. In this respect, special attention has been paid to the formation of phosphate conversion coatings containing Ca [5], Mg [6], Zn [7–10], Ba [11], Ni [12], Mn [13–15], V [16], and Ce [17]. In addition, various nanoparticle additions have been proposed, such as ZrO_2 [18], K_2O/TiO_2 [19], ZnO/TiO_2, [20], $WO_3/BiVO_4$, [21], Al_2O_3/Mo [22], MoS_2 [23], Nd modified $ZnAl_2O_4$ [24], Bi-doped $FeVO_4$ [25], etc. Furthermore, this approach has been proposed for the improvement of zinc coatings on steels [26] and for enhancing the adhesion of organic coatings [27].

For this reason, some authors have paid special attention to pH as a technological parameter for the successful deposition of reliable Zn–P conversion coatings on steel [28] and magnesium alloys [29, 30]. In some of these studies, the authors propose strongly acidic conditions. However, such conditions are not suitable for magnesium and aluminum alloy treatments due to the high solubility of these metals in strongly acidic or alkaline media. Therefore, nearly neutral borate and phosphate buffer solutions were proposed for the sealing of cerium conversion coatings deposited on preliminarily anodized aluminum alloys [31]. The compositions of these buffers and their pH ranges are described elsewhere [32].

Other authors have proposed the deposition of Mo-Mn-V conversion coatings under weakly acidic conditions [33], or the use of borate buffer solutions for the passivation of aluminum alloys [34]. Moreover, the use of boron-containing compounds has been shown to have a beneficial effect on the electrochemical film formation of aluminum alloys [35].

The necessity of developing buffers that contain both boron and phosphorus becomes even more evident, given the recent trend toward the development of Ni–B layers [36, 37], doped and reinforced Ni–B composites [38, 39], and Ni–Co–P layers [40–43], as well as the important role of B-compounds in the respective electrolytes. Indeed, according to some authors [44, 45], boron incorporation in Ni-based layers decreases the grain size and changes the morphology from faceted to dome-like. Additionally, borate buffers have recently

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been studied for water oxidation in hydrogen production [46, 47] and for water purification [48].

Consequently, more detailed research regarding the pH ranges and potential buffering properties of mixtures of relatively easily accessible boron- and phosphorus-containing compounds is necessary.

In this context, the present brief study is devoted to the investigation of the pH ranges and buffering effects of mixtures of borax (as the alkaline component) with orthophosphoric or metaphosphoric acid (as the acidic components). It is part of a wider systematic study aiming to provide valuable data on the pH ranges of various boron- and phosphorus-containing compounds.

EXPERIMENTAL

pH Range determination

A set of phosphate/borate mixtures was obtained by mixing the initial solutions in defined volume ratios. The compositions of the initial solutions are summarized in Table 1. The alkaline component (CAS 1303-96-4) was a product of Merck (Germany). The orthophosphoric acid (CAS 7664-38-2) was also a product of Merck (Germany), whereas the metaphosphoric acid (Art. No. 01-320) was a product of Ferak GmbH (Germany). According to the manufacturer, the latter product is 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, manufactured by Hanna Instruments, equipped with an 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 involved a 5-min immersion of the electrode in the stirred solution at room temperature. The solutions were pre-stirred for another 5 min immediately prior to each measurement.

The mean pH values were obtained from the raw data from each of the five measurements for every volume ratio. The calculations were performed according to the following expression:

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

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

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

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

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

The standard deviation was calculated by Equation (3):

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

All designations are similar to those in Equation (2). For clarity, the data in Tables 2 and 3 are illustrated in Figure 2. The figure was constructed after determining the ratios of the used solution volumes, following 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, forming the buffer mixture (mL); V_2 – volume of the acidic solution, forming the buffer mixture (mL).

Table 1. Exact buffer solution component compositions.

Buffer	Component type	Calculated concentration	Actual content
BPB-1	Alkaline component	$Na_2B_4O_7.10H_2O$ - 0.05 M (borax)	19.2663 g of 99.5 % pure compound to 1 dm^3 aqueous solution
	Acidic component	o-H_3PO_4 - 0.05 M (orthophosphoric acid)	3.40 ml of 85 % acid to 1 dm^3 aqueous solution
BPB-2	Alkaline component	$Na_2B_4O_7.10H_2O$ - 0.05 M (borax)	19.2663 g of 99.5 % pure compound to 1 dm^3 aqueous solution
	Acidic component	HPO_3 / $NaPO_3$ mixture* (metaphosphoric acid)	5.4560 g of industrial product to 1 dm^3 aqueous solution

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

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 acquired values from the direct measurements were combined with the calculated average pH values and their standard deviations.

Buffering capacity determination

The buffering capacity determination was performed after defining the volume ratios between the alkaline and the acidic borate or phosphate solutions, which correspond to buffer mixtures with pH ≈ 7. The experimental activities were 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%), provided by Chim-spectar Ltd. (Bulgaria), in 1 dm^3 of distilled water in a volumetric flask. The need for standardization using a primary standard solution is predetermined by the susceptibility of the NaOH precursor 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 alkaline and acidic standard solutions:

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

where: BC is the buffering capacity (mol pH^{-1}); MV_{ss} is the quantity of the added standard solution of a known alkaline or acidic compound (mol). In the present case, the data for the standard solution molarity are shown in Table 1, whereas, their volumes, expended for the titrations are summarized in Table 4. Δ(pH) is the pH change (dimensionless). In this 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) is attributed to the compound, whose solution is subjected to pH measurement. If it is alkaline, then n is the number of OH^- anions per molecule of the compound. If it is acidic, then n is the 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 alkaline and acidic standard solutions described above.

RESULTS AND DISCUSSION

Results from pH range determination

The pH range determination was performed consecutively for the $Na_2B_4O_7$ / o-H_3PO_4 system (denoted as BPB-1) and subsequently for the $Na_2B_4O_7$ / $(HPO_3)_n$ system (denoted as BPB-2). The results for the former case are shown in Table 2 and Fig. 1, respectively.

The data in Table 2 show that the pH interval of BPB-1 buffer is rather large, ranging from about pH ≈ 9.6 down to nearly pH ≈ 1.7. When the mixture is composed by equal volumes of both alkaline and acidic component solutions, the resulting mixture exhibits a slightly alkaline reaction. Neutral BPB-1 type solutions can be obtained when the amount of orthophosphoric acid predominates. At higher acid contents, the pH drops sharply. Probably, $(B_4O_7)^{2-}$ ions decompose in acidic media, but detailed analysis of such processes is beyond the scope of the present research.

The images in Fig. 1 show that the pH dependence on the borax / orthophosphoric acid content ratios can be divided into three regions. In the most alkaline range, down to pH ≈ 8.5, the line has a rather weak slope. In the middle range, including the neutral pH, this dependence reaches unity (i.e., 45°). Below pH ≈ 6, the curve slope becomes much steeper, along with a slight decrease in the curve overlap rate. At the lowest pH values, the curves become almost horizontal again.

Table 2. Volumes of added component solutions and resulting pH values of the BPB-1 buffer

Component solution volumes (ml)		Volume ratios		Consecutive measurement number					Calculated pH mean values
$Na_2B_4O_7$	o-H_3PO_4	VR_1	VR_2	pH_1	pH_2	pH_3	pH_4	pH_5	
40	0	1.000	0.000	9.592	9.585	9.587	9.584	9.589	9.587 ± 0.033
20	10	0.667	0.333	9.126	9.110	9.128	9.114	9.117	9.119 ± 0.085
20	20	0.500	0.500	8.328	8.322	8.326	8.324	8.321	8.324 ± 0.034
15	25	0.375	0.625	6.876	6.863	6.861	6.859	6.865	6.865 ± 0.097
10	20	0.333	0.667	6.472	6.473	6.468	6.459	6.456	6.466 ± 0.119
10	30	0.250	0.750	5.847	5.836	5.831	5.832	5.832	5.836 ± 0.114
5	35	0.125	0.875	2.107	2.099	2.089	2.081	2.072	2.090 ± 0.666
0	40	0.000	1.000	1.747	1.760	1.754	1.750	1.749	1.752 ± 0.263

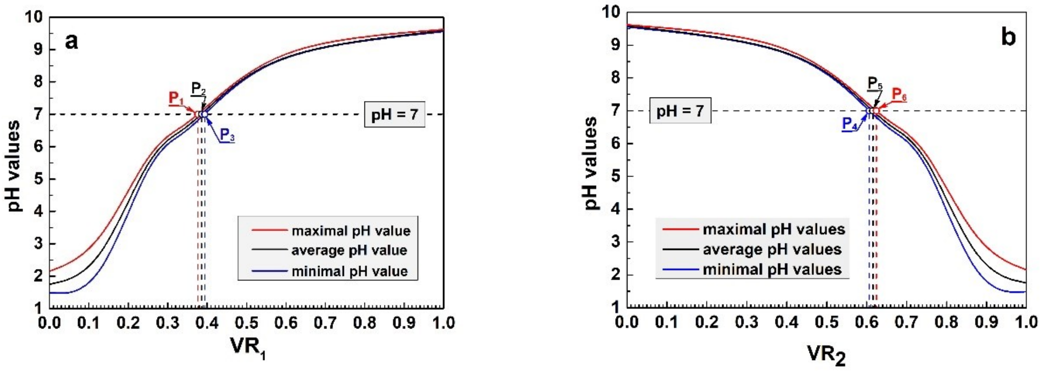

Fig. 1. Correlation between the pH value ranges for $Na_2B_4O_7$/ o-H_3PO_4 potential buffer volume ratios and the primary component solutions: (a) for VR_1 and (b) for VR_2.

Table 3. Added volumes of the component solutions and resulting pH values of BPB-2 buffer.

Solution component volumes (ml)		Volume ratios		Consecutive measurement number					Calculated pH mean values
$Na_2B_4O_7$	$(HPO_3)_n$	VR_1	VR_2	pH_1	pH_2	pH_3	pH_4	pH_5	
40	0	1.000	0.000	9.592	9.585	9.587	9.584	9.589	9.587 ± 0.033
20	10	0.667	0.333	9.308	9.292	9.290	9.298	9.293	9.296 ± 0.078
20	20	0.500	0.500	8.859	8.858	8.853	8.857	8.858	8.857 ± 0.026
15	25	0.375	0.625	8.108	8.107	8.115	8.112	8.114	8.111 ± 0.044
10	20	0.333	0.667	7.421	7.425	7.422	7.422	7.424	7.423 ± 0.022
10	30	0.250	0.750	5.758	5.759	5.764	5.766	5.768	5.763 ± 0.076
5	35	0.125	0.875	2.377	2.364	2.354	2.349	2.345	2.358 ± 0.546
0	40	0.000	1.000	1.906	1.910	1.909	1.904	1.889	1.904 ± 0.447

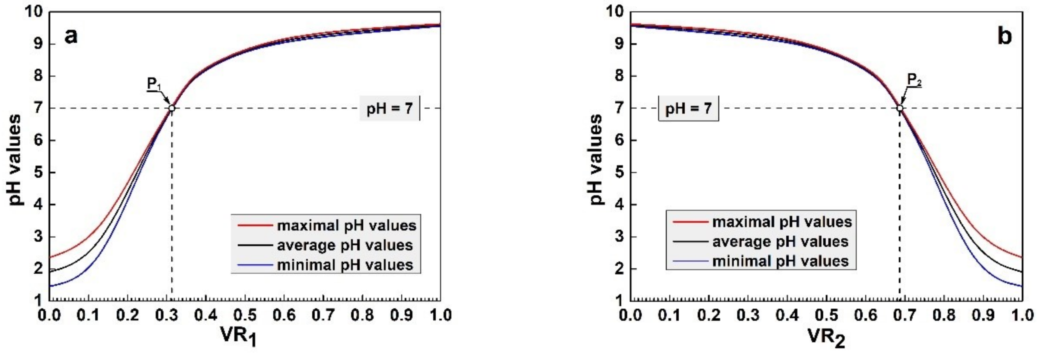

Fig. 2. Correlation between the pH value ranges for BPB-2 potential buffer volume ratios and the primary component solutions: (a) for VR_1 and (b) for VR_2.

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)	
BPB-1	NaOH,	3.85	3.90	3.90	3.90	3.90	3.89 ± 0.57
	HCl	3.55	3.55	3.50	3.50	3.50	3.52 ± 0.78
BPB-2	NaOH,	3.15	3.10	3.15	3.10	3.20	3.12 ± 1.83
	HCl	3.55	3.60	3.50	3.55	3.55	3.55 ± 1.00

The curves show that neutral mixtures can be obtained within rather narrow VR_l and VR_2 intervals. In the former case, the neutral pH range is enclosed between P_1 and P_3 (Fig. 1a), corresponding to VR_l between 0.37 and 0.40. The highest probability of obtaining a neutral pH is indicated by P_2. It corresponds to a mixture prepared by combining 38.5 mL of 0.05 M $Na_2B_4O_7$ solution and adding 0.05 M o-H_3PO_4 solution up to 100 mL. In turn, analysis of Fig. 1b shows that a neutral pH can be obtained by mixing 62 mL of 0.05 M o-H_3PO_4 solution and adding 0.05 M borax solution up to 100 mL, corresponding to P_5. However, preparation of such a neutral mixture requires high precision due to the narrowness of the range enclosed between P_4 and P_6.

Identical analyses were carried out for the borax / metaphosphoric acid, and the respective data are summarized in Table 3 and illustrated in Fig. 2.

The data in Table 3 are quite similar to those of the previous system described above. In brief, the pH range is rather wide, and neutral pH is achievable when the acidic component predominates. The respective curves in Fig. 2 are simpler in shape compared to those of the previous system. Here, no intermediate range is observable; instead, the low slope at pH above 8 directly transitions to a sharp decline down to the most acidic values. Final curve bends, combined with curve splitting similar to those in the previous figure, are also observable.

Here, juxtapositions of the maximal, average, and minimal pH value curves are observable at the pH = 7 line. According to VR_l (P_1, Fig. 2a), 31 mL of 0.05 M borax solution should be mixed with 69 mL of 0.05 M metaphosphoric acid solution, and *vice versa,* according to VR_2 (P_2, Fig. 2b).

Results from the buffering capacity determination

Prior to the definition of the buffering capacity (BC), the exact concentrations of the secondary standard solutions were determined by titration with the $(COOH)_2$ primary standard solution. The titrations were performed instrumentally using the pH meter described in the experimental part. The respective titrations with 15 mL of the primary standard solution required 30.66 ± 0.32 mL of the NaOH solution. The respective calculations resulted in an average NaOH concentration value of 49.156×10^{-3} M. Knowing this value, it was possible to define the HCl concentration. It was determined by five titrations of the HCl solution with the NaOH secondary standard. The average volume of the HCl solution expended for these titrations was 14.69 ± 0.28 mL. Hence, the calculations showed that the HCl secondary standard solution had average concentration values of 50.193×10^{-3} M.

Both secondary solutions were used to determine the buffering capacity of BPB-1 and BPB-2 mixtures, described in Table 1. Again, instrumental titrations were applied to 15 mL neutral pH solutions of BPB-1 and BPB-2. The obtained values are shown in Table 4.

Similar titrations were performed with the commercial *Reagecon* (UK) buffer for neutral media. The respective expended solution volumes were 7.40 mL for the NaOH solution and 11.10 mL for the HCl standard. Thus, comparison with the results in Table 4 shows that, when titrated with the alkaline (NaOH) standard solution, both investigated mixtures exhibit buffering properties approximately twice weaker than those of the commercial buffer. In turn, titrations with the acidic (HCl) standard revealed that both investigated mixtures have about three times weaker buffering properties.

The data in Table 4 were used for BC definition using Equation (5). The calculations revealed the buffering capacities of the investigated mixtures. Accordingly, using the NaOH standard solution, the buffering capacities of investigated mixtures were: $BC_{BPB\text{-}1}^{NaOH} = 12.75\times10^{-3}$ mol pH^{-1} and $BC_{BPB\text{-}2}^{NaOH} = 10.22\times10^{-3}$ mol pH^{-1}, respectively. In turn, the buffering capacities of these mixtures determined with the HCl standard solution were: $BC_{BPB\text{-}1}^{HCl} = 11.78\times10^{-3}$ mol pH^{-1} and $BC_{BPB\text{-}2}^{HCl} = 11.88\times10^{-3}$ mol pH^{-1}. These results revealed that the neutral mixtures of borax with either orthophosphoric or metaphosphoric acid possess almost identical buffering capacity values.

The relatively weak buffering effect of the proposed $Na_2B_4O_7$ - o-H_3PO_4 and $Na_2B_4O_7$ - $(HPO_3)_n$ systems could be explained by considering the difference between the standard reduction potentials [49-51] of the respective anions, as shown in Equations (6 – 9):

$$(B(OH)_4)^- + 3e^- \rightarrow B_{(s)} + 4OH^- \quad E^0 = -1.811\ V_{SHE} \qquad (6)$$

$$B(OH)_3 + 3H^+ + 3e^- \rightarrow B_{(s)} + 3H_2O \quad E^0 = -0.890\ V_{SHE} \qquad (7)$$

$$H_3PO_3 + 2H^+ + 2e^- \rightarrow H_3PO_2 + H_2O \quad E^0 = -0.50\ V_{SHE} \qquad (8)$$

$$H_3PO_4 + 2H+ + 2e- \rightarrow H_3PO_3 + H_2O \quad E^0 = -0.28\ V_{SHE} \qquad (9)$$

The differences among these standard reduction potential values predetermine that redox couples appear between the boron- and the phosphorus-containing anions. This fact probably results in decomposition of the tetraborate anions and formation of other water-soluble compounds.

However, their analysis is not among the main objects of the present research.

In turn, the similarity between the weak buffering capacities of both systems can be explained by the fact that, in aqueous media, the metaphosphoric acid (HPO_3) converts to orthophosphoric acid (H_3PO_4), following reaction (Eq. 10):

$$HPO_3 + H_2O \rightarrow H_3PO_4 \qquad (10)$$

Finally, analysis of all facts described above leads to the inference that both systems possess rather similar properties and could substitute each other in real technological processes.

CONCLUSIONS

The present brief study is part of a wider systematic research effort aiming to provide valuable data for the pH ranges of various boron- and phosphorus-containing compounds. It is devoted to defining the pH ranges and the buffering effects of mixtures between borax (as the alkaline component) and orthophosphoric or metaphosphoric acid (as the acidic components).

In both cases, the pH range is rather wide, and a neutral pH is achievable when the acidic component predominates.

For the former investigated mixture, neutral pH could be achieved at a rather narrow initial component solution ratio. Most probably, a mixture prepared by 38.5 mL of 0.05 M $Na_2B_4O_7$ solution and addition of 0.05 M o-H_3PO_4 solution up to 100 mL should possess neutral pH. In turn, neutral pH can be also obtained by 62 mL of 0.05 M o-H_3PO_4 solution and further addition of 0.05 M borax solution up to 100 mL.

For the latter investigated system, 31 mL of 0.05 M borax solution should be mixed with 69 mL of 0.05 M metaphosphoric acid solution, and *vice versa*, in order to reach neutral pH value.

Finally, the buffering capacities of both systems were calculated after multiple titrations with secondary standard solutions of NaOH or HCl. Comparison with the results from titrations using a commercial buffer showed that the proposed here potential buffers possess relatively weak buffering properties.

Further analysis of the result indicated that both systems possess almost identical buffering capacities.

Finally, both systems, proposed in the present study, can be used as additives to electrolytes for the electrochemical deposition of active layers for corrosion protection, alternative energy sources and environmental protection purposes. However, their unsatisfactory buffering properties necessitate pH monitoring of electrolytes containing BPB-1 and BPB-2.

In this sense, the present study provides data regarding the pH ranges and the respective contents of the components (i.e., borax, ortho- or metaphosphoric acids) composing these mixtures.

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