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SYSTEMATIC STUDY OF THE PH RANGES AND BUFFERING CAPACITY OF MIXTURES OF TRISODIUM ORTHOPHOSPHATE OR TETRASODIUM PYROPHOSPHATE WITH BORIC ACID

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Abstract: *This study presents a systematic investigation of the pH ranges and buffering capacity of two systems composed of phosphate alkaline components and boric acid as the acidic counterpart. The alkaline components selected were trisodium orthophosphate dodecahydrate ($Na_3PO_4.12H_2O$) and tetrasodium pyrophosphate decahydrate ($Na_4P_4O_7.10H_2O$). The experimental work was carried out in two stages: (i) determination of pH ranges and (ii) evaluation of buffering capacity. All measurements were performed in quintuplicate using a high-precision pH meter. The results, including the complete set of raw data, are provided to serve as a useful reference for future studies. Detailed descriptions of the experimental procedures and calculation methods are also included, enabling reproducibility and further exploration. Although the investigated phosphate/borate mixtures displayed limited buffering capacity, they may nevertheless find application in chemical and electrochemical surface treatment processes.*

Keywords: *$Na_3PO_4.12H_2O$, $Na_4P_2O_7.10H_2O$, H_3BO_3, pH ranges, Buffering Capacity.*

INTRODUCTION

pH control is a crucial factor in numerous processes occurring in aqueous media. The significance of pH regulation for biotechnological processes has been discussed in detail in a previous study (Georgieva et al., 2025-1). Moreover, the application of phosphate-based pH buffers for the pretreatment of industrial alloys has also been demonstrated (Georgieva et al., 2025-2).

In this context, several researchers have investigated the phosphating of mild steel, examining different bath compositions with promising practical potential for the formation of reliable primer coatings (Ilieva et al., 2021; Rumyantseva et al., 2021; Fachikov et al., 2021; Liubenova et al., 2023).

The present study therefore focuses on the characterization of the pH ranges and potential buffering properties of two phosphate/borate mixtures:

- M_1: $Na_3PO_4.12H_3O$ with H_3BO_3
- M_2: $Na_4P_2O_7.10H_2O$ with H_3BO_3

The experimental procedures are described in detail, and the raw data are included, with the aim of providing a useful reference for future research.

EXPERIMENTAL

The experimental work was organized into two main stages:
(1) determination of the pH ranges
(2) evaluation of the potential buffering capacity of neutral phosphate/borate solutions.

For stage (i), pH measurements were performed in quintuplicate on solutions prepared in nine different proportions. The measurements were carried out using a HI 255 combined meter (*Hanna Instruments*) equipped with a HI 1131 commercial universal glass electrode.

Before conducting the experiments, stock solutions of the individual compounds were prepared. The compositions of these solutions are given in Table 1.

Table 1. Initial solutions used for the pH range determinations of the studied borate-phosphate mixtures

Component type	Estimated solution content	Real content (weighted)	Exact compound concentration
First alkaline component	0.05 M solution of $Na_3PO_4.12H_2O$	19.3954 g of product (CAS-2570) with 98 %	52.066×10^{-4} mol dm^{-3}
Second alkaline component	0.05 M solution of $Na_4P_2O_7.10H_2O$	22.6196 g of product (CAS 13472-36-1) with 99 %.	51.222×10^{-4} mol dm^{-3}
Acidic component	0.05 M solution of H_3BO_3	3.1328 g of product (CAS-10043-35-3) with 99.8 %.	50.567×10^{-4} mol dm^{-3}

The determination of the pH ranges was performed by mixing the alkaline and acidic components in defined proportions (described in the next paragraph), followed by measurement of the pH of the resulting solutions. This approach enabled the monitoring of pH variations with gradual increases or decreases in the acidic component relative to the alkaline one.

For further data analysis, the volume ratios (VR) of the alkaline and acidic parts of the mixtures were calculated according to Equation 1:

$$VR_1 = \frac{V_1}{V_1 + V_2} \qquad \text{or} \qquad VR_2 = \frac{V_2}{V_1 + V_2}, \qquad (1)$$

where VR – volume ratio of the used primary solutions; $\mathbf{V_1}$ – volume of the alkaline solution, composing the buffer mixture (mL); $\mathbf{V_2}$ – volume of the acidic solution, composing the buffer mixture (mL).

The buffering capacity was determined by titrating the phosphate/borate mixtures prepared at neutral pH. Titrations were performed using secondary standard alkaline (NaOH) and acidic (HCl) solutions. Due to the susceptibility of NaOH to absorb CO_2 from air and the volatility of HCl, both solutions were standardized against a primary standard. Specifically, NaOH was standardized using oxalic acid, and subsequently, HCl was standardized against the NaOH solution. All titrations were performed in quintuplicate with the same pH meter described above, and continued until a neutral pH was reached. The exact concentrations of the standardized solutions are listed in Table 2.

Table 2. Concentrations of the standard solutions

Solution type	Preparation details	Calculated concentration (mol dm^{-3})	Standardized concentration (mol dm^{-3})
Primary standard	6.3226 g of $(COOH)_2.2H_2O$ with 99.5% purity grade in 1 dm^3	0.05040	Primary standard
Secondary solution	4.0375 g of NaOH with 99.5% purity grade in 2 dm^3	0.04795	48.648×10^{-3} mol dm^{-3}
Secondary solution	8.60 mL Concentrated hydrochloric acid in 2 dm^3	0.05149	49.255×10^{-3} mol dm^{-3}

The secondary standard solutions (NaOH and HCl) were used for the titration of mixtures of H_3BO_3 with either $Na_3PO_4.12H_2O$, (M_1) or $Na_4P_2O_7.10H_2O$ (M_2), both prepared at nearly neutral pH. The proportions of acidic and alkaline components necessary to obtain neutral mixtures were determined from the results of the pH range measurements (Stage 1). Aliquots of 25 mL from each neutral mixture were titrated with the standardized NaOH or HCl solutions (Table 2). Each titration was performed five times using the same pH meter setup.

The buffering capacity (BC) was calculated according to Equation 2:

$$BC = \frac{MV_{ss}}{\Delta(pH)Vb_{uff}} \cdot \frac{1}{n}, \tag{2}$$

where: BC is the buffering capacity (mol pH^{-1}), MV_{ss} is the amount of the added standard solution of known alkaline or acidic compound (represented in moles). In the present case, the data for the standard solution molarity are shown Table 2, whereas, their volumes, expended for the titrations are summarized in Tables 5 and 6. $\Delta(pH)$ is the change in pH (dimensionless). In the present case, its value is assumed to be unit. V_{buff} is the volume of the buffer solution submitted to titration (25 mL in the present case). The coefficient ($1/n$) is attributed to the compound, whose solution is submitted to pH measurement. If it is alkaline, then n = number of OH^-, anions from any compound molecule. If it is acidic, then n = number of H_3O^+ (i.e., H^+ cations) moieties from each molecule of the dissolved compound. In both cases of NaOH and HCl, its value is: $1/n = 1$.

RESULTS AND DISCUSSION

Determination of the pH ranges

The experimental results are summarized in Table 3 for the M_1 system and in Table 4 for the M_2 system.

Table 3. Volume ratios and the resulting pH values, of M_1 system

Components (mL)		**Volume ratios**		**Raw data acquired from each measurement**					**Avg. Val.**	**St. Dev.**
Alkaline	**Acidic**									
$Na_3PO_4.12H_2O$	**H_3BO_3**	**VR_1**	**VR_2**	**pH_1**	**pH_2**	**pH_3**	**pH_4**	**pH_5**		
50	**0**	**1.00**	**0.00**	12.008	12.007	12.001	11.998	11.995	12.002	0.006
40	**10**	**0.80**	**0.20**	10.974	10.975	10.969	10.963	10.958	10.968	0.007
30	**10**	**0.75**	**0.25**	10.412	10.405	10.404	10.399	10.397	10.403	0.006
30	**20**	**0.60**	**0.40**	9.635	9.632	9.631	9.623	9.627	9.630	0.005
25	**25**	**0.50**	**0.50**	9.311	9.309	9.306	9.304	9.301	9.306	0.004
20	**30**	**0.40**	**0.60**	9.294	9.289	9.295	9.286	9.295	9.292	0.004
10	**30**	**0.25**	**0.75**	8.663	8.648	8.655	8.657	8.662	8.657	0.006
10	**40**	**0.20**	**0.80**	8.500	8.494	8.501	8.495	8.497	8.497	0.003
0	**50**	**0.00**	**1.00**	5.630	5.628	5.618	5.618	5.620	5.623	0.006

Table 4. Volume ratios and the resulting pH values, of M_2 system

Components (mL)		**Volume ratios**		**Raw data acquired from each measurement**					**Avg. Val.**	**St. Dev.**
Alkaline	**Acidic**									
$Na_4P_2O_7.10H_2O$	**H_3BO_3**	**VR_1**	**VR_2**	**pH_1**	**pH_2**	**pH_3**	**pH_4**	**pH_5**		
50	**0**	**1.00**	**0.00**	10.794	10.797	10.795	10.792	10.788	10.793	0.003
40	**10**	**0.80**	**0.20**	9.740	9.742	9.745	9.744	9.749	9.744	0.003
30	**10**	**0.75**	**0.25**	9.672	9.663	9.639	9.630	9.648	9.650	0.017
30	**20**	**0.60**	**0.40**	9.441	9.453	9.463	9.466	9.47	9.459	0.012
25	**25**	**0.50**	**0.50**	9.328	9.333	9.336	9.340	9.339	9.335	0.005
20	**30**	**0.40**	**0.60**	9.220	9.226	9.233	9.232	9.234	9.229	0.006
10	**30**	**0.25**	**0.75**	8.998	8.999	9.008	9.012	9.009	9.005	0.006
10	**40**	**0.20**	**0.80**	8.903	8.907	8.894	8.891	8.896	8.898	0.007
0	**50**	**0.00**	**1.00**	5.630	5.628	5.618	5.618	5.620	5.623	0.006

The visualization of the data in Tables 3 and 4 allows the definition of the volume ratio (VR) ranges suitable for achieving of neutral pH. For this purpose, the dependencies *pH = f(VR)* were plotted, as shown in Figure 1.

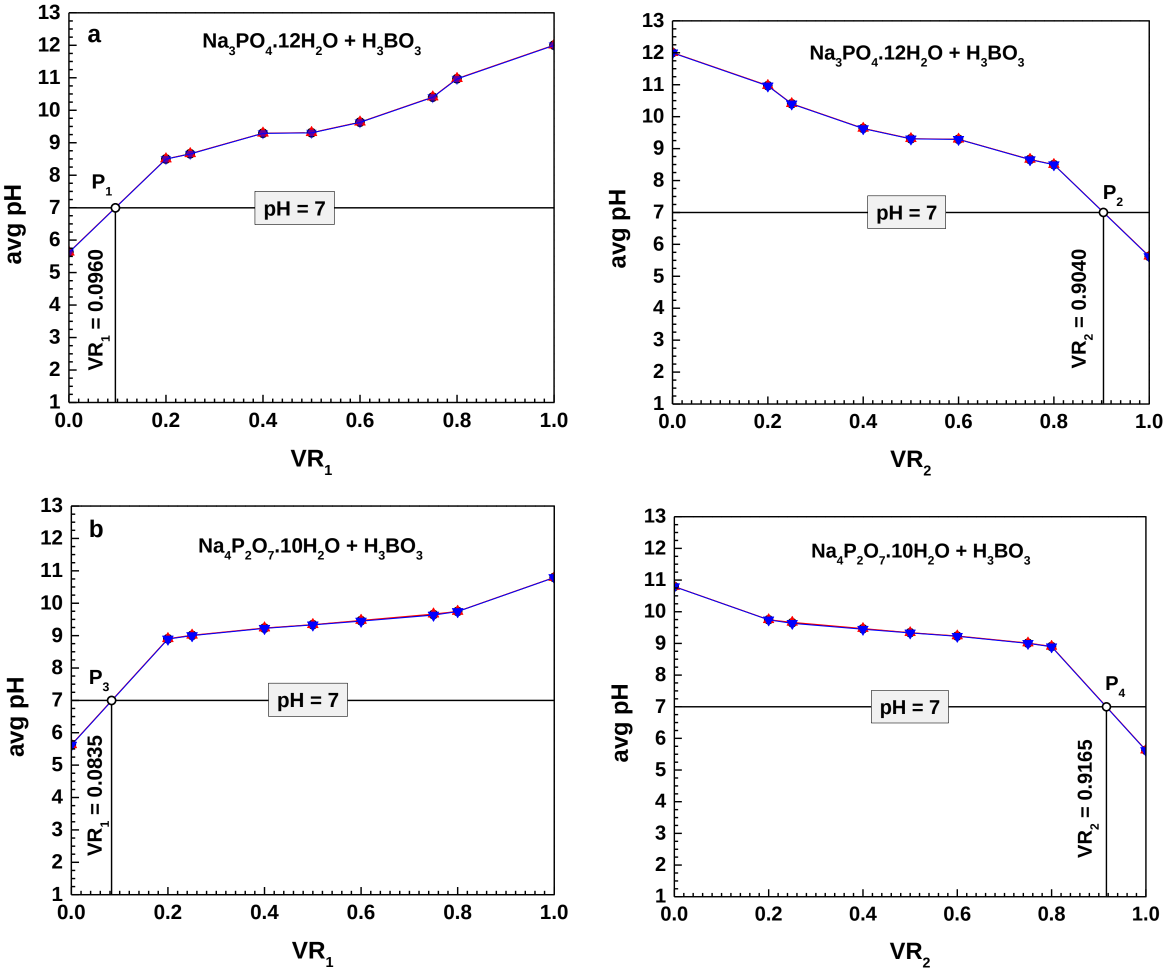

Fig. 1. Trends in pH variation as a function of the volume ratios between alkaline and acidic components: a) System M_1, b) system M_2.

The plots in Figure 1 reveal rather narrow VR intervals that permit the preparation of solutions with nearly neutral pH. For the system M_1, the neutral region lies between points P_1 and P_3 corresponding to $VR_1 = 0.09$ and $VR_1 = 0.12$. Practically, this means that a neutral M_1 system can be obtained by adding several milliliters (not exceeding 10 mL) of 0.05 M $Na_3PO_4.12H_2O$ to approximately 90 mL of 0.05 M H_3BO_3 solution. A similar conclusion can be drawn from the pH / VR_2 dependence.

In turn, for the M_2 system shown in Fig. 1b the interval is even narrower, lying between P_7 and P_9. In this case, a neutral mixture can be prepared by adding about 6-10 mL of 0.05 M $Na_4P_2O_7.10H_2O$ solution to nearly 92 mL of 0.05 M H_3BO_3 solution.

In both cases, the alkaline components must be added dropwise, and fine pH adjustment should be carried out on the following day to ensure stability.

Buffering capacity of neutral phosphate/borate solutions:

The buffering capacity was assessed by fivefold titration of 25 mL aliquots of the near-neutral mixtures with the standardized secondary solutions described in the experimental section. The obtained results these titrations are presented in Tables 5 and 6.

Table 5. Results of the potential buffering capacity of neutral $Na_3PO_4.12H_2O$ / H_3BO_3

Number	Expended NaOH (mL)	pH before titration	pH after titration	Expended HCl (mL)	pH before titration	pH after titration
I	**1.30**	**6.959**	**7.959**	**0.25**	**6.923**	**5.904**
II	**1.35**	**6.962**	**7.963**	**0.25**	**6.987**	**5.936**
III	**1.40**	**6.970**	**7.962**	**0.22**	**6.925**	**5.896**
IV	**1.40**	**6.984**	**7.974**	**0.22**	**6.947**	**5.870**
V	**1.45**	**6.972**	**7.968**	**0.30**	**6.944**	**5.857**
Avg. val.	**1.38 ± 0.06**	**6.969 ± 0.010**	**7.965 ± 0.010**	**0.25 ± 0.03**	**6.945 ± 0.026**	**5.893 ± 0.031**

Table 6. Results of the potential buffering capacity of neutral $Na_4P_4O_7.10H_2O$ / H_3BO_3

Number	Expended NaOH (mL)	pH before titration	pH after titration	Expended HCl (mL)	pH before titration	pH after titration
I	**1.65**	**6.971**	**7.968**	**0.25**	**6.913**	**5.925**
II	**1.50**	**6.887**	**7.886**	**0.30**	**6.936**	**5.880**
III	**1.65**	**6.960**	**7.969**	**0.25**	**6.918**	**5.950**
IV	**1.70**	**6.963**	**7.966**	**0.20**	**6.926**	**5.882**
V	**1.70**	**6.958**	**7.956**	**0.35**	**6.996**	**5.838**
Avg. val.	**1.64 ± 0.08**	**6.948 ± 0.034**	**7.949 ± 0.036**	**0.27 ± 0.06**	**6.938 ± 0.034**	**5.895 ± 0.043**

The data in both tables clearly show that only very small volumes of the diluted NaOH and HCl solutions are required to induce measurable pH changes in the investigated mixtures. This indicates that the studied systems exhibit negligible buffering properties.

Their buffering capacities were calculated, using Equation 2. It was applied, using the results, obtained from the above-described procedures. Hence, for the $Na_3PO_4.12H_2O$ - H_3BO_3, system (M_1) the calculations were done, considering: (i) the molarity of NaOH, shown in Table 2 is 48.648×10^{-3} mol.dm^{-3}; (ii) the average volume of this solution, expended for the titrations was about 1.64 mL, as is shown in Table 5; (iii) the volume of the titrated buffer solutions was 25 mL, until reaching (iv) almost a unit of pH change ($\Delta pH \approx 0.996$), as also shown in Table 5. All this yielded a buffering capacity for the $Na_3PO_4.12H_2O$ / H_3BO_3 neutral system M_1 of $BC^{NaOH}_{M1} = 26.96\times10^{-4}$ mol pH^{-1}.

For the $Na_4P_2O_7.10H_2O$ - H_3BO_3 system (M_2), similar calculations were performed using the data in Table 6 (average volume of the expended NaOH solution was about 1.64 mL, and the average change in pH was $\Delta pH \approx 1.001$. The obtained value for M_2 was close to the previous one, namely: $BC^{NaOH}_{M2} = 31.88\times10^{-4}$ mol pH^{-1}.

In a similar way, the buffering capacities of M_1, (based on $Na_3PO_4.12H_2O$ and H_3BO_3) and M_2 (based on $Na_4P_2O_7.10H_2O$ and H_3BO_3) were calculated by Equation 2, using the respective data in Tables 2, 5 and 6. The obtained results are: $BC^{HCl}_{M1} = 46.82\times10^{-5}$ mol pH^{-1} and $BC^{HCl}_{M2} = 51.00\times10^{-5}$ mol pH^{-1}, respectively.

A comparison of these values with results reported in previous studies confirms that the mixtures investigated in the present work cannot be considered effective buffers.

CONCLUSION

The present work provides valuable systematic data on the pH ranges and potential buffering properties of two phosphate/borate systems: $\mathbf{M_1}$ (composed of $Na_3PO_4.12H_2O + H_3BO_3$) and $\mathbf{M_2}$ (composed of $Na_4P_2O_7.10H_2O + H_3BO_3$). The experimental procedures, including direct measurements and raw data, are presented in detail to ensure reproducibility and to serve as a useful reference for further studies. Although the examined systems demonstrated poor buffering capacity, the proposed mixtures may still find practical use in preliminary surface treatments and primer coating formation on various industrial alloys.

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