

Investigation of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O Water-Salt Ternary System at Room Temperature

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Abstract

Objective: In this study, the solubility, density, conductivity and phase equilibria of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary system located in the structure of the Na^+ , Ba^{2+} , $(\text{H}_2\text{PO}_2)^-//\text{H}_2\text{O}$ quaternary reciprocal water-salt system were investigated using physicochemical analysis methods.

Material and Methods: Riedel-de Haen and Merck salts were used to investigate the solubility and phase equilibria of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system at room temperature

Results: It was determined that the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system belongs to the simple eutonic system type and the compositions corresponding to the eutonic point, expressed as mass %, were 50.73, 0.53 and 48.74 (w/w %) for $\text{Na}_2(\text{H}_2\text{PO}_2)_2$, $\text{Ba}(\text{H}_2\text{PO}_2)_2$ and H_2O , respectively

Keywords: $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O Ternary Water-Salt System, Isothermic System, Density, Solubility, Conductivity

Introduction

“Physicochemical analysis”, a term introduced by N. S. Kurnakov, based on various properties of a system (solubility, viscosity, density, conductivity, etc.), is one of the research methods used to reveal reciprocal interactions among compounds of the system in question (1)

Gibbs’s phase rule, V. F. Alekseyev’s reciprocal solubility of fluids (2), and I. F. Schrader’s relationship between the melting points of solids, specific melting heats and solubility in fluids (2, 3), along with other studies, have played a major role in the development of the theoretical basis of physicochemical analysis.

To obtain hypophosphites in a simpler and more practical manner compare to physicochemical methods, research in the solubility and phase equilibria of A^+ , $\text{M}^{++} / \text{X}^-$, $(\text{H}_2\text{PO}_2)^- // \text{H}_2\text{O}$ ($\text{A}^+=\text{Na}^+$, K^+ , NH_4^+ , etc.), ($\text{M}^{++}=\text{Ba}^{++}$, Mn^{++} , Zn^{++} , Ni^{++} , etc.), and ($\text{X}^- = \text{Cl}^-$, Br^- , NO_3^- , etc.) quaternary reciprocal water-salt systems carries a certain theoretical and practical importance (4, 3).

By investigating, through physicochemical analysis methods, the ternary, quaternary and quinary systems established for salts which several sea, lake and underground water sources contain, and proceeding from the basis of “Composition-Characteristic” diagrams, the acquisition, recovery and separation of a few valuable chemical substances have been realized (5).

In the present paper, the experimental results obtained at room temperature of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system, which takes place within the structure of the Na^+ , $\text{Ba}^{2+} / \text{Cl}^-$, $(\text{H}_2\text{PO}_2)^-//\text{H}_2\text{O}$ quaternary reciprocal water-salt system, and phase diagrams based on those results are shown.

Material and Methods

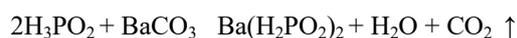
Riedel-de Haen and Merck salts were used to investigate the solubility and phase equilibria of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system at room temperature. The $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt was obtained purely through the below reaction and crystallized twice (6).

Received: 18-08-2016 Accepted 28-10-2016 Available Online: 15-11-2016

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The process of investigating the solubility and phases in a state of equilibrium in this ternary system was carried out using a special lens inserted into an electric thermostat. Analysis of the liquid phase was performed by determining the Ba^{++} , Na^+ , $(\text{H}_2\text{PO}_2)^-$ ions found in solution. Of these ions, the Ba^{++} ion was analyzed using complexometry (as well as the gravimetric method), while the $(\text{H}_2\text{PO}_2)^-$ ion was determined using the spectrophotometric method (7).

Determination of the system's solid phase composition was carried out using Schreinemaker's dry residue method (8).

Results

During investigation of the solubility, density, conductivity and phase equilibria of the $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system at room temperature, 10 experimental data points per $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O were determined until reaching the eutonic point in the direction of $\text{Na}_2(\text{H}_2\text{PO}_2)_2$, and 3 data points per $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - H_2O were determined until the eutonic point was reached in the direction of $\text{Ba}(\text{H}_2\text{PO}_2)_2$.

The experimental results obtained, relating to the compositions of the system's liquid phase and solid phase at equilibrium, are given in Table 1.

Table 1. The solubility of $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system and composition of the solid phases at equilibrium, at room temperature.

No	Liquid Phase (Mass %)			Solid Residue (Mass %)		Composition of Solid Phase
	NaH_2PO_2	$\text{Ba}(\text{H}_2\text{PO}_2)_2$	H_2O	NaH_2PO_2	$\text{Ba}(\text{H}_2\text{PO}_2)_2$	
1	51.96	0.00	48.04	100.00	0.00	NaH_2PO_2 , H_2O
2	51.07	0.32	48.61	73.24	0.26	NaH_2PO_2 , H_2O
3	50.73	0.53	48.74	67.17	16.32	NaH_2PO_2, H_2O + $\text{Ba}(\text{H}_2\text{PO}_2)_2$·$\text{H}_2\text{O}$
4	50.73	0.53	48.74	48.31	28.62	NaH_2PO_2, H_2O + $\text{Ba}(\text{H}_2\text{PO}_2)_2$·$\text{H}_2\text{O}$
5	48.61	1.08	50.31	11.26	70.90	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
6	38.92	1.49	59.59	9.47	72.53	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
7	33.49	1.60	64.91	6.47	74.53	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
8	24.43	3.03	72.54	4.41	76.09	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
9	21.97	3.25	74.78	3.50	77.80	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
10	10.71	7.36	81.93	2.06	79.04	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
11	6.87	10.17	2.96	0.80	81.80	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
12	4.17	12.20	83.63	0.50	82.20	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O
13	0.00	16.23	83.77	0.00	100.00	$\text{Ba}(\text{H}_2\text{PO}_2)_2$ · H_2O

Table 2. Composition and change in solubility, density and conductivity of $\text{Na}_2(\text{H}_2\text{PO}_2)_2$ - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system at room temperature.

No	Liquid Phase (Mass %)			In 100 Mol Salt Mixture		H_2O Mol Count versus 100 Mol Salt	Density ($\text{kg}\cdot\text{m}^{-3}$)	Conductivity ($\text{mS}\cdot\text{cm}^{-1}$)
	NaH_2PO_2	$\text{Ba}(\text{H}_2\text{PO}_2)_2$	H_2O	NaH_2PO_2	$\text{Ba}(\text{H}_2\text{PO}_2)_2$			
1	51.96	0.00	48.04	100.00	0.00	904	1394	6480
2	51.07	0.32	48.61	99.58	0.42	927	1390	6360
3	50.73	0.53	48.74	99.31	0.69	933	1385	5960
4	50.73	0.53	8.74	99.31	0.69	933	1385	5960
5	48.61	1.08	50.31	98.55	1.45	997	1384	5900
6	38.92	1.49	59.59	97.53	2.47	1460	1383	5880
7	33.49	1.60	64.91	96.94	3.06	1837	1381	5860
8	24.43	3.03	72.54	92.44	7.56	2684	1380	5850
9	21.97	3.25	74.78	91.11	8.89	3032	1378	5810
10	10.71	7.36	81.93	68.82	31.18	5148	1360	5220
11	6.87	10.17	82.96	50.61	49.39	5976	1341	4400
12	4.17	12.20	83.63	34.14	65.86	6696	1316	3600
13	0.00	16.23	83.77	0.00	100.00	7656	1255	935

Based on the data given in Table 1, a phase diagram was constructed for the $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary water-salt system using the Rozeboun method.

The results of the mathematical calculations as mol %, based on the composition of the $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary water-salt system expressed as mass %, are shown in Table 3.

Table 3. Solubility of $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary water-salt system at room temperature.

No	Liquid Phase (Mass %)			In 100 Mol Salt Mixture		H ₂ O Mol Count versus 100 Mol Salt
	NaH ₂ PO ₂	Ba(H ₂ PO ₂) ₂	H ₂ O	NaH ₂ PO ₂	Ba(H ₂ PO ₂) ₂	
1	51.96	0.00	48.04	100.00	0.00	904
2	51.07	0.32	48.61	99.58	0.42	927
3	50.73	0.53	48.74	99.31	0.69	933
4	50.73	0.53	48.74	99.31	0.69	933
5	48.61	1.08	50.31	98.55	1.45	997
6	38.92	1.49	59.59	97.53	2.47	1460
7	33.49	1.60	64.91	96.94	3.06	1837
8	24.43	3.03	72.54	92.44	7.56	2684
9	21.97	3.25	74.78	91.11	8.89	3032
10	10.71	7.36	81.93	68.82	31.18	5148
11	6.87	10.17	82.96	50.61	49.39	5976
12	4.17	12.20	83.63	34.14	65.86	6696
13	0.00	16.23	83.77	0.00	100.00	7656

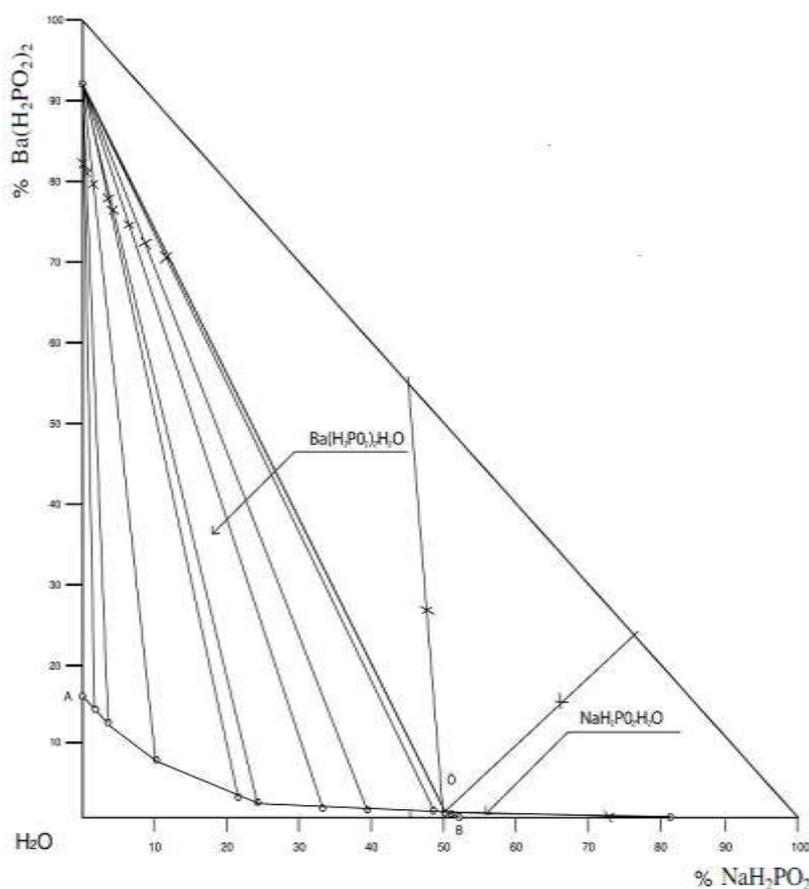


Figure 1. Solubility and phase equilibria diagram of $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary water-salt system at room temperature (the Rozeboun method).

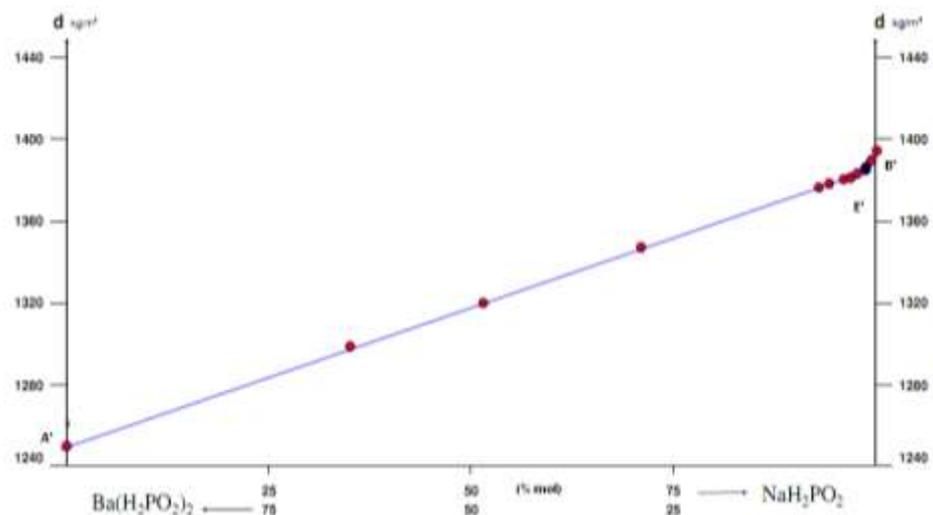


Figure 2. Yeneke – Le Chatelier diagram of the density of $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary system.

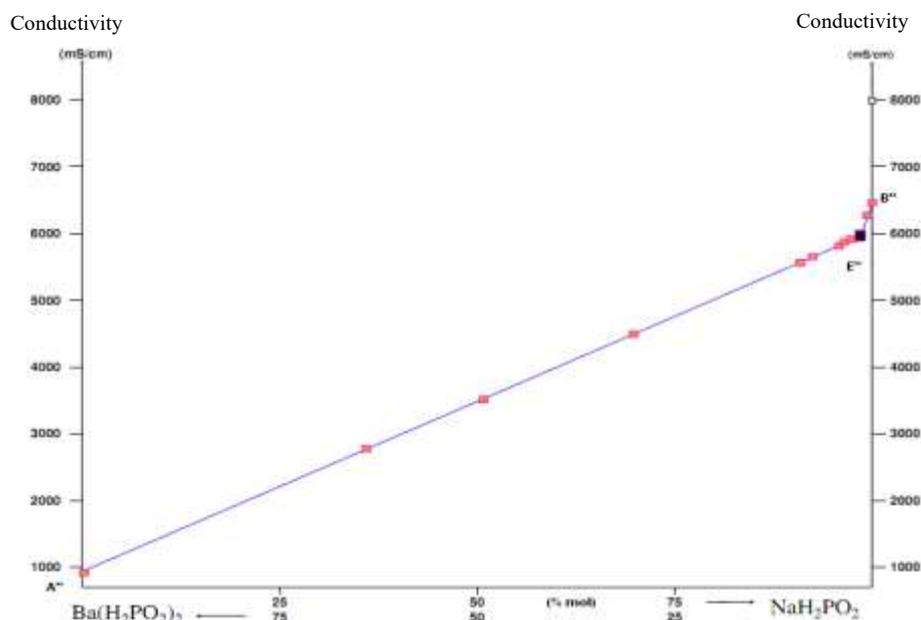


Figure 3. Yeneke – Le Chatelier diagram of the conductivity of $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary system.

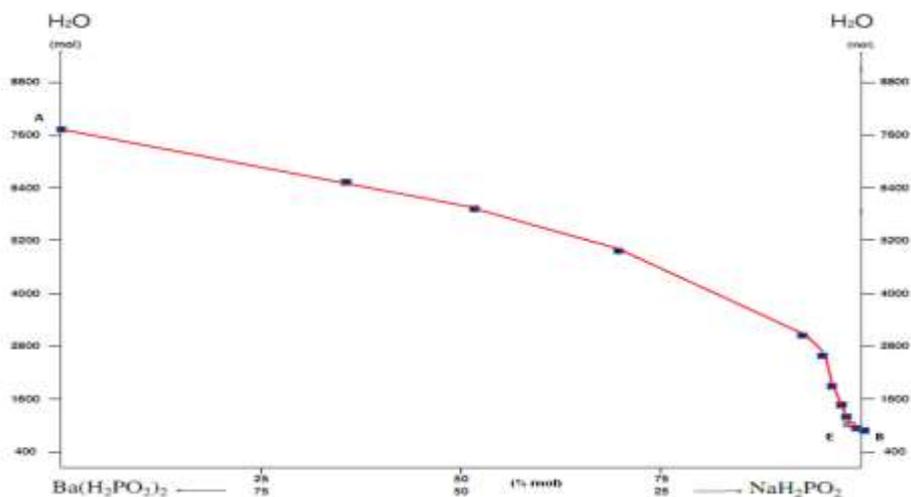


Figure 4. Solubility of $\text{NaH}_2\text{PO}_2\text{-Ba}(\text{H}_2\text{PO}_2)_2\text{-H}_2\text{O}$ ternary water-salt system at room temperature using the Yeneke – Le Chatelier method.

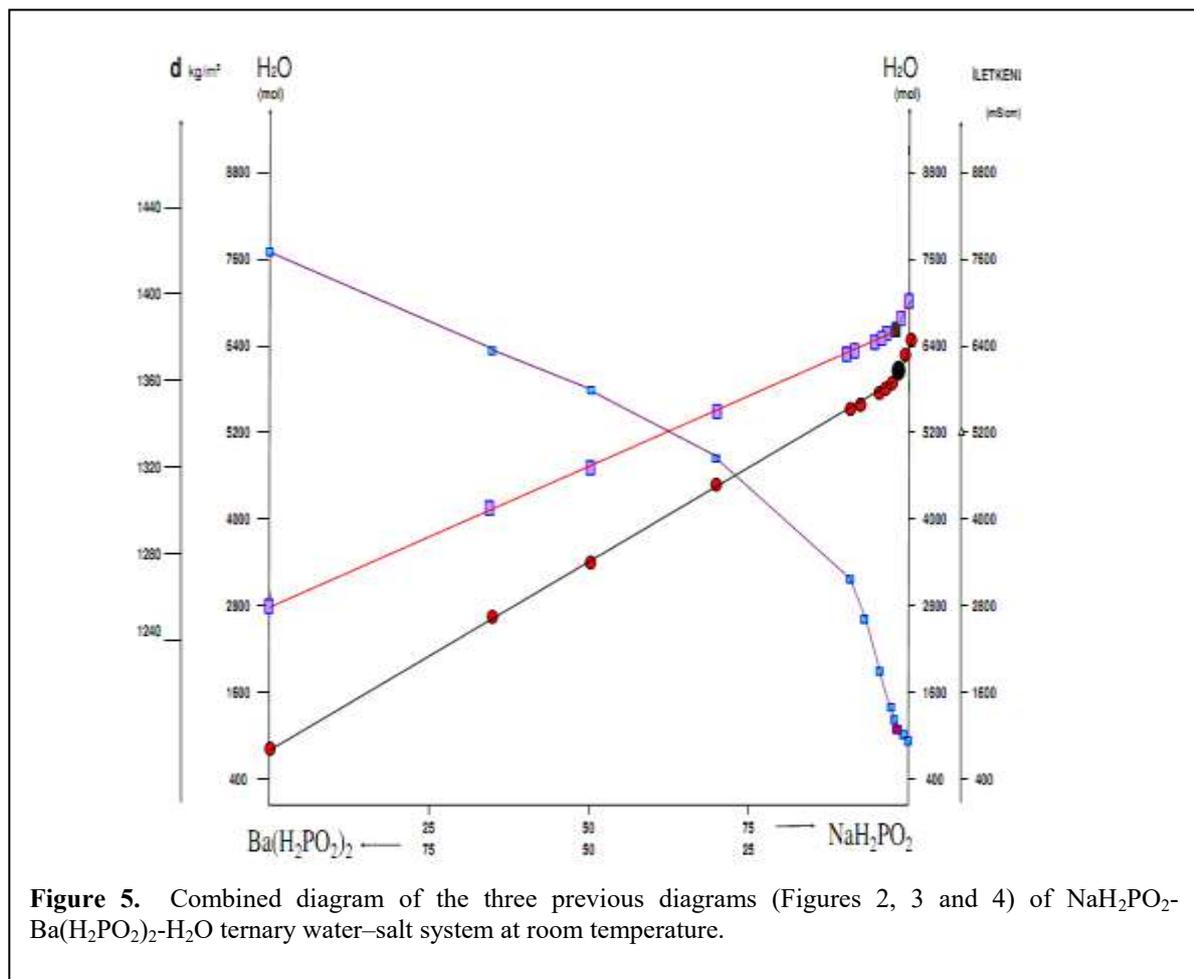


Figure 5. Combined diagram of the three previous diagrams (Figures 2, 3 and 4) of NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system at room temperature.

Conclusion

According to the experimental results obtained from the NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary water-salt system (Tables 1-3 and Figures 1-5), it was determined that the system belongs to the simple eutonic type.

The composition, expressed as mass %, of the eutonic point of the system investigated was found to be 50.73 for NaH_2PO_2 , 0.53 for $\text{Ba}(\text{H}_2\text{PO}_2)_2$, and 48.74 for H_2O . $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and $\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ crystal hydrate were found to be in equilibrium with the liquid phase of the system at the eutonic point.

As seen in Table 1 and Figure 1, examination of the NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary system at room temperature shows that, when moving towards the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ corner of the triangle along the NaH_2PO_2 - H_2O curve, the reciprocal solubility of the NaH_2PO_2 salt decreased from 51.96% (the solubility of NaH_2PO_2 salt in pure water) to 50.73% (the solubility of NaH_2PO_2 salt at the eutonic point) under the influence of the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt added to the solution.

According to calculations from studying the NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary system at room temperature, when approaching the NaH_2PO_2 corner of the triangle along the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O curve, the reciprocal solubility of the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt was

reduced from 16.23% (the solubility of $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt in pure water) to 0.53% (the solubility of $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt at the eutonic point) due to the influence of the NaH_2PO_2 salt added to the solution. In this case, it can be concluded that each salt reduced the other's solubilities at room temperature.

In studying of the NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary system at room temperature it was found that, when moving in the direction of the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ corner of the triangle along the NaH_2PO_2 - H_2O curve, the density of the liquid phase decreased from 1394 kg/m^3 (the density of the saturated solution of the NaH_2PO_2 salt) to 1385 kg/m^3 (the density of the liquid phase of the system at the eutonic point) with the addition of the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt to the system.

Study of the NaH_2PO_2 - $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O ternary system at room temperature determined that,

proceeding along the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ - H_2O curve in the direction of the NaH_2PO_2 corner of the triangle, the density of the liquid phase increased from 1255 kg/m^3 (the density of the saturated solution of the $\text{Ba}(\text{H}_2\text{PO}_2)_2$ salt) to 1385 kg/m^3 (the density of the liquid phase of the system at the eutonic point) with the addition of the NaH_2PO_2 salt to the system.

At room temperature, the fact that the value of the density of the liquid phase of the NaH_2PO_2 -

Ba(H₂PO₂)₂-H₂O ternary system at the eutonic point is lower than the density of the saturated solution of the NaH₂PO₂ salt in pure water is related to the total salt content (NaH₂PO₂+Ba(H₂PO₂)₂) (which was dissolved at the eutonic point) of the system being less.

The experimental results obtained by investigating the conductivity of the liquid phase of the NaH₂PO₂-Ba(H₂PO₂)₂-H₂O ternary system at room temperature are shown in Table 2, and a diagram of the change in conductivity associated with the Ba(H₂PO₂)₂ composition is shown in Figure 3.

Study of the NaH₂PO₂-Ba(H₂PO₂)₂-H₂O ternary water-salt system at room temperature showed that, advancing toward the Ba(H₂PO₂)₂ corner of the triangle along the NaH₂PO₂- H₂O curve, the conductivity of the liquid phase decreased from 6480 mS/cm (the conductivity of the saturated solution of the NaH₂PO₂ salt) to 5960 mS/cm (the conductivity of the liquid phase of the system at the eutonic point) with the addition of the Ba(H₂PO₂)₂ salt to the system.

Study of the NaH₂PO₂-Ba(H₂PO₂)₂-H₂O ternary water-salt system at room temperature determined that, moving in the direction of the NaH₂PO₂ corner of the triangle along the Ba(H₂PO₂)₂-H₂O curve, the conductivity of the liquid phase increased from 935 mS/cm (the conductivity of the saturated solution of the Ba(H₂PO₂)₂ salt) to 5960 mS/cm (the conductivity of the liquid phase of the system at the eutonic point) with the addition of the NaH₂PO₂ salt to the system.

In conclusion, in using physicochemical methods to research the NaH₂PO₂-Ba(H₂PO₂)₂-H₂O ternary water-salt system, it is critical that the analytical methods applied in the analysis of the compositions of the liquid and solid phases, as well as in other experimental work, and other be carried out as accurately as possible so that the results obtained are accepted as sound and trustworthy to a high degree (Figure 5).

Conflict of interest: The authors declare they have no potential conflicts of interest with respect to the research, authorship, and/or publication of this article, and declare study has ethical permissions if required.

Acknowledgement: Contribution of authors; HE, HT: Concept and design, **HT:** Data Analysis, **ARK:** Statistical analysis, **HT:** Writing, **HE, HT and ARK:** Editing

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