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ORIGINAL PAPER

# Solubility, density, conductivity, and phase equilibrium of NaBr - $Ba(H_2PO_2)_2$ - $H_2O$ ternary system at 298 K*

**Hasan Erge**

**Department of Chemistry**
**Van Yüzüncü Yıl University, Türkıye**

**Abstract**

Composition-property diagrams of NaBr-$Ba(H_2PO_2)_2$ -$H_2O$ ternary water-salt system, which is contained within $A^+$, $B^{++}$/ $X^-$, $(H_2PO_2)^-$ // $H_2O$ ($A^+$= $Na^+$, $Li^+$, $K^+$, $NH4^+$ etc.); ($B^{++}$= $Ba^{++}$, $Fe^{++}$, $Mg^{++}$, $Cu^{++}$, $Ni^{++}$ etc.); ($X^-$ = $Cl^-$, $I^-$, $Br^-$ etc.) $Na^+$, $Ba^{++}$/ $Br^-$, $(H_2PO_2)^-$//$H_2O$ quaternary water-salt system were drawn with the isothermal method. In this study, the phase equilibria of the NaBr -$Ba(H_2PO_2)_2$- $H_2O$ triple system that are included in the quaternary mutual water-salt system containing $Na^+$, $Ba^{+2}$/$Br^-$, $(H_2PO_2)^-$//$H_2O$, at 298 K were investigated. The physicochemical properties of the liquid phase, which is in equilibrium with the solid phases of the system, such as density and conductivity were also studied. The system's solubility, density, conductivity, and equilibrium phases were studied, with the use of a special glass container placed in an electro-thermostat. We used titrimetric analysis in analytical chemistry and physicochemical phase diagram techniques to test the developed system. In the ternary water-salt system studied (% mass), an invariant point having a composition of NaBr – 46.27%, Ba $(H_2PO_2)_2$ – 5.75%, $H_2O$ – 47.98% was determined. It has been seen that in the indicated invariant point, the liquid phase is equilibrated with two solid phases: $Ba(H_2PO_2)_2$. $H_2O$ and NaBr. The methods for separating NaBr and $Ba(H_2PO_2)_2$ salts from natural salts and salt mixtures in industrial wastes can be applied and used in the processing and preparation of physicochemical principles.

**Keywords:** ternary water-salt system, isothermal method, conductivity, solubility

Hasan Erge, Ast. Prof. (ORCID ID: 0000-0002-7696-3300), Department of Chemistry, Faculty of Science, Van Yüzüncü Yıl University, Türkıye, e-mail: ergehasan@hotmail.com
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# INTRODUCTION

Hypophosphite salts have a wide range of use. Hypophosphites are used in chemistry, medicine, food, pharmacology, and in the textile industry (Robertson 2006, Noisong et al. 2008).

Compound-property diagrams drawn from experimental data obtained by investigating phase equilibria of water-salt systems with physicochemical methods are used widely in the salt industry (Alişoğlu 1998). The separation of the crystals of $Na_2SO_4 \cdot 10H_2O$ from the mirabilite crystal hydrate from the Caspian Sea Kara-Boğazgöl waters was possible owing to the investigation of the solubility and equilibrium phases in the $Na^+$, $Mg^{2+}$//$Cl^-$, $SO_4^{2-}$// $H_2O$ quaternary water-salt system carried out with physicochemical methods (Anasov, Pogodin 1948).

In the isothermal method, the $K_2(NO_3)_2$-$Mn(H_2PO_2)_2$-$H_2O$ ternary system was investigated at 20°C. As a result, it has been determined that there is a eutonic point with the following composition on the solubility curve of the system in question: $KNO_3$ – 20.12%, $Mn(H_2PO_2)_2$ – 6.88%, and $H_2O$ 73.00%. It has been shown that the crystals of $KNO_3$ and $Mn(H_2PO_2)_2 \cdot H_2O$ salts are in equilibrium with the liquid phase at the said eutonic point (Aliev et al. 1989).

The isothermal method investigated the solubility and phase balances of the NaBr-$Mn(H_2PO_2)_2$–$H_2O$ system at 25°C. As a result, eutonic points on the isothermic curve of the system were determined, with the following composition of NaBr – 46.92%, $Mn(H_2PO_2)_2$ – 2.30%, and $H_2O$ – 50.78% (Aliev et al. 1991).

The solubility and phase equilibria of the $Na_2(NO_3)_2$-$Na_2(H_2PO_2)_2$-Mn $(H_2PO_2)_2$-$H_2O$ quaternary system at 0°C were investigated with the isothermal method. As a result, its composition (in mass%) for the investigated quartet system was identified. Four eutonic points were determined, namely $NaNO_3$ – 11.36%, $NaH_2PO_2$ – 42.88%, $Mn(H_2PO_2)_2$ – 0.13%, and $H_2O$ – 45.63% (Alişoğlu, Necefoğlu 1997).

Erge and his research team have studied the ternary and quaternary systems of barium and sodium-containing hypophosphite salts at 0°C (Erge et al. 2013). Alişoğlu and Adıgüzel have examined the manganese and potassium hypophosphites at 273.15 K (Alişoğlu, Adigüzel 2008). Demirci et al. have studied the solubility and physicochemical properties of the ternary and quaternary systems containing $NaH_2PO_2$, $Zn(H_2PO_2)_2$ at 298.15 K (Demirci et al. 2016). Tan and co-authors have observed the ternary systems with the content of $Ca(H_2PO_2)_2$ and $NaH_2PO_2$ at 298.15 K (Tan et al. 2015).

$ZnCl_2$, the other salt in our study, is a salt with very high solubility, which increases with the temperature increase, and therefore has high viscosity in the solution condition (Kirilenko 2013, Zhang et al. 2017).

It is known that the applicability of some inorganic chemistry compounds is limited because the methods in which certain salts are obtained are multi-step and expensive. One of those salts is hypophosphite. Hypophosphites are obtained with the following methods, such as the salts of $H_3PO_2$.

$P_4 + 3NaOH + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$

Hypophosphites of alkaline earth metals have also been obtained with this method,. But another method with multiple steps is used to obtain hypophosphites of the elements which have water-insoluble hydroxides.

For example, synthesis of manganese hypophosphite is a three-step chemical reaction. In general, it can be shown as follows:

i) $2P_4 + 3Ba(OH)_2 + 6H_2O \rightarrow 3Ba(H_2PO_2)_2 + 2PH_3$

ii) $Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ H_3PO_2$

iii) $2H_3PO_2 + MnCO_3 \rightarrow Mn(H_2PO_2)_2 + CO_2 + H_2O$

When multi-step reactions are used, the efficiency of obtaining the final product hypophosphite will not be high, which is why the product is expensive. A method to produce such hypophosphites that can be easier, practical and cheaper, for example a method based on displacement reaction, has been developed. Physicochemical analysis of water-salt systems containing hypophosphite obtained with an easy and inexpensive method is important to develop the physicochemical basis for such a method (Alişoğlu 2004).

## MATERIAL AND METHODS

For the formation of $Na^+$, $Ba^{2+}/Br^-(H_2PO_2)^-//H_2O$ quaternary water-salt system, salts of Riedel-de Haen and Merck were used.

$Ba(H_2PO_2)_2 \cdot H_2O$ salt was obtained purely in the laboratory from the following reaction:

$2H_3PO_2 + BaCO_3 \rightarrow Ba(H_2PO_2)_2 \cdot H_2O + CO_2$

The resulting salts were subjected to the crystallization process twice (Erge et al. 2011, 2012).

A special glass container with an electro-thermostat was used to investigate the solubility, density, conductivity, and phase in equilibrium in the system (Alişoğlu 1973). The liquid phase concentration in the system was determined using a pycnometer with a volume of 5 mL. Conductivity was measured using a Cond 315İ/SET conductometer (Adigüzel et al. 2014). The $Ba^{2+}$ ion in the solution was determined by complexometry, $Br^-$ ion was determined by the argentometric method, and the $H_2PO_2^-$ ion was determined by the titrimetry method (Gündüz 1993, Gülensoy 2003).

# RESULTS AND DISCUSSION

During the investigation of the solubility, density, conductivity, and phase equilibria of NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary water-salt system at 298K, nine experimental points were determined until the system reached the invariant point in the NaBr direction by $Ba(H_2PO_2)_2$-$H_2O$. Five practical points were confirmed until the invariant point was reached in the $Ba(H_2PO_2)_2$ direction by NaBr. The experimental results concerning the liquid phase in the system and the solid phase compounds in equilibrium are given in Table 1.

Table 1

Solid-liquid phase equilibria of the NaBr -$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298 K

| Liquid phase (% mass) | | | | The solid phase (% mass) | | Equilibrium composition |
|---|---|---|---|---|---|---|
| No | NaBr | $Ba(H_2PO_2)_2$ | $H_2O$ | NaBr | $Ba(H_2PO_2)_2$ | |
| 1 | 49.67 | 0.00 | 50.33 | 94.3 | 0.00 | NaBr |
| 2 | 48.74 | 1.32 | 49.94 | 92.10 | 0.70 | NaBr |
| 3 | 47.8 | 2.58 | 49.62 | 88.80 | 0.95 | NaBr |
| 4 | 47.32 | 3.54 | 49.14 | 83.00 | 1.90 | NaBr |
| 5E | 46.27 | 5.75 | 47.98 | 66.00 | 18.7 | NaBr+$Ba(H_2PO_2)_2 \cdot H_zO$ |
| 6E | 46.27 | 5.75 | 47.98 | 53.00 | 31.0 | NaBr +$Ba(H_2PO_2)_2 \cdot H_zO$ |
| 7 | 44.56 | 6.37 | 49.07 | 15.50 | 62.4 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 8 | 38.44 | 7.15 | 54.41 | 14.00 | 63.2 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 9 | 32.05 | 8.84 | 59.11 | 10.20 | 67.1 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 10 | 23.92 | 10.74 | 65.34 | 6.30 | 72.4 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 11 | 18.58 | 11.89 | 69.53 | 4.00 | 76.7 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 12 | 13.37 | 12.95 | 73.68 | 2.20 | 80.3 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 13 | 7.51 | 14.28 | 78.21 | 0.90 | 85.0 | $Ba(H_2PO_2)_2 \cdot H_2O$ |
| 14 | 0.00 | 16.05 | 83.95 | 0.00 | 93.2 | $Ba(H_2PO_2)_2 \cdot H_2O$ |

Based on the information given in Table 1, the phase diagram of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system was plotted with the Rozeboum method (Figure 1). Based on the information given in Table 2, diagrams of the density and conductivity of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298K were drawn using the Yeneke-Le Chatelier method (Figures 2-3).

The result of the mathematical operations based on the % mass expression of the composition of NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary water-salt system

Table 2

Exchange of the solubility, density, and conductivity of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298 K with the composition of the system

| Liquid phase (% mass) | | | | 100 mole salt composition | | 100 mole $H_2O$ composition (equal 100-mole salt) | Density (kg $m^{-3}$) | Conductivity (mS $cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| No | NaBr | $Ba(H_2PO_2)_2$ | $H_2O$ | NaBr | $Ba(H_2PO_2)_2$ | | | |
| 1 | 49.67 | 0.00 | 50.33 | 100.00 | 0.00 | 1160 | 1527 | 7980 |
| 2 | 48.74 | 1.32 | 49.94 | 97.95 | 2.05 | 1149 | 1540 | 7860 |
| 3 | 47.8 | 2.58 | 49.62 | 96.00 | 3.99 | 1141 | 1555 | 7774 |
| 4 | 47.32 | 3.54 | 49.14 | 94.54 | 5.46 | 1124 | 1560 | 7700 |
| 5E | 46.27 | 5.75 | 47.98 | 91.25 | 8.75 | 1083 | 1578 | 7540 |
| 6E | 46.27 | 5.75 | 47.98 | 91.25 | 8.75 | 1083 | 1578 | 7540 |
| 7 | 44.56 | 6.37 | 49.07 | 90.06 | 9.93 | 1135 | 1573 | 7425 |
| 8 | 38.44 | 7.15 | 54.41 | 87.45 | 12.55 | 1417 | 1562 | 7242 |
| 9 | 32.05 | 8.84 | 59.11 | 82.45 | 17.55 | 1740 | 1524 | 6870 |
| 10 | 23.92 | 10.74 | 65.34 | 74.27 | 25.73 | 2322 | 1486 | 6285 |
| 11 | 18.58 | 11.89 | 69.53 | 66.94 | 33.05 | 2867 | 1454 | 5770 |
| 12 | 13.37 | 12.95 | 73.68 | 57.23 | 42.77 | 3609 | 1403 | 5065 |
| 13 | 7.51 | 14.28 | 78.21 | 40.53 | 59.46 | 4831 | 1318 | 3840 |
| 14 | 0.00 | 16.05 | 83.95 | 0.00 | 100.00 | 7759 | 1121 | 1020 |

at 298 K is shown in Table 3 as % mol salt mixture and mole numbers of salt against 1000 moles of water.

Based on the information given in Table 3, a diagram of the solubility of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298 K was drawn with the Yeneke-Le Chatelier method, and the exchange of solubility, density, and conductivity (three in one) was illustrated in a composite graph (Figures 4 and 5).

The solubility, density, conductivity, and phase equilibria of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system in the $Na^+$, $Ba^{2+}$/$Br^-$, $(H_2PO_2)^-$//$H_2O$ quaternary mutual water salt system were investigated with physicochemical methods. The experimental results are shown in Tables (1-3) and Figures (1-5).

According to the experimental results (Tables 1-3 and Figures 1-5), the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system belonged to simple invariant

Table 3

Solubility of $NaBr-Ba(H_2PO_2)_2-H_2O$ ternary water-salt system at 298 K

| Liquid phase (% mass) | | | | 100 mole salt composition | | 100 mole $H_2O$ composition (equal 100-mole salt) | Salt composition (equal 100 mole $H_2O$) | |
|---|---|---|---|---|---|---|---|---|
| No | NaBr | $Ba(H_2PO_2)_2$ | $H_2O$ | NaBr | $Ba(H_2P_2)_2$ | | NaBr | $Ba(H_2PO_2$ |
| 1 | 49.67 | 0.00 | 50.33 | 100.00 | 0.00 | 1160 | 86.23 | 0.00 |
| 2 | 48.74 | 1.32 | 49.94 | 97.95 | 2.05 | 1149 | 85.28 | 1.78 |
| 3 | 47.8 | 2.58 | 49.62 | 96.00 | 3.99 | 1141 | 84.17 | 3.51 |
| 4 | 47.32 | 3.54 | 49.14 | 94.54 | 5.46 | 1124 | 84.14 | 4.86 |
| 5E | 46.27 | 5.75 | 47.98 | 91.25 | 8.75 | 1083 | 84.26 | 8.08 |
| 6E | 46.27 | 5.75 | 47.98 | 91.25 | 8.75 | 1083 | 84.26 | 8.08 |
| 7 | 44.56 | 6.37 | 49.07 | 90.06 | 9.93 | 1135 | 79.35 | 8.75 |
| 8 | 38.44 | 7.15 | 54.41 | 87.45 | 12.55 | 1417 | 61.73 | 8.86 |
| 9 | 32.05 | 8.84 | 59.11 | 82.45 | 17.55 | 1740 | 47.38 | 10.08 |
| 10 | 23.92 | 10.74 | 65.34 | 74.27 | 25.73 | 2322 | 31.99 | 11.08 |
| 11 | 18.58 | 11.89 | 69.53 | 66.94 | 33.05 | 2867 | 23.35 | 11.53 |
| 12 | 13.37 | 12.95 | 73.68 | 57.23 | 42.77 | 3609 | 15.86 | 11.85 |
| 13 | 7.51 | 14.28 | 78.21 | 40.53 | 59.46 | 4831 | 8.39 | 12.31 |
| 14 | 0.00 | 16.05 | 83.95 | 0.00 | 100.00 | 7759 | 0.00 | 12.89 |

systems. The composition of this invariant point (% mass) was determined as NaBr – 46.27%, $Ba(H_2PO_2)_2$ – 5.75%, $H_2O$ – 47.98%. In this invariant point system, the liquid phase of the system was in equilibrium with the crystal hydrate of NaBr and $Ba(H_2PO_2)_2.H_2O$.

As shown in Table 1 and Figure 1, when the triangle is made towards the $Ba(H_2PO_2)_2$ corner by NaBr, investigation of $NaBr-Ba(H_2PO_2)_2-H_2O$ ternary system at 298 K shows that the NaBr salt counterpart solution decreases from 49.67% (NaBr salt pure water solubility) to 46.27% (NaBr salt invariant solubility) under the effect of $Ba(H_2PO_2)_2$ salt added to the solution. When the investigation of the $NaBr-Ba(H_2PO_2)_2-H_2O$ ternary system at 298 K was carried out while the triangle was made towards the NaBr corner by $Ba(H_2PO_2)_2-H_2O$, the relative solubility of $Ba(H_2PO_2)_2$ salt was calculated to decrease from 16.05% [solubility in $Ba(H_2PO_2)_2$ pure salt water] to 5.75% [invariant point solubility of $Ba(H_2PO_2)_2$ salt] under the influence of NaBr salt added to the solution.

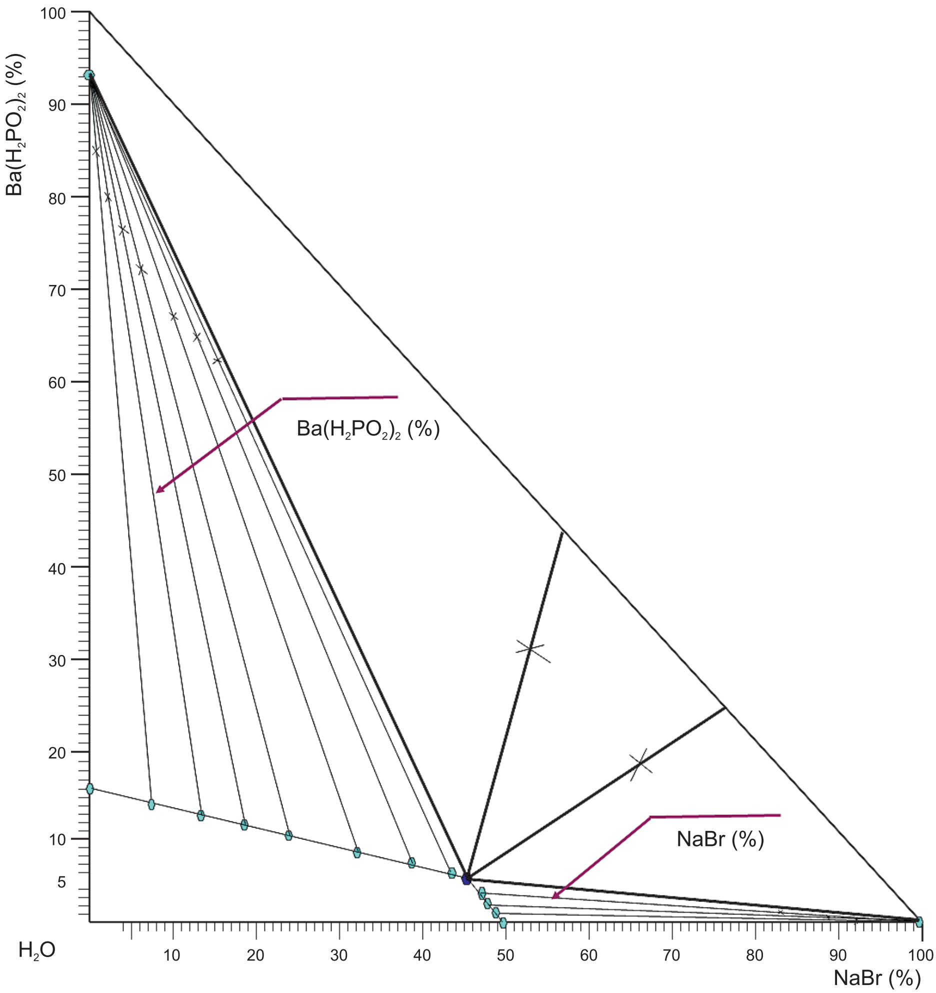


Fig. 1. Solubility and phase diagrams of the NaBr -$Ba(H_2PO_2)_2$-$H_2O$ triple water-salt system at 298 K (Rozeboum method)

To employ the Yeneke-Le Chatelier method for testing the solubility of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298K, based on the % mass expression of the composition of the system, the result of mathematical operations, the composition of the subject system is expressed in terms of moles of NaBr and $Ba(H_2PO_2)_2$ salts in a 100 moles salt mixture and mole number of water in the solution compared to a mol% salt mixture (Table 3 and Figure 4).

The experimental results obtained from the investigation of the liquid phase density of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system at 298 K are shown in Table 2. The diagram of the exchange of $Ba(H_2PO_2)_2$ with the compound in the dense system is shown in Figure 2.

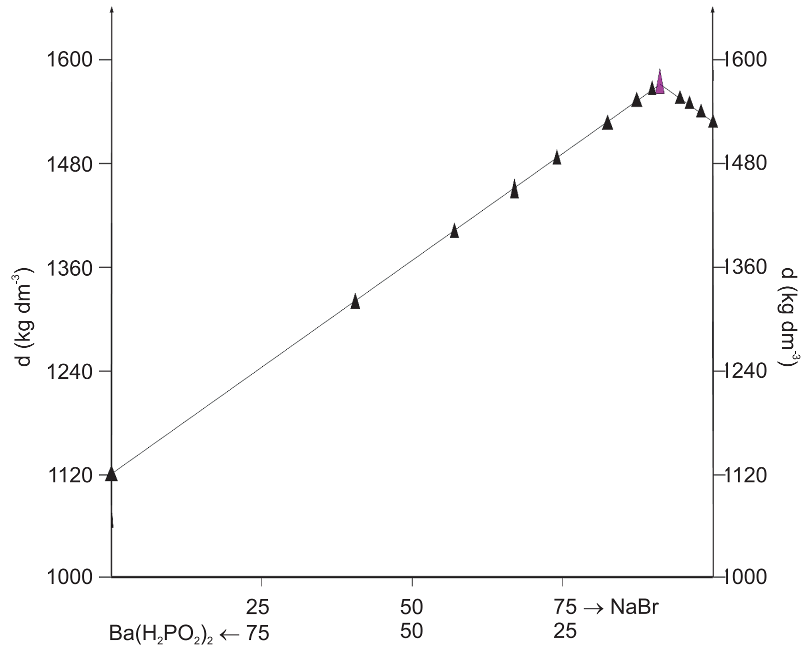


Fig. 2. Yeneke-Le Chatelier diagram of the density of NaBr-$Ba(H_2PO_2)_2$-$H_2O$ triple system at 298 K

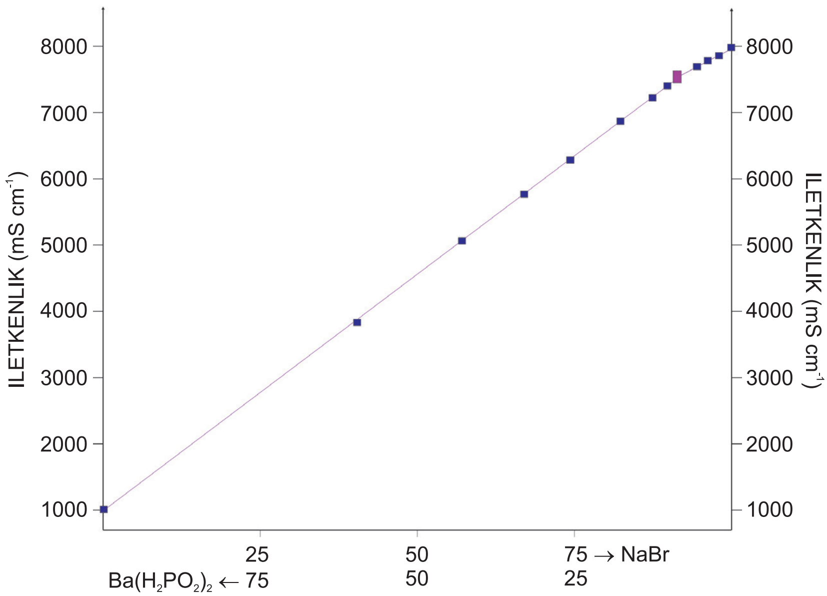


Fig. 3. Yeneke-Le Chatelier diagram of the conductivity of NaBr-$Ba(H_2PO_2)_2$-$H_2O$ triple system at 298 K

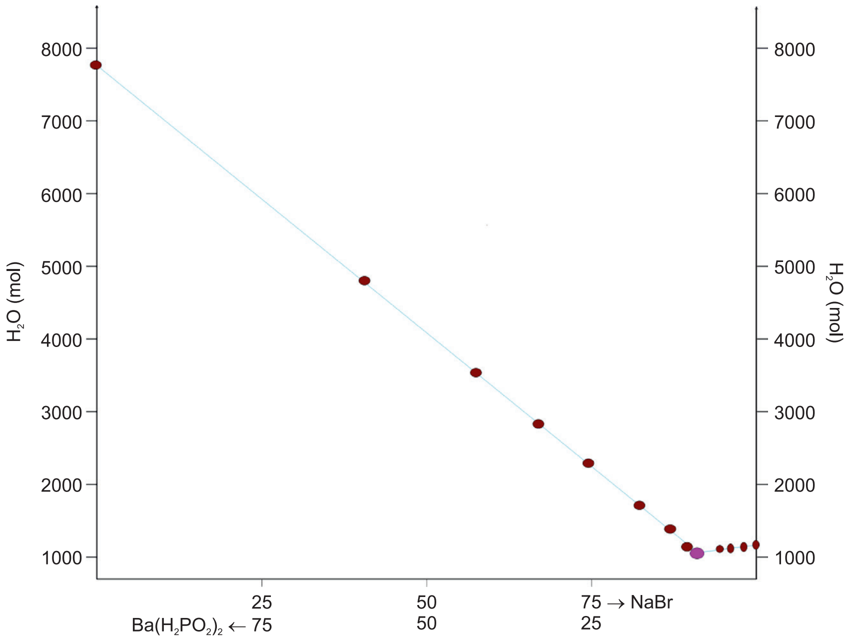


Fig. 4. Yeneke-Le Chatelier diagram of the resolution of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ triple system at 298 K

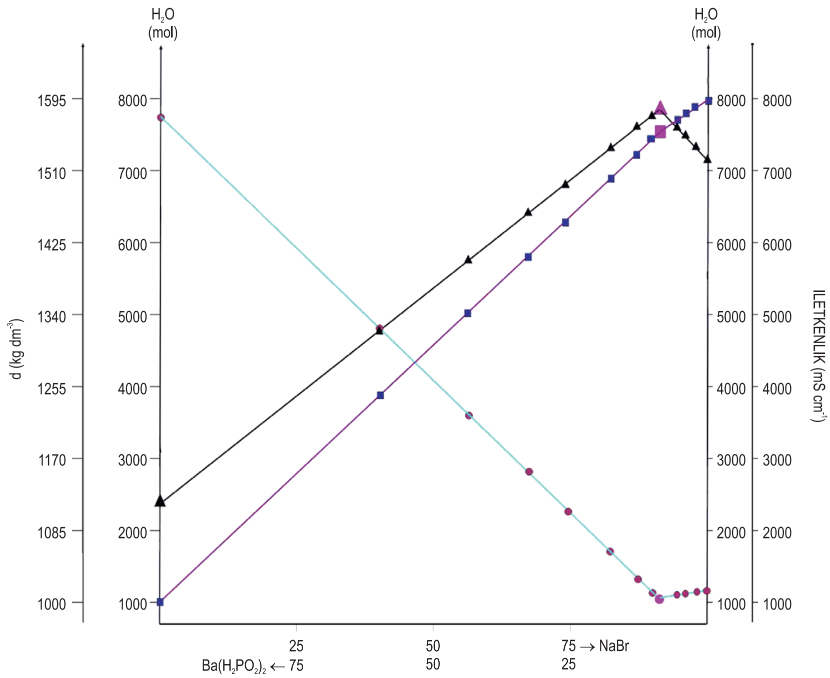


Fig. 5. Diagram of the exchange of the solubility, density, and conductivity (three in one) of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ triple water-sal system with the composition of the system at 298 K

During the investigation of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system at 298 K, while the triangle is made towards the Ba$(H_2PO_2)_2$ corner by NaBr, it was found that the addition of the Ba$(H_2PO_2)_2$ salt to the system increased the concentration of the liquid phase from 1527 kg $m^{-3}$ (the density of the saturated solution of the NaBr salt) to 1578 kg $m^{-3}$ (the density of the liquid phase at the invariant point of the system).

During the investigation of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system at 298K, while the triangle was made towards the NaBr corner by Ba$(H_2PO_2)_2$-$H_2O$, it was found that the density of the liquid phase increased from 1121 kg $m^{-3}$ [density of the saturated solution of Ba$(H_2PO_2)_2$] to 1578 kg $m^{-3}$ (density of the liquid phase at the invariant point of the system) after the addition of NaBr salt to the system.

At 298 K, the invariant value of the liquid phase density of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system is higher than that of the NaBr salt pure water saturated solution, and this depends on the amount of dissolved total salt [NaBr + Ba$(H_2PO_2)_2$] in the invariant point of the system.

The experimental results obtained during the investigation of the liquid phase conductivity of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system at 298 K are shown in Table 2, and the exchange in conductivity of the system with the composition of Ba$(H_2PO_2)_2$ is shown in Figure 3.

During the investigation of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system at 298 K, while the triangle was made towards the Ba$(H_2PO_2)_2$-$H_2O$ corner by NaBr, the addition of Ba $(H_2PO_2)_2$ salt to the system decreased the conductivity of the liquid phase from 7980 mS $cm^{-1}$ (the conductivity of the saturated solution of NaBr salt) to 7540 mS $cm^{-1}$ (the conductivity of the liquid phase at the invariant point of the system).

During the investigation of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system at 298 K, while the triangle was made towards the NaBr corner by Ba$(H_2PO_2)_2$-$H_2O$, the conductivity of the liquid phase increased from 1020 mS $cm^{-1}$ to the value of 7540 mS $cm^{-1}$ (the conductivity of the liquid phase at the invariant point of the system) after the addition of the NaBr salt to the system [conductivity of the saturated solution of Ba$(H_2PO_2)_2$].

## CONCLUSIONS

As a result of these evaluations, it can be concluded that the physicochemical methods used for the investigation of the NaBr-Ba$(H_2PO_2)_2$-$H_2O$ ternary system, the analytical techniques used in the analysis of the liquid and solid phase compositions, and other experimental work have been performed accurately and as accurately as possible, and that the results obtained are considered to be a clear indication of their robustness and reliability at a high level.

In addition, the experimental results were obtained from the investigations of solubility, density, conductivity, and phase equilibria of the NaBr-$Ba(H_2PO_2)_2$-$H_2O$ ternary system located in the $Na^+$, $Ba^{2+}$/$Br^-$($H_2PO_2$)$^-$// $H_2O$ quaternary mutual water salt system with physicochemical methods at 298K. The diagrams that are drawn on the basis of this experiment can be applied and expected to be used for separating NaBr and Ba $(H_2PO_2)_2$ salts, which can be applied in the HALLURJI plant (salt industry) from natural salt mixtures and salt mixtures in industrial wastes.

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