**Journal:** Journal of the Serbian Chemical Society

# Title: "Solid- Liquid Phase Equilibria of (H2O-Mn(H2PO2)2-MnCl2-NaCl), (H2O-Mn(H2PO2)2-MnCl2) and (H2O-NaCl- MnCl2) Systems at 323.15 K"

**Author(s):** Adiguzel, Vedat

**Dear editor and reviewers:**

I have studied the valuable comments from reviewers carefully and tried our best to revise the manuscript. Required corrections are marked in red in the article. The point to point responds to reviewer’s comments are listed as following:

**Responds to the reviewer A comments:**

**Comment** **1**- the analysis of the solubility data in the quaternary system and comparison with literature is transferred to the main body of the manuscript, but the Figure 5 and the comments should be placed in a Discussion of the results not in the Conclusion (again, some short, precise conclusion should be drawn from this Discussion as well). So, in a document 9533-55158-3-RV from page 11, the part starting with ' Then, the quaternary systems of this study and ref. 8 were compared (Figure 5)....' right to the end please, do transfer it to the Discussion.

**Reply 1:** Figure 5 and discussion of it were moved into Discussion.

**Comment** **2**- Furthermore, for the data presented in Figure 5, the explanation of the composition should be given (for the wider scientific community) not just 'salt composition, 100 moles' and figure caption should contain more details (for example that the comparison of data is performed in a way that literature data are referring to temperature 298,15 K).

**Reply 2:** In Figure 5,The explanation of the composition, 'salt composition, 100 moles', was changed as ‘total salt composition in 100 mole’.

In addition, caption of Figure 5 was changed as “Comparison of the data obtained in this study with those of reference 8 related to the same salts studied at 298.15 K”.

**Comment** **3**- suggestion for the title (if the author finds it appropriate) since he analyses the solubility in this quaternary system and its subsystems then the title should be simply: Solid-Liquid Equilibria of H2O+Mn(H2PO2)2+MnCl2+NaCl System at 323.15 K;

**Reply 3:** Since the title suggested by the reviewer does not fully express all the quaternary and ternary systems studied in the study, I think that the existing title should not be changed**.**

**Comment** **4**- running title should be more concrete

**Reply 4:** Running Title was changed as “WATER SALT SYSTEMS CONTAINING Mn(H2PO2)2”.

**Comment** **5**- page 4, after Analytical methods: add (aq) after ions, like Cl-(aq) , H2PO2-(aq) and Mn2+(aq)

**Reply 5:** On page 4, after Analytical methods, “(aq)” was added right after ions.

**Comment** **6**- throughout the text, the composition should be given as mass % or mol.%, not just %

**Reply 6:** The article was completely revised according to the reviewer’s comments. **Comment** **7**- in Table III, maybe it will be favourable to emphasize that No.1 is point A in Figure 1, No. 10 is point F in Figure 1, ...

**Reply 7:** Table III-V were revised according to the comments of the reviewer.

**Comment** **8**- on page 6. after Figure 1. where is the explanation for point B?

**Reply 8:** On page 6, Point B and C were explained after Figure 1.

**Comment** **9**- on page 8, in Figure 3. where is the explanation for points H and B?

**Reply 9:** On page 8, Point H and B in Figure 3 were explained.

**Comment** **10**- in Table V,  in the Table title give the explanation of w

**Reply 10:** The expression, **“**w is the mass fraction”, was added to the footnote of Table V.

**Comment** **11**- on page 10., rephrase the sentence, ' As it is seen in Figure 4 which shows the crystallization area of the quaternary system, Mn(H2PO2)2 80.75 %, NaCl 11.63 %, and MnCl2 7.62 % cover the area.' How this can be seen from Figure4?

**Reply 11:** all the necessary explanation was added to the related part of manuscript on page 10.

**I look forward to hearing from you.**

# Solid-Liquid Phase Equilibria of (H2O-Mn(H2PO2)2-MnCl2-NaCl), (H2O-Mn(H2PO2)2-MnCl2) and (H2O-NaCl- MnCl2) Systems at 323.15 K

VEDAT ADIGUZEL[[1]](#footnote-1)\*

*Department of Chemical Engineering, Kafkas University, Kars 36100, Turkey*

*Abstract:* The solid-liquid phase equilibria (SLE) and densities of H2O-NaCl-MnCl2-Mn(H2PO2)2 quaternary system, H2O-NaCl-MnCl2 and H2O-MnCl2-Mn(H2PO2)2 ternary systems were investigated at 323.15 K by the isothermal solution saturation method. The analyses of the liquid and solid phases were used to determine the composition of the solid phase using the Schreinmakers graphic method.

The ternary systems contain one invariant point, two invariant curves and two crystallization regions.

In the quaternary system, there is one invariant point, three invariant curves, and three crystallization areas corresponding to NaCl, MnCl2.4H2O, and Mn(H2PO2)2.H2O.

The crystallization area of Mn(H2PO2)2.H2O, being the largest in comparison with those of other salts, occupied 80.75 % of the total crystallization area.

*Keywords:* Manganese hypophosphite; Manganese chloride; Ternary system; Schreinmakers method; Density*.*

RUNNING TITLE: WATER SALT SYSTEMS CONTAINING Mn(H2PO2)2.

INTRODUCTION

Apart from being environmental friendly, metal hypophosphite salts M(H2PO2)n draw great attention due to their high thermal and chemical stabilities, good reducing, and mechanical features.1 These salts are used as reductive, antioxidant, anticorrosive, animal feed, flame retardant in polymer, medicine, metal, and food industry.1-7

Mn(H2PO2)2 is used as a chemical intermediate in pharmacy and polymer technology, and to increase fiber quality in nylon carpet fiber production.4,5 In a study, Yang et al. has determined that Mn(H2PO2)2 has high flame-retardant effect.2

In the laboratory, hypophosphites are generally synthesized from sulphate, hydroxide, oxide, and nitrates of metals. The synthesis of hypophosphites obtained from hydroxides of insoluble elements in the water is generally synthesized both via multi-step reactions and expensively.4,8-15

Phase equilibriums are widely used as a method in the study of equilibrium relationships. In the salt industry, they are used to increase production efficiency, and also for the recovery of valuable chemicals. Besides, they are used in the recycling and disposal of harmful wastes in terms of environmental pollution. In addition to all of these, they are used in economic synthesis by obtaining chemicals that can be obtained by multi-step reactions in fewer reaction steps in the laboratory.16,17

In this study, H2O-Mn(H2PO2)2-MnCl2-NaCl, H2O-Mn(H2PO2)2-MnCl2 andH2O-NaCl-MnCl2 systems were analyzed, and an economic method was proposed for the separation process of Mn(H2PO2)2 salt used in the industrial field.

SLE data of salts including H2PO2- ion were given in Table I.8-15,18-22

**Table I** SLE ternary and quaternary systems including H2PO2 ion

|  |  |  |
| --- | --- | --- |
| Researchers | Systems | Ref. |
| Alisoglu and Necefoglu | Na+, Mn2+//NO3−, (H2PO2)−−H2O at 273.15 K | 9 |
| Alişoglu | K+, Mn2+//Br−, (H2PO2)−−H2O at 298.15 K | 11 |
| Alişoglu | Na+, Mn2+//Cl−, (H2PO2)−−H2O at 298.15 K | 8 |
| Alişoglu | Na+, Mn2+//Br−, (H2PO2)−−H2O at 298.15 K | 10 |
| Alisoglu and Adıguzel | K+, Mn2+/Br-, (H2PO2)-//H2O at 298.15 K | 12 |
| Erge et al. | Na+, Ba2+//(H2PO2)−−H2O at 273.15 K | 13 |
|  | Na+//Cl-, (H2PO2)−−H2O at 273.15 K | 13 |
|  | Ba2+//Cl−, (H2PO2)−−H2O at 273.15 K | 13 |
|  | Na+, Ba2+//Cl-, (H2PO2)−−H2O −H2O at 273.15 K | 13 |
| Adıguzel et al. | Na+, Zn2+//(H2PO2)−−H2O at 273.15 K | 14 |
|  | Zn2+//Cl−, (H2PO2)−−H2O at 273.15 K | 14 |
|  | Na+, Zn2+//Cl−, (H2PO2)−−H2O at 273.15 K | 14 |
| Demirci et al. | NaH2PO2−NaCl−H2O at 298.15 K | 15 |
|  | NaH2PO2−Zn(H2PO2)2−H2O at 298.15 K | 15 |
|  | NaCl−Zn(H2PO2)2−H2O at 298.15 K | 15 |
|  | NaH2PO2−NaCl−Zn(H2PO2)2−H2O at 298.15 K | 15 |
| Tan et al. | Ca(H2PO2)2 − CaCl2 − H2O at 298.15 K | 18 |
|  | Ca(H2PO2)2−NaH2PO2−H2O at 298.15 K | 18 |
| Cao et al. | Ca(H2PO2)2 + CaCl2 + H2O at 323.15 K | 22 |
|  | Ca(H2PO2)2 + NaH2PO2 + H2O at 323.15 K | 22 |
| Gao et al. | Mg(H2PO2)2 + NaH2PO2 + H2O at 298 K | 20 |
|  | Mg(H2PO2)2 +MgCl2 + H2O at 298 K | 20 |
| Yin et al. | Ca(H2PO2)2 +CaCl2 + H2O | 19 |
|  | Ca(H2PO2)2 + NaH2PO2 + H2O | 19 |
| Shi et al. | Mg(H2PO2)2 + NaH2PO2 + H2O | 21 |
|  | Mg(H2PO2)2 + MgCl2 + H2O | 21 |

EXPERIMENTAL

*Apparatus and reagents*

The commercial chemicals used in the study were given in Table II. The solution condition was provided with the use of pure water whose pH was 6.6 and conductivity was <10-4 S m-1.

**Table II** Provenance and mass fraction concentration of the used chemicals.

|  |  |  |  |
| --- | --- | --- | --- |
| **Chemical** | **CAS No** | **Source** | **Mass fraction concentrationa** |
| NaCl | 7647-14-5 | Merck | 0.999 |
| MnCl2.4H2O | 13446-34-9 | Merck | 0.999 |
| Mn(H2PO2)2.H2O | 7783-16-6 | Sigma-Aldrich | ≥0.985 |
| CuCl2.2H2O | 10125-13-0 | Sigma-Aldrich | 0.999 |
| C10H14N2Na2O8 | 6381-92-6 | Rİedel-de Haen | 0.98 |
| HCl | 7647-01-0 | Rİedel-de Haen | 0.37 |
| K2Cr2O7 | 7778-50-9 | Merck | 0.98 |
| K2CrO4 | 7789-00-6 | Merck | 0.98 |
| a Mass fraction concentration values were measured by the supplier of the chemicals. |

Density analyses were detected with the device of Mettler Toledo 30PX (accuracy ± 0.001 g cm-3).

Titration measurements were conducted with Hirscmann Solarus automatic burette (accuracy 0.2 %). Stabile experimental temperature was provided with a Polyscience branded cooler and a mixer water bath (accuracy ± 0.05 K).

*Experimental Methods*

Phase equilibria were determined according to isothermal solubility saturation method.12,15

All the experiments were carried out at atmospheric pressure (0.1025 MPa).

The general procedure of the experiment is as below:

(1) In the ternary system, the binary system saturated solution was prepared in a waterproof isolated tube, and placed in a water bath stabilized at 323.15 K.

(2) The second salt was added at a certain amount to this solution. The solution was stirred for one day.

(3) The solution was kept until the phase separation was observed clearly.

(4) Later on, samples were obtained from solid and liquid phases, and necessary analyses were done.

(5) The first forth steps of the procedure were repeated until the invariant point was reached.

(6) In quaternary systems, the process was completed with the invariant point solution of the ternary system in the first step. In the second step, the third salt was added, and the whole process was done, respectively.

All the density measurements were taken by using a density measurement device which was stabilized at 323.15 K. The measurements were carried out in triplicate, and the calibration of the device was controlled by using pure water.

The solid phase compositions were detected according to the wet residue method of Schreinmakers.12,15,23

All the tests were repeated three times for the reliability of the test results, and the results were expressed as ± standard deviation value.

All the tables and graphics were formed after the mathematical calculations necessary for all the data were conducted, and results were interpreted.

*Analytical methods*

Cl-(aq), H2PO2-(aq) and Mn2+(aq) ion analyses were respectively determined by titration with standard solutions of AgNO3, K2Cr2O7, and EDTA.24,25 The expanded uncertainties (ur) for Mn2+, Cl−, and H2PO2− analyses were respectively 1.32 mass %, 2.99 mass %, and 1.92 mass % (at the level of confidence of 0.95). Na+ amounts were calculated according to the total ion balance.

RESULTS AND DISCUSSION

*Solubility data of H2O-MnCl2-NaCl ternary system at 323.15 K*

The solubility and density values of NaCl-H2O and MnCl2-H2O binary systems were respectively detected as 26.86 mass % NaCl and 49.54 mass % MnCl2, 1.191 g cm-3, and 1.568 g cm-3 at 323.15 K. The solid phases belonging to these compositions were found as NaCl and MnCl2.4H2O. NaCl, MnCl2, and H2O compositions and the density in the invariant point of the H2O-MnCl2-NaCl system at 323.15 K were respectively 3.14 mass %, 47.48 mass %, 49.38 mass %, and 1.583 g cm-3. The solid phase of the invariant point consists of NaCl and MnCl2.4H2O salts.

The solubility and density data belonging to this system are given in Table III, Figure 1, and 2.

**Table III** SLE data for the H2O-MnCl2-NaCl ternary system at 323.15 K

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Liquid Phase (% mass)** | **Solid Phase (%mass)** | **100 mole composition of salts in the liquid phase** | ***ρ*/ g cm-3** | **Solid Phasec** |
| No | MnCl2 | NaCl | MnCl2 | NaCl | MnCl2 | NaCl |  |  |
| 1A | 0.00 | 26.86 | 0.00 | 93.44 | 0.00 | 100 | 1.191 | N |
| 2 | 6.21 | 20.65 | 1.64 | 81.01 | 12.24 | 87.76 | 1.225 | N |
| 3 | 14.69 | 15.29 | 3.22 | 82.15 | 30.85 | 69.15 | 1.279 | N |
| 4 | 21.39 | 11.33 | 5.52 | 77.9 | 46.71 | 53.29 | 1.325 | N |
| 5 | 27.86 | 9.00 | 6.51 | 79.68 | 58.98 | 41.02 | 1.383 | N |
| 6 | 36.01 | 6.18 | 8.43 | 78.39 | 73.02 | 26.98 | 1.460 | N |
| 7E | 47.48 | 3.14 | 39.76 | 49.82 | 87.54 | 12.46 | 1.583 | N+M |
| 8E | 47.48 | 3.14 | 59.42 | 18.97 | 87.54 | 12.46 | 1.583 | N+M |
| 9 | 48.60 | 1.63 | 56.16 | 1.17 | 93.26 | 6.74 | 1.572 | M |
| 10B | 49.54 | 0.00 | 58.36 | 0.00 | 100 | 0.00 | 1.568 | M |

a Standard uncertainties *u* are *u(ρ)*=0.001 g cm-3, *u(T)*=0.05 K, *ur(P)*= 5 % and *u(w)*=0.01w, c N, NaCl; M, MnCl2.4H2O.



**Figure 1** SLE diagram for the H2O-MnCl2-NaCl ternary system at 323.15 K.

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**Figure 2** Density vs composition diagram for the ternary systems at 323.15 K.

In Figure 1, there are two crystallization areas. The first one is CAE corresponding to the crystallization area of NaCl, and the second is BFE corresponding to the crystallization area of MnCl2.4H2O. Point A and F are the invariant points of the binary systems of NaCl−H2O and MnCl2−H2O. Point E represents the invariant of the system. Point C and Point B show the amount of salt by weight of NaCl and MnCl2.4H2O salt molecules and the amount of water as hydrate, respectively. The areas of AEB0 and CEBD represent the unsaturated and saturated solutions of both salts, respectively. The curves AE and EB represent the saturation curves of NaCl and MnCl2, respectively.

*Solubility data of H2O-MnCl2-Mn(H2PO2)2 ternary system at 323.15 K*

The solubility and density values of Mn(H2PO2)2-H2O and MnCl2-H2O binary systems were respectively detected as 11.14 mass % Mn(H2PO2)2 and 49.54 mass % MnCl2, 1.067 g cm-3, and 1.568 g cm-3 at 323.15 K. The solid phases belonging to these compositions were found as Mn(H2PO2)2.H2O and MnCl2.4H2O.

Mn(H2PO2)2, MnCl2 and H2O compositions and the density in the invariant point of H2O+ MnCl2+Mn(H2PO2)2 system at 323.15 K were respectively 15.34 mass %, 21.02 mass %, 63.64 mass % and 1.334 g cm-3. The solid phase of the invariant point consists of Mn(H2PO2)2.H2O and MnCl2.4H2O salts.

The solubility and density data belonging to this system are given in Table IV, Figure 2 and 3.

**Table IV** SLE data for the H2O-MnCl2-Mn(H2PO2)2 ternary system at 323.15 K.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Liquid Phase****(% mass)** | **Solid Phase****(%mass)** | **100 mole composition of salts in liquid phase** | ***ρ*/ g cm-3** | **Solid Phasec** |
| No | MnCl2 | Mn(H2PO2)2 | MnCl2 | Mn(H2PO2)2 | MnCl2 | Mn(H2PO2)2 |  |  |
| 1A | 0.00 | 11.14 | 0.00 | 90.13 | 0.00 | 100 | 1.067 | H |
| 2 | 6.73 | 11.77 | 0.58 | 88.57 | 45.45 | 54.55 | 1.133 | H |
| 3 | 11.07 | 12.50 | 1.2 | 84.72 | 56.55 | 43.45 | 1.185 | H |
| 4 | 15.02 | 13.26 | 3.4 | 74.58 | 62.46 | 37.54 | 1.239 | H |
| 5 | 20.76 | 15.23 | 2.83 | 82.42 | 66.72 | 33.28 | 1.327 | H |
| 6E | 21.02 | 15.34 | 28.02 | 52.46 | 66.82 | 33.18 | 1.334 | H+M |
| 7E | 21.02 | 15.34 | 56.35 | 32.15 | 66.82 | 33.18 | 1.334 | H+M |
| 8 | 25.1 | 12.63 | 50.29 | 4.13 | 74.48 | 25.52 | 1.357 | M |
| 9 | 36.7 | 6.17 | 55.24 | 1.91 | 89.75 | 10.25 | 1.452 | M |
| 10 | 43.4 | 3.03 | 56.09 | 0.91 | 95.46 | 4.54 | 1.504 | M |
| 11F | 49.54 | 0.00 | 60.86 | 0.00 | 100 | 0.00 | 1.568 | M |

aStandard uncertainties *u* are *u(ρ)*=0.001 g cm-3, *u(T)*=0.05 K, *ur(P)*= 5 % and *u(w)*=0.01w,c M, MnCl2.4H2O; H, Mn(H2PO2)2.H2O.



**Figure 3** SLE diagram for the H2O-MnCl2-Mn(H2PO2)2 ternary system at 323.15 K.

In Figure 3, there are two crystallization areas. The first one is HAE corresponding to the crystallization area of Mn(H2PO2)2.H2O, and the second is BFE corresponding to the crystallization area of MnCl2.4H2O. Point A and F are the invariant points of the binary systems of Mn(H2PO2)2−H2O and MnCl2−H2O. Point E represents the invariant of the system. Point H and Point B show the amount of salt by weight of Mn(H2PO2)2.H2O and MnCl2.4H2O salt molecules and the amount of water as hydrate, respectively. The areas of AEF0 and CHEBD represent the unsaturated and saturated solutions of both salts, respectively. The curves AE and EF represent the saturation curves of Mn(H2PO2)2 and MnCl2, respectively.

*Solubility data of H2O- Mn(H2PO2)2-NaCl-MnCl2 system at 323.15 K*

The solubility data belonging to the quaternary system are given in Table V and Figure 4.

**Table V** SLE data for the quaternary H2O-Mn(H2PO2)2-NaCl-MnCl2 system at 323.15 K.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **composition of the solution, 100.w(B)b** | **Jänecke index/mol·100 mol−1** (2Na++Mn2+=100mol) |  |
| No | w(Mn2+) | w(Na+) | w(Cl-) | w(H2PO2) | J(Mn2+) | J(2Cl-) | J (H2O) | Solid Phasec |
| 1 | 20.73 | 1.23 | 28.63 | 0.00 | 93.98 | 99.90 | 680.67 | N+M |
| 2 | 18.28 | 2.37 | 26.60 | 1.19 | 86.58 | 97.60 | 746.93 | N+M |
| 3 | 16.08 | 2.59 | 23.94 | 1.47 | 83.85 | 96.73 | 891.89 | N+M |
| 4E | 14.28 | 2.95 | 21.91 | 1.95 | 80.19 | 95.33 | 1011.86 | N+M+H |
| 5 | 13.72 | 0.00 | 11.83 | 10.78 | 100 | 66.80 | 1419.43 | M+H |
| 6 | 13.29 | 1.45 | 16.26 | 5.73 | 88.46 | 83.85 | 1288.10 | M+H |
| 7 | 12.76 | 2.00 | 17.62 | 3.52 | 84.21 | 90.05 | 1293.63 | M+H |
| 8E | 14.28 | 2.95 | 21.91 | 1.95 | 80.19 | 95.33 | 1011.86 | N+M+H |
| 9 | 1.79 | 9.61 | 14.85 | 4.23 | 13.46 | 86.62 | 1601.20 | H+N |
| 10 | 4.32 | 7.36 | 14.94 | 3.67 | 32.91 | 88.22 | 1625.10 | H+N |
| 11 | 5.49 | 7.02 | 15.97 | 3.59 | 39.54 | 89.10 | 1496.39 | H+N |
| 12 | 7.57 | 4.76 | 15.73 | 2.53 | 57.07 | 91.87 | 1600.66 | H+N |
| 13E | 14.28 | 2.95 | 21.91 | 1.95 | 80.19 | 95.33 | 1011.86 | N+M+H |

aStandard uncertainties *u* are *u(ρ)*=0.001 g cm-3, *u(T)*=0.05 K, *ur(P)*= 5 % and *u(w)*=0.01w, , w is the mass fraction, bw(B) is the mass fraction of component B, cN, NaCl; M, MnCl2.4H2O; H, Mn(H2PO2)2.H2O.

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**Figure 4** SLE diagram for the H2O-Mn(H2PO2)2-NaCl-MnCl2 system at 323.15 K.

The invariant point data of H2O-Mn(H2PO2)2-NaCl system are respectively 69.52 mass %, 6.02 mass %, and 24.46 mass %.

The invariant point data of H2O-Mn(H2PO2)2-NaCl-MnCl2 quaternary system are respectively 58.89 mass %, 2.77 mass %, 7.5 mass % and 30.84 mass %.

In Figure 4, there are three crystallization areas. The first one is AECH corresponding to the crystallization area of Mn(H2PO2)2.H2O, the second one is DBEA corresponding to the crystallization area of NaCl, and the third is BECF corresponding to the crystallization area of MnCl2.4H2O. Point A, B and C are the invariant points of the ternary systems. Point E represents the invariant of the quaternary system.

As it is seen in Figure 4 which shows the crystallization area of the quaternary system, Mn(H2PO2)2 80.75 %, NaCl 11.63 %, and MnCl2 7.62 % cover the area. These values were obtained by calculating the area of the DFH triangle in Figure 4. When the study is compared with literature data of the binary, ternary and quaternary systems, it is seen that the solubility of Mn(H2PO2)2 and NaCl in binary systems slightly change with the increase in temperature, but the solubility of MnCl2 increases significantly with the increase in temperature.26

The solubility of MnCl2 changed as respectively 49.54 and 56.1 mass % between 273 and 373K.The solubility of NaCln changed as respectively 26.28 and 28.05 mass % between 273 and 373K.26

There is limited data available for Mn(H2PO2)2 solubility. According to the data, the solubility of it is between 12.20 and 11.14 mass % at between 273 and 298K.8-12

The quaternary systems of this study and ref. 8 were compared (Figure 5). When the temperature increased from 298.15 to 323.15 K, the crystallization areas of NaCl and Mn(H2PO2)2 decreased; thus, their corresponding solubilities increased. In contrast to this, the crystallization area of MnCl2 increased and its solubility decreased.



**Figure 5** Comparison of the data obtained in this study with those of reference 8 related to the same salts studied at 298.15 K

In this study, the invariant points of the quaternary system were respectively 30.84,7.5 and 2.77 mass % (MnCl2, NaCl and Mn(H2PO2)2). According to this, there is mostly MnCl2 and at least Mn(H2PO2)2 in the solution. Because of this, this is important data for the separation of Mn(H2PO2)2 from the solution.

CONCLUSION

Two ternary systems and one quaternary system were investigated in this study.

First of all, in the MnCl2-NaCl-H2O system, NaCl solubility reduced from 26.86 mass % to 3.14 mass % in the existence of MnCl2, and MnCl2 solubility reduced from 49.54 mass % to 47.48 mass % in the existence of NaCl. It is clearly seen that MnCl2 has a sharp salting-out effect on NaCl. The density of the invariant point was determined as 1.583 g cm-3.

Secondly, in MnCl2-Mn(H2PO2)2-H2O system, the solubility of Mn(H2PO2)2 increased from 11.14 mass % to 15.34 mass % in the existence of MnCl2, and MnCl2 decreased from 49.54 mass % to 21.02 mass %. Here, MnCl2 has a salting-on effect on Mn(H2PO2)2. The density of the invariant point was 1.334 g cm-3.

Thirdly, as the crystallizing area of the quaternary system is clearly observed in the graphic (Fig 3), Mn(H2PO2)2 has the greatest area with 80.75 %, NaCl follows it with 11.63 % and MnCl2 has the smallest area with 7.62 % in the solution including all the three salts.

When literature data is analyzed, it is seen that the solubility and density of Mn(H2PO2)2-H2O binary system are respectively 12.20 mass % and 1.089 g cm-3 at 273 K. This result was found by Alisoğlu and Necefoğlu.9 Furthermore, it has been found that solubility is 12.48 mass % and density is 1.086 g cm-3 at 298 K.8,10-12 It is apparently seen that solubility and densities of Mn(H2PO2)2-H2O binary system changed slightly at 273 K and 298 K, but when the temperature reached 323.15 K, the solubility and densities decreased to 11.14 mass % and 1.067 g cm-3, respectively.

It has been seen in the literature that MnCl2-H2O binary system has 43.60 mass % solubility and 1.491 g cm-3 density at 298 K8, and 49.40 mass % solubility at 323 K.26 When it is compared with the data obtained from this study and cited literature above, it can be concluded that the solubility of MnCl2-H2O binary system is in the range 43.60 to 49.54 mass %. Moreover, the density of the system increased from 1.491 g cm-3 to 1.568 g cm-3 in parallel with the increase in the temperature.

Finally, it has been observed that solubility of NaCl-H2O binary system at 273 K, 298 K and 323 K is respectively 26.25 mass %, 26.42 mass %, and 26.84 mass %, and the density is respectively 1.201, 1.199, 1.191 g m-3 again.14,15,27

Mn(H2PO2)2 is obtained by a displacement reaction of MnCl2 with NaH2PO2 to produce Mn(H2PO2)2 and NaCl. The salts can be separated from each other as a result of their solubility differences by creating Na+, Mn2+/Cl-, (H2PO2)-//H2O reciprocal quaternary system. In this study, a method has been proposed for purification of Mn(H2PO2)2 by separating it from the solution medium by using phase equilibrium method, which enables the synthesis of Mn(H2PO2)2 more economically and easily than the synthesis method used in the traditional laboratory.

In the study with the same quaternary system at 298 K of Alisoğlu 8, it is seen that the crystallizing area of Mn(H2PO2)2 covers 82.9 % of the total area (Figure 5). A method can be proposed to separate these salts by using temperature and phase changes with the joint evaluation of Alişoğlu and this study. Especially, the separation of Mn(H2PO2)2 which has the highest crystallization area is an important result since it is more economical than the traditional method. According to this, it has been concluded that Mn(H2PO2)2 can be separated via temperature change.

Therefore, this study suggests an economic method for the separation of Mn(H2PO2)2 which solves the least (2.77 %) and covers the most crystallizing area (80.75 %) in the solution including three salts mentioned.

REFERENCES

1. W. Wu, S. Lv, X. Liu, H. Qu, H. Zhang, J. Xu, *J. Therm. Anal. Calorim.* **118** (2014) 1569 ([https://doi.org/](https://doi.org/10.1109/5.771073)10.1007/s10973-014-4085-8)

2. W. Yang, W. J. Yang, B. Tawiah, Y. Zhang, L. L. Wang, S. E. Zhu, T. B. Y. Chen, A. C. Y. Yuen, B. Yu, Y. F. Liu, *Compos. Sci. Technol.* **164** (2018) 44 (<https://doi.org/10.1016/j.compscitech.2018.05.023>)

3. G. A. Bhat, P. Vishnoi, S. K. Gupta, R. Murugavel, *Inorg. Chem. Commun.* **59** (2015) 84 (<https://doi.org/10.1016/j.inoche.2015.07.006>)

4. P. Noisong, C. Danvirutai, *Spectrochim. Acta, Part A* **77** (2010) 890 (<https://doi.org/10.1016/j.saa.2010.08.028>)

5. P. Noisong, C. Danvirutai, T. Srithanratana, B. Boonchom, *Solid State Sci.* **10** (2008) 1598 (<https://doi.org/10.1016/j.solidstatesciences.2008.02.020>)

6. A. Suekkhayad, P. Noisong, C. Danvirutai, *J. Therm. Anal. Calorim.* **129** (2017) 123 (https://doi.org/10.1007/s10973-017-6156-0)

7. Y. Zeng, J. Yi, H. Wang, G. Zhou, S. Liu, *J. Mol. Struct.* *THEOCHEM* **724** (2005) 81 (<https://doi.org/10.1016/j.theochem.2005.03.014>)

8. V. Alisoğlu, *C.R. Chim.* **5** (2002) 547 ([https://doi.org/10.1016/S1631-0748(02)01411-X](https://doi.org/10.1016/S1631-0748%2802%2901411-X))

9. V. Alisoglu, H. Necefoglu, *C.R. Acad. Sci., Ser. IIb: Mec., Phys., Chim., Astron.* **324** (1997) 139 ([https://doi.org/10.1016/S1251-8069(99)80017-7](https://doi.org/10.1016/S1251-8069%2899%2980017-7))

10. V. Alisoğlu, *C.R. Chim.* **8** (2005) 1684 (<https://doi.org/10.1016/j.crci.2004.11.041>)

11. V. Alisoglu, *C.R. Acad. Sci., Ser. IIc: Chim.* **1** (1998) 781 ([https://doi.org/10.1016/S1251-8069(99)80046-2](https://doi.org/10.1016/S1251-8069%2899%2980046-2))

12. V. Alisoglu, V. Adiguzel, *C.R. Chim.* **11** (2008) 938 (<https://doi.org/10.1016/j.crci.2007.12.001>)

13. H. Erge, V. Adiguzel, V. Alisoglu, *Fluid Phase Equilib.* **344** (2013) 13 (<https://doi.org/10.1016/j.fluid.2012.12.033>)

14. V. Adiguzel, H. Erge, V. Alisoglu, H. Necefoglu, *J. Chem. Thermodyn.* **75** (2014) 35 (<https://doi.org/10.1016/j.jct.2014.04.014>)

15. S. Demirci, V. Adıgüzel, Ö. Şahi̇n, *J. Chem. Eng. Data* **61** (2016) 2292 (<https://doi.org/10.1021/acs.jced.5b00988>)

16. Y. Mastai, *Advances in Crystallization Processes,* InTech, Rijeka, Croatia, 2012, 400-413 ([https://doi.org/](https://doi.org/10.1109/5.771073)10.5772/2672)

17. H. Civelekoğlu, R. Tolun, N. Bulutçu, *İnorganik teknolojiler*, İTÜ Maden Fakültesi Ofset Atölyesi, İstanbul, Turkey, 1987, 80-103 (<http://www.ituyayinlari.com.tr/kitapdetay.asp?KitapID=34&inorganik-Teknolojiler>)

18. L. Tan, J. Wang, H. Zhou, L. Wang, P. Wang, X. Bai, *Fluid Phase Equilib.* **388** (2015) 66 (<https://doi.org/10.1016/j.fluid.2014.12.047>)

19. J. Yin, X. Shi, H. Zhou, J. Tang, Y. Dai, X. Bai, *J. Chem. Eng. Data* **62** (2017) 744 (<https://doi.org/10.1021/acs.jced.6b00813>)

20. S. Gao, X. Shi, J. Yin, Z. Wan, H. Zhou, G. Li, *Fluid Phase Equilib.* **411** (2016) 7 (<https://doi.org/10.1016/j.fluid.2015.11.033>)

21. X. Shi, J. Yin, H. Zhou, X. Gu, Y. Dai, J. Tang, *J. Chem. Eng. Data* **62** (2017) 1011 (<https://doi.org/10.1021/acs.jced.6b00828>)

22. H. Cao, H. Zhou, X. Bai, R. Ma, L. Tan, J. Wang, *J. Chem. Thermodyn.* **93** (2016) 255 (<https://doi.org/10.1016/j.jct.2015.09.006>)

23. H. Schott, *J. Chem. Eng. Data* **6** (1961) 324 (<https://doi.org/10.1021/je00103a002>)

24. J. R. Van Wazer, *Phosphorus and its Compounds*, Interscience Publishers, New York, London, 1958, 60-62 (<https://doi.org/10.1002/ange.19610731513>)

25. T. Gündüz, *Kantitatif analiz laboratuvar kitabı*, Gazi Büro Kitabevi, Ankara, Turkey, 2012, 280-282 (ISBN 9799757313457)

26. D. R. Lide, *CRC handbook of chemistry and physics*, CRC Boca Raton, 2012, 468-469 (<https://doi.org/10.1080/08893110902764125>)

27. A. R. Kul, H. Erge, İ. Meydan, *Yüzüncü Yıl Üniversitesi Fen Bilim. Enstitüsü Derg.* **19** (2014) 62 (<https://dergipark.org.tr/en/download/article-file/204648>).

FIGURE CAPTIONS

**Figure 1** SLE diagram for the H2O-MnCl2-NaCl ternary system at 323.15 K.

**Figure 2** Density vs composition diagram for the ternary systems at 323.15 K.

**Figure 3** SLE diagram for the H2O-MnCl2-Mn(H2PO2)2 ternary system at 323.15 K.

**Figure 4** SLE diagram for the H2O-Mn(H2PO2)2-NaCl-MnCl2 system at 323.15 K.

**Figure 5** Comparison of the data obtained in this study with those of reference 8 related to the same salts studied at 298.15 K

1. \*Corresponding author. E-mail: vedatnursen@gmail.com [↑](#footnote-ref-1)