Ternary SLE Measurements for the Systems $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ at T= (298, 313 and 333) K

[1]Sevilay DEMİRCİ, [1]Vedat ADIGÜZEL*, [2]Ömer SAHİN and [3]Hasan ERGE
[1]*Department of Chemical Engineering, Kafkas University, Kars 36100, Turkey*.
[2]*Department of Chemical Engineering, Siirt University, Siirt 56100, Turkey*.
[3]*Department of Chemistry, Yüzüncüyıl University, Van 65000, Turkey*.
vedatnursen@gmail.com*

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Summary: The solid-liquid equilibrium (SLE) of $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ ternary system at 298, 313 and 333 K have been studied with the use of isothermal method. Solid phase compositions have been determined with Schreinemaker's method. $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ ternary systems have simple eutectic type in 298, 333K. One invariant point, two invariant curves and two crystallization region have been observed in the phase diagrams at 298, 333K. Otherwise, One invariant point, three invariant curves and two crystallization region have been observed in the phase diagrams in 313K. In the crystallization regions; (i) $Zn(H_2PO_2).H_2O$ and $ZnCl_2$, (ii) $Zn(H_2PO_2)_2$, $Zn(H_2PO_2).H_2O$ and $ZnCl_2$, (iii) $Zn(H_2PO_2)_2$ and $ZnCl_2$ salts have been observed at 298 K, 313K, and 333 K, respectively. In $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ ternary system, the increasing salting-out effect of $Zn(H_2PO_2)_2$ on $ZnCl_2$ with temperature.

Keywords: Phase equilibria, Ternary system, Density, Zinc chloride, Zinc hypophosphite.

Introduction

Hypophosphite salts have a wide usage area. Hypophosphites are used in the fields of pharmacology, textile industry, medicine, food and chemistry [1-8].

Despite these common usages, the synthesis of some hypophosphites attained from the water-insoluble metal hydroxides is both expensive and it has many steps. The production of the mentioned hypophosphites is more economical and easier with the help of physicochemical methods [9-12].

The recent studies belonging to SLE systems in various temperatures containing Hypophosphite ion are as follows:

Shi *et al.*, have studied the ternary systems containing $Mg(H_2PO_2)_2$ and NaH_2PO_2 at 323,15K [13]. Yin *et al.*, have examined the ternary systems containing $Ca(H_2PO_2)_2$ and NaH_2PO_2 at 373,15 and 273,15 K [14].

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 298,15K [12].

Tan and co-authors have observed the ternary systems with the content of $Ca(H_2PO_2)_2$ and NaH_2PO_2 at 298,15K [15].

Adiguzel *et al.*, have examined the viscosity, density and solubility equilibrium of the ternary and quaternary systems containing NaH_2PO_2 and $Zn(H_2PO_2)_2$ salts at 273.15K [11].

Erge and his study group have studied the ternary and quaternary systems of barium and sodium containing hypophosphite salts at 0°C [10].

Alişoğlu and Adiguzel have examined the manganese and potassium hypophosphites at 273,15K [9].

$ZnCl_2$ which is the other salt in our study is a salt with very high solubility, whose solubility increases with the temperature increase and therefore, which has a high viscosity in the solution condition [16, 17].

In this study; the solubility and density changes have been examined with the temperature changes at 298, 313, 333K belonging to the ternary system of $H_2O+ZnCl_2+Zn(H_2PO_2)_2$. The attained test data, formed graphics and tables suggest a separation method for a solution containing these salts.

Experimental

Reagent and Instruments

The chemicals used in the study are shown in Table 1. The deionized water pH used is 6.6 and conductivity is lower than 10^{-4} Sm^{-1}. $Zn(H_2PO_2)_2$ has been synthesized and purified in our lab [12].

Density measurements have been analyzed with Mettler Toledo 30PX device (accuracy ± 0.001g/cm^3).

Titration measurements have been conducted with 50 mL Hirscmann Solarus automatic burette (accuracy 0,2%) and stabile test temperature has been conducted with Polyscience branded heater, cooler and mixer water bath (accuracy ± 0,05K).

*To whom all correspondence should be addressed.

Table-1: Physical properties of the chemicals used in this work.

Chemical	Source	Mass fraction purity	Purification method
$Zn(H_2PO_2)_2$	Synthesis	98%	Crystallization
$[Fe(C_{12}H_8N_2)_3]SO_4$	Merck		Used as purchased
H_3PO_2	Riedel-de Haen	50%	Used as purchased
$CuCl_2.2H_2O$	Merck	98%	Used as purchased
$C_{10}H_{14}N_2Na_2O_8.2H_2O$	Riedel-de Haen	98%	Used as purchased
HCl	Riedel-de Haen	37%	Used as purchased
$K_2Cr_2O_7$	Merck	98%	Used as purchased
K_2CrO_4	Merck	98%	Used as purchased
$ZnCl_2$	Merck	98%	Used as purchased

Table-2: SLE data for the ternary $ZnCl_2$-$Zn(H_2PO_2)_2$-H_2O system at 298 K

	Liquid Phase (% mass)		Solid Phase (% mass)		100 mole composition of salts		Density $\rho(kg/m^3)$	Equilibrium Salt[b]
No	$ZnCl_2$	$Zn(H_2PO_2)_2$	$ZnCl_2$	$Zn(H_2PO_2)_2$	$ZnCl_2$	$Zn(H_2PO_2)_2$		
1	0.00	18.61	0.00	89.20	0.00	100	1154	ZHyp
2	18.70	11.59	1.20	86.00	69.89	30.11	1283	ZHyp
3	24.13	11.65	2.20	86.05	75.00	25.00	1348	ZHyp
4	33.30	12.89	2.57	84.80	78.96	21.04	1465	ZHyp
5	39.30	14.05	3.04	84.20	80.00	20.00	1561	ZHyp
6	41.30	14.46	6.18	80.11	80.37	19.63	1595	ZHyp
7	51.90	17.91	12.10	74.07	80.54	19.46	1841	ZHyp
8E	52.54	18.11	42.70	43.50	80.72	19.28	1874	ZHyp+ZC
9E	52.54	18.11	62.50	23.18	80.72	19.28	1874	ZHyp+ZC
10	60.60	11.55	64.80	10.68	88.21	11.79	1951	ZC
11	67.80	5.54	71.10	4.70	94.60	5.40	2168	ZC
12	73.20	2.08	78.11	1.60	98.06	1.94	2400	ZC
13	80.13	0.00	82.30	0.00	100	0.00	2696	ZC

[a]Standard uncertainties u are $u(\rho)$=0.001g/cm^3, $u(T)$=0.05K, $u_r(P)$= 5% and $u(w)$=0.01w. [b]ZHyp: $Zn(H_2PO_2)_2.H_2O$, ZC: $ZnCl_2$

Experimental Methods

SLE experiments have been conducted according to the classical isothermal solubility equilibrium method [9-12].

40 mL saturated $ZnCl_2$ solutions have been added to the insulated tubes in the temperature desired to form the ternary system of $ZnCl_2$-$Zn(H_2PO_2)_2$-H_2O, and $Zn(H_2PO_2)_2$ have been added to the tubes in respectively increasing amounts. Then all the tubes have been put into a disc. The disc has been placed to heater and cooler circulator for stabilized in the desired temperatures and they have been mixed for one day (Fig. 1). They have been kept waiting until the phases have separated. In the same way; $ZnCl_2$ have been added in increasing amounts on the saturated $Zn(H_2PO_2)_2$ solution tubes and the process has continued until the invariant point. After that; samples have been taken from the liquid and solid phases of all the tubes and the salt compositions and densities have been examined. Then, the moles of the salts in the liquid phase composition were calculated. By using these calculated values, the moles of each salt in 100 mol salt composition were calculated. Graphics have been drawn and interpreted from the attained data after the conduction of necessary mathematical processes. Chemical structure of the salts identified according to Schreinemaker's method which is known as wet solid phase method [9-12]. This procedure has been carried out separately at 298, 313, 333K. All the experiments have been repeated three times. Results have been expressed as ± standard deviation value.

Cl^-, $H_2PO_2^-$ and Zn^{2+} ion concentrations have been determined with the help of respectively $AgNO_3$, $K_2Cr_2O_7$ and EDTA standard solutions [9-12, 18].

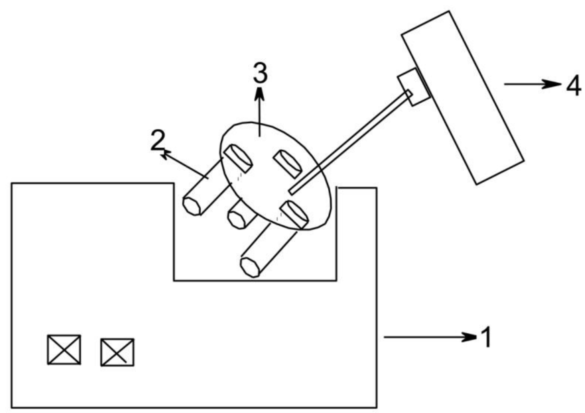

Fig. 1: Experimental apparatus of SLE: (1) heated circulating bath, (2) tube, (3) turning disc, and (4) mechanical stirrer.

Result and Discussion

The water-solubility of $ZnCl_2$ at 298, 313 and 333K is respectively 80.13%, 81.1% and 83.2%. On the other hand; the solubility change of $Zn(H_2PO_2)_2$ at 298, 313 and 333K has been observed as 18.61%, 22.22% and 27.23%. As it could be seen; the solubility of both salts has increased in the mentioned temperatures. However;

When the invariant point compositions have been considered, it has been observed that the solubility of $ZnCl_2$ has decreased with increase in the temperature. The reason for this is the salting-out effect of $Zn(H_2PO_2)_2$ on $ZnCl_2$; because, the increase in the solubility of $Zn(H_2PO_2)_2$ with temperature from 18.11% to 47.72% in the invariant point has caused $ZnCl_2$ to rapidly proceed to the solid phase from the solution. $ZnCl_2$, $Zn(H_2PO_2)_2$ and H_2O % compositions in the invariant point have been respectively detected as 52.54%, 18.11%, 29.35% at 298K; 37.88%, 31.22%, 30.9% at 313K and 33.92%, 47.72% and 18.36% at 333K.

It has been observed that the solubility of $ZnCl_2$ has decreased from 80.13% to 52.54% at 298K and $Zn(H_2PO_2)_2$ has almost never changed from 18.61% to 18.11% at the invariant point. The decrease in the solubility of $ZnCl_2$ stems from the salting out effect of $Zn(H_2PO_2)_2$ on $ZnCl_2$ at this temperature (Fig.2, Table 2). The density of this invariant point has 1874 kg/m^3 (Fig. 5, Table 2).

It has been observed in 313 K that the solubility of $ZnCl_2$ has decreased from 81.1% to 37.88% at the invariant point and the solubility of $Zn(H_2PO_2)_2$ has increased from 22.22% to 31.22%. It could be seen here that while the solubility of $ZnCl_2$ has rapidly decreased, the solubility of $Zn(H_2PO_2)_2$ has increased; in other words, the salting out effect of $Zn(H_2PO_2)_2$ has become stronger (Fig. 3, Table 3). The density of this invariant point has 1811 kg/m^3 (Fig. 5, Table-3).

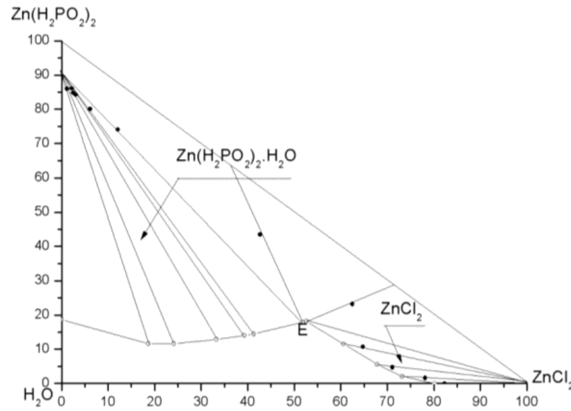

Fig. 2: SLE diagram for the ternary $ZnCl_2$ - $Zn(H_2PO_2)_2$-H_2O system at 298 K.

Table-3: SLE data for the ternary $ZnCl_2$ -$Zn(H_2PO_2)_2$-H_2O system at 313 K.

	Liquid Phase (% mass)		**Solid Phase (% mass)**		**100 mole composition of salts**		**Density**	**Equilibrium Salt[b]**
No	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**ρ(kg/m^3)**	
1	**0.00**	**22.22**	**0.00**	**79.18**	**0.00**	**100**	**1165**	**ZHyp**
2	**9.13**	**24.00**	**2.07**	**79.33**	**35.28**	**64.72**	**1292**	**ZHyp**
3	**14.04**	**25.30**	**5.09**	**69.70**	**44.30**	**55.70**	**1352**	**ZHyp**
4	**16.45**	**26.75**	**4.18**	**77.45**	**46.85**	**53.15**	**1402**	**ZHyp**
5	**24.12**	**36.24**	**5.72**	**80.97**	**48.82**	**51.18**	**1630**	**ZHyp**
6	**25.17**	**38.80**	**5.20**	**83.06**	**48.18**	**51.82**	**1692**	**ZHyp**
7	**26.66**	**36.82**	**14.67**	**66.47**	**50.92**	**49.08**	**1709**	**ZHyp2**
8	**31.01**	**33.20**	**19.65**	**58.40**	**57.24**	**42.76**	**1734**	**ZHyp2**
9	**34.10**	**31.40**	**24.69**	**50.14**	**60.88**	**39.12**	**1767**	**ZHyp2**
10E	**37.88**	**31.22**	**38.15**	**34.93**	**63.49**	**36.51**	**1811**	**ZC+ ZHyp2**
11E	**37.88**	**31.22**	**52.50**	**30.12**	**63.49**	**36.51**	**1811**	**ZC+ ZHyp2**
12	**51.60**	**12.60**	**63.11**	**9.96**	**85.44**	**14.56**	**1790**	**ZC**
13	**62.90**	**4.40**	**72.11**	**3.56**	**95.35**	**4.65**	**1900**	**ZC**
14	**69.80**	**1.90**	**79.01**	**1.42**	**98.14**	**1.86**	**2030**	**ZC**
15	**81.10**	**0.00**	**89.33**	**0**	**100**	**0**	**2120**	**ZC**

[a]Standard uncertainties *u* are *u(ρ)*=0.001kg/m^3, *u(T)*=0.05K, $u_r(P)$= 5% and *u(w)*=0.01w, [b]ZHyp: $Zn(H_2PO_2)_2.H_2O$, ZHyp2: $Zn(H_2PO_2)_2$, ZC: $ZnCl_2$.

Table-4: SLE data for the ternary $ZnCl_2$ -$Zn(H_2PO_2)_2$-H_2O system at 333 K.

	Liquid Phase (% mass)		**Solid Phase (% mass)**		**100 mole composition of salts**		**Density**	**Equilibrium Salt[b]**
No	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**$ZnCl_2$**	**$Zn(H_2PO_2)_2$**	**ρ(kg/m^3)**	
1	**0.00**	**27.23**	**0.00**	**89.13**	**0.00**	**100**	**1194**	**ZHyp2**
2	**15.92**	**34.60**	**4.03**	**80.46**	**39.74**	**60.26**	**1538**	**ZHyp2**
3	**20.92**	**37.20**	**7.28**	**77.68**	**44.63**	**55.37**	**1642**	**ZHyp2**
4	**26.70**	**39.30**	**7.29**	**83.85**	**49.33**	**50.67**	**1790**	**ZHyp2**
5	**29.38**	**40.57**	**20.46**	**58.51**	**50.92**	**49.08**	**1827**	**ZHyp2**
6E	**33.92**	**47.72**	**32.70**	**52.42**	**50.45**	**49.55**	**2013**	**ZHyp2+ZC**
7E	**33.92**	**47.72**	**41.32**	**52.29**	**50.45**	**49.55**	**2013**	**ZHyp2+ZC**
8	**46.80**	**19.40**	**84.50**	**5.90**	**77.57**	**22.43**	**1880**	**ZC**
9	**67.90**	**5.50**	**86.12**	**2.25**	**94.12**	**5.88**	**2032**	**ZC**
10	**83.20**	**0.00**	**85.33**	**0.00**	**100**	**0.00**	**2200**	**ZC**

[a]Standard uncertainties *u* are *u(ρ)*=0.001kg/m^3, *u(T)*=0.05K, $u_r(P)$= 5% and *u(w)*=0.01w, ZHyp2: $Zn(H_2PO_2)2$, ZC2: $ZnCl_2$.

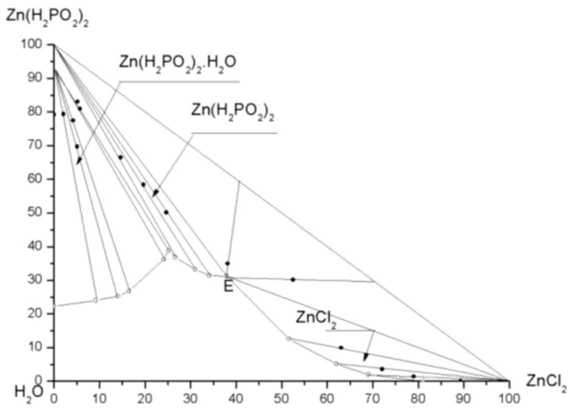

Fig. 3: SLE diagram for the ternary $ZnCl_2$ - $Zn(H_2PO_2)_2$-H_2O system at 313 K.

It has been detected at 333 K that the solubility of $ZnCl_2$ has changed between 83.2%-33.92% until the invariant point and the solubility of $Zn(H_2PO_2)_2$ has changed between 27.23%-47.72% until the invariant point. As it could be seen; it has been observed that the solubility of Zn $(H_2PO_2)_2$ is the highest at 333 K at the invariant point when compared to other temperatures and also the solubility of $ZnCl_2$ is the least (Fig. 4, Table-4). The density of this invariant point has 2013 kg/m^3 (Fig. 5, Table 4).

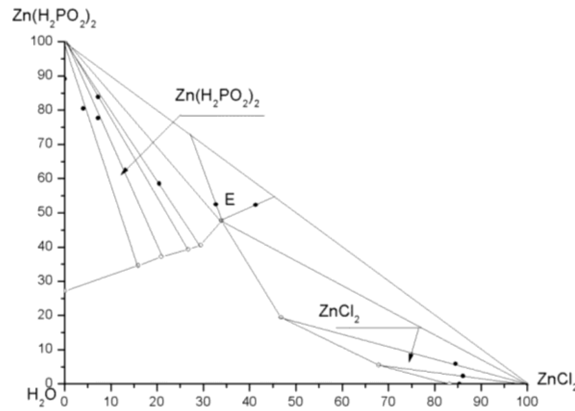

Fig. 4: SLE diagram for the ternary $ZnCl_2$ - $Zn(H_2PO_2)_2$-H_2O system at 333 K.

Solid phase compositions have been calculated with the help of Schreinemaker's method as $Zn(H_2PO_2)_2.H_2O$ and $ZnCl_2$ at 298 K, and $Zn(H_2PO_2)_2.H_2O$, $Zn(H_2PO_2)_2$ and $ZnCl_2$ at 313 K, and $Zn(H_2PO_2)_2$ and $ZnCl_2$ at 333 K.

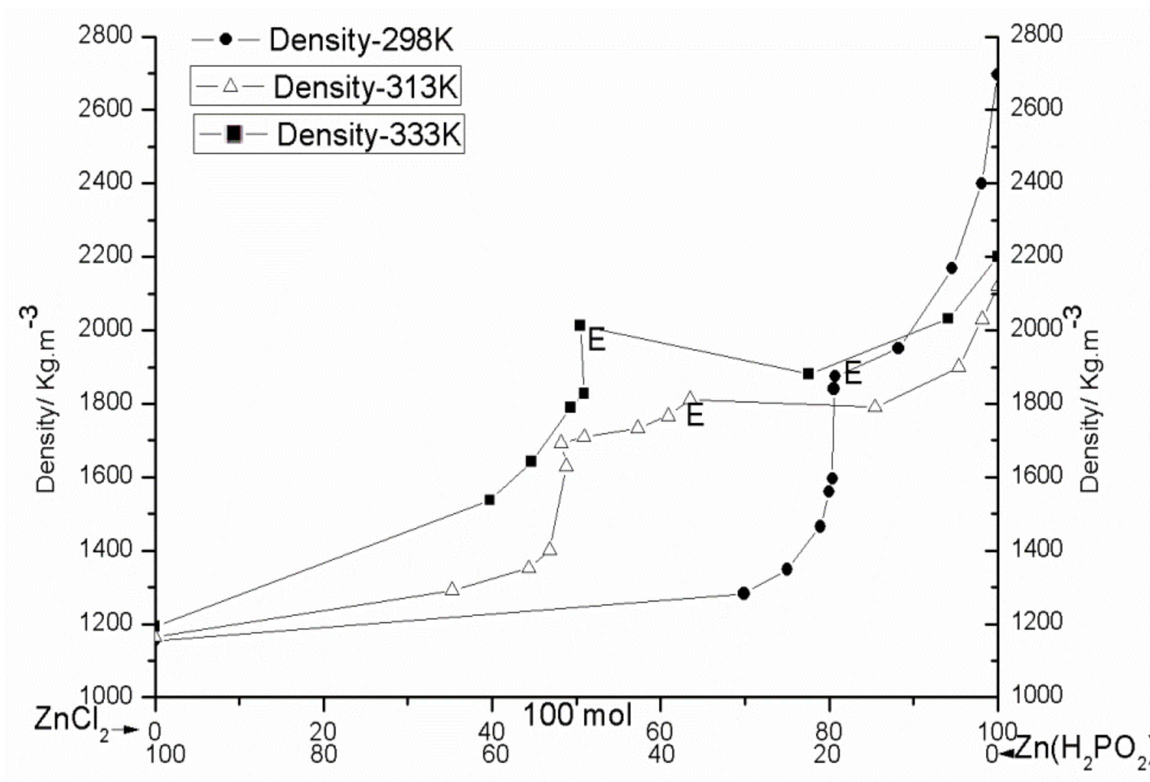

Fig. 5: Density diagram for the ternary $ZnCl_2$ -$Zn(H_2PO_2)_2$-H_2O system at 298-333 K.

Conclusions

In this study; the phase equilibrium of $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ ternary system have been studied at the temperatures of 298, 313 and 333 K for the purpose of examining the change in the solubility of $ZnCl_2$ and $Zn(H_2PO_2)_2$ with temperature. No study belonging to the salts mentioned in these temperatures has been encountered according to the literature review.

When this study is compared with ref 11, the $Zn(H_2PO_2)_2$ and $ZnCl_2$ solubility at 273 K are 13.79% and 66.6%, respectively. It is clearly seen that the solubility of both salts increases with the temperature between 273 and 333 K. With the increase in temperature from 273K to 333K, the solid phases $Zn(H_2PO_2)_2.H_2O$ and $ZnCl_2.2H_2O$ hydrate salts at the 273K were converted to the anhydrous $Zn(H_2PO_2)_2$ and $ZnCl_2$ forms.

One of the most important results of $H_2O+ZnCl_2+Zn(H_2PO_2)_2$ ternary system is the salting out effect of $Zn(H_2PO_2)_2$ increasing on $ZnCl_2$ with temperature. The other one is the salting in effect of $ZnCl_2$ on $Zn(H_2PO_2)_2$; because, while the solubility of $Zn(H_2PO_2)_2$ is between 18.61%-27.23% with temperature in the binary system, this has increased between 18.11%-47.72% with the existence of $ZnCl_2$ in this ternary system at invariant point.

This study suggests a process for the easy separation of $ZnCl_2$ by using phase diagrams from a solution including the mentioned salts, by adding $Zn(H_2PO_2)_2$ to the solution and/or by changing the temperature according to these data.

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