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Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O Sisteminin Fiziko-Kimyasal Analizi

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Özet

Na^+ , Ba^{2+} // Cl^- , $H_2PO_2^-$ // H_20 dörtlü karşılıklı sistemin bünyesinde yer alan Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O dörtlü sistemin 0^0C de çözünürlüğü ve faz dengeleri araştırılmıştır. Araştırma sırasında söz konusu sistemin aşağıdaki bileşime sahip bir ötonik noktası tespit edilmiştir (% kütle olarak) NaCl–15.03, $BaCl_2$–12.36, $Ba(H_2PO_2)_2$–2.86 ve H_2O-69.75. Bu ötonik noktada sistemin sıvı fazı ile $BaCl_2.2H_2O$ ve $Ba(H_2PO_2)_2.H_2O$ kristallerinin dengede bulunduğu saptanmıştır.

Anahtar kelimeler: sistem, hipofosfit, kristallenme alanı, doygun çözelti.

Physico-Chemical Analysis of The System

Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O

Abstract

To elaborate a new method of synthesis of barium hypophosphite based on an exchange reaction, the solubility in the Na_2Cl_2/$BaCl_2$/$Ba(H_2PO_2)_2$/H_2O system has been investigated by isothernal method at 0°C.

For the system in question the one quaternary eutonic points have been established. The composition of it has been determined as: NaCl–15.03, $BaCl_2$–12.36, $Ba(H_2PO_2)_2$–2.86 and H_2O-69.75%. The fields of the crystallization of the pure components are outlined. The field of crista11isation of the $Ba(H_2PO_2)_2.H_2O$ occupies 77 % of the total.

Key words: Fields of Crystallisation, Hypophosphite, Barium, Quaternary System.

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INTRODUCTION

Literature data show that hypophosphites of the alkaline elements are obtained by treating the warm solutions of alkaline hydroxides by some white phosphor:

(1)$P_4+3NaOH+3H_2O \rightleftarrows 3NaH_2PO_2+PH_3$

In the same way, one obtains the hypophosphites of the elements hydroxides of which are soluble enough, for example: that $Ca(H_2PO_2)_2$ and $Ba(H_2PO_2)_2$ [1].

The obtaining of the hypophosphite of elements (such as elements d-Mn, Zn, Cu) the hydroxide of which isn't soluble, is realized by another method, more complicated and more expensive. For that purpose, the acid hypophosphoreux is prepared by reaction of the hypophosphite of barium with the sulphuric acid for 100 % [2]; one makes, then, the acid act obtained on the oxide or on the carbonate of the metal.

For example, the obtaining of the $Mn(H_2PO_2)_2$ can be represented by the following reactions:

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

(3)$Ba(H_2PO_2)_2+H_2SO_4 \rightleftarrows BaSO_4+2H_3PO_2$

(4)$2H_3PO_2+MnCO_3 \rightleftarrows Mn(H_2PO_2)_2+CO_2+H_2O$

Physico-Chemical study of the mutual quartet system

$A^+,Ba^{2+}/X^-,(H_2PO_2)^-//H_2O$ (A= Na, K, NH_4; X= NO_3, Cl, Br)

presents certain practical importance, because the obtained results can be used to prepare of the hypophosphite of manganese by basing itself on the reaction of exchange. However, to obtain the wished results, it's necessary that the reaction of exchange in the studied mutual quartet system

(5)$2AH_2PO_2+MnX_2 \rightleftarrows 2AX+Mn(H_2PO_2)_2+H_2O$

occurs in the direction of the forming of the hypophosphite of manganese.

As a first steep in this direction was the investigation of ternary systems containing

$Ba(H_2PO_2)_2$ and the hypophosphites of alkaline and alkaline earth metals [3].

A further advance in the problem of the preparation of $Ba(H_2PO_2)_2$ by a reaction of exchange is the study of quaternary systems containing the hypophosphites and other salts of Ba^{2+} and alkaline metals [4,5].

In the present paper the solubility and field of crystallization of $Ba(H_2PO_2)_2$ in the quartet system Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O is discussed. The investigation of this system was carried out by the isothermal method at the temperature of 0°C.

MATERIAL AND METHODS

To realize the experimental party of this study, one used sa1ts NaCl, $BaCl_2$ and $Ba(H_2PO_2)_2$ crystallized twice. Schreinemaker's [6] method of isothermal recording of the saturation was used to attain the equilibrium in the systems. The experiments were carried out in a glass vessel fitted with an aqueous mantle. The temperature was kept constant with a precision of ± 0.050 ^{0}C by an ultra thermostat. Stirring was realized by means of a magnetic stirrer. After the equilibrium in the system was attained, samples were taken from the liquid phase and the wet solid residue and were analyzed for the content of ions Ba^{2+}, Cl^- and $(H_2PO_2)^-$. The analysis of the solid phases in balance is realized by the method of the "rests" of Schreinemaker's . The ions constituting the studied systems are doses by the classic analytical methods. The amount of Ba^{2+} in the samples was determined complexometrically with EDTA standard solution and Eriochrom Black T as indicator. The amount of Cl^- in the samples was determined argentometrycally and of $(H_2PO_2)^-$ spectrophotometrically [7-9].

At first one studied the mutual solubility in the systems ternaires $Na_2Cl_2/BaCl_2/H_2O$ (I), $BaCl_2/Ba(H_2PO_2)_2/H_2O$ (II) and in the diagonal cutting $Na_2Cl_2/Ba(H_2PO_2)_2/H_2O$ (III) of the mutual quartet system $Na^+,Ba^{2+}/Cl^-,(H_2PO_2)^-//H_2O$ (IV).

RESULTS

Table 1. The $Na_2Cl_2/BaCl_2/Ba(H_2PO_2)_2/H_2O$ system at 0 ^0C.Composition of the liquid phase. Nature of the solid phases in equilibrium.

	Liquid phase,(wt.%)				Sıvı Fazın Bileşimi 100 Mol Tuz Karışımında			100 Mol Tuza Karşı H_2O Mol Sayısı	Solid phase (*)
No	NaCl	$BaCl_2$	$Ba(H_2PO_2)_2$	H_2O	Na_2Cl_2	$BaCl_2$	$Ba(H_2PO_2)_2$		
1	0.00	22.53	7.88	70.61	0.00	78.60	21.40	2847	B+C
2	22.80	0.00	8.33	68.87	86.20	0.00	13.80	1692	A+C
3	15.17	12.43	0.00	72.40	68.44	31.56	0.00	2122	A+C
4	2.53	21.52	7.06	68.89	14.26	68.32	17.42	2526	B+C
5	5.05	20.50	6.25	68.20	26.15	59.66	14.19	2294	B+C
6	7.58	19.49	5.44	67.49	36.22	52.38	11.40	2096	B+C
7	10.11	18.48	4.63	66.78	44.87	46.13	9.00	1926	B+C
8	12.64	17.27	3.82	66.27	52.61	40.43	6.96	1793	B+C
9	13.88	16.68	3.28	66.16	56.18	37.99	5.83	1741	B+C
10	**15.03**	**12.36**	**2.86**	**69.75**	**64.70**	**29.91**	**5.39**	**1951**	**(A+B+C)****
11	19.40	10.30	4.29	66.01	71.65	21.40	6.95	1585	A+C
12	21.10	5.15	6.31	67.44	77.88	11.92	10.20	1619	A+C

(*) A-NaCl, B-$BaCl_2.2H_2O$, C-$Ba(H_2PO_2)_2.H_2O$;

( )** quartet eutonic point.

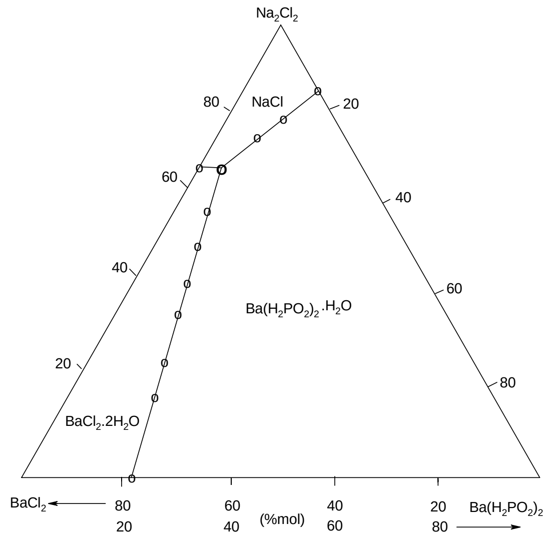

Figure 1.Fields of crystallization of the system $Na_2Cl_2/BaCl_2/Ba(H_2PO_2)_2/H_2O$ at the 0 ^0C.

(Gibbs-Rozeboum Method)

DISCUSSION

It was found, that in system I the solubility of NaCl decreases with addition of $BaCl_2$ to the saturated solution from the 21.10 wt.% to the 15.03 wt.% in the eutonic point (NaCl–15.03 wt.% and $BaCl_2$–12.36 wt.%). Under the same condition the solubility of $BaCl_2$ varyes with addition of NaCl to the saturated solution from the 22.53 wt.% to the 12.36 wt.%. Two fields of crystallization (of NaCl and of $BaCl_2.2H_2O$) are established in the solubility diagram of this system.

In system II the solubility of $Ba(H_2PO_2)_2$ decreases with addition of $BaCl_2$ to the saturated solution from 7.88 wt.% to the 2.86 wt.% in the eutonic point [$Ba(H_2PO_2)_2$-2.86 wt.% and $BaCl_2$–12.36 wt.%]. Under the same condition the solubility of $BaCl_2$ varyes with addition of $Ba(H_2PO_2)_2$ to the saturated solution from the 22.53 wt.% to the 12.36 wt.%. Two fields of crystallization [of $Ba(H_2PO_2)_2.H_2O$ and of $BaCl_2.2H_2O$] are established in the solubility diagram of this system.

In system III the solubility of $Ba(H_2PO_2)_2$ decreases with addition of NaCl to the saturated solution from 7.88 wt.% to the 2.86

wt.% in the eutonic point [$Ba(H_2PO_2)_2$-2.86 wt.% and NaCl–15.03 wt.%). Under the same condition the solubility of NaCl varyes with addition of $Ba(H_2PO_2)_2$ to the saturated solution from the 22.80 wt.% to the 15.03 wt.%. Two fields of crystallization [of $Ba(H_2PO_2)_2.H_2O$ and NaCl] are established in the solubility diagram of this system. In system III crystallization fields of $Ba(H_2PO_2)_2$ and Na_2Cl_2 as components of the exchange reaction does not exist.

To connaitre the solubility of the hypophosphite of barium in the presence of the other two salts (NaCl and $BaCl_2$), we studied by the method isothermal, the solubility of the hypophosphite of barium in the quartet system Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O (IV) at the temperature of 0°C. For it a mixture corresponding to the point of double saturation in salts of every constituent ternaire of the studied quaternary system is prepared. This mixture contains an excess of not dissolved salts and the fourth constituent is then added to has saturation and appearance of this one has the solid state. The experimental results for the system IV given in the Table 1 and are plotted in Figure 1.

Three fields of crystallization are observed in the phase diagram of quartet system Na_2Cl_2/ $BaCl_2$/$Ba(H_2PO_2)_2$/H_2O :

- field of crystallization of NaCl which begins at a concentration of the same 22.80 wt. % and ends at the quaternary eutonic point;

-field of crystallization of $BaCl_2.2H_2O$ which begins at a concentration of the $BaCl_2$ 22.53 wt. % and ends at the quaternary eutonic point;

-field of crystallization of $Ba(H_2PO_2)_2$. H_2O which begins at a concentration of the $Ba(H_2PO_2)_2$ 7.88 wt. % and ends at the quaternary eutonic point.

The composition of the quaternary eutonic point has been determined as following:

NaCl–13.03, $BaCl_2$–12.36, $Ba(H_2PO_2)_2$-2.86 and H_2O–69.75 %. In this quartet eutonic point, the following phases solids were observed in the equilibrium with the investigated solution: NaCl, $BaCl_2.2H_2O$ and $Ba(H_2PO_2)_2.H_2O$.The field of crystallization of the $Ba(H_2PO_2)_2.H_2O$ occupies 77 % of the total. On the basis of the experimental results obtained, it can be concluded that reaction of exchange

$$2NaH_2PO_2+BaCl_2 \rightleftharpoons 2NaCl+Ba(H_2PO_2)_2+H_2O$$

will occurs on the direction of the formation of the $Ba(H_2PO_2)_2$ and this salt can be obtained by using of the reaction of exchange in question.

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