Equilibria Data for the Chloropinnoite + Boric Acid + Water System at 273 K

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Solid–liquid phase equilibria have been studied at 273 K for the chloropinnoite + boric acid + water system. The equilibria solid phases identified by infrared spectra and X-ray diffraction were inderite ($2MgO\cdot3B_2O_3\cdot15H_2O$) when the mass percentage of H_3BO_3 was in the range from (0 to 1.5) %, hungtsaite ($MgO\cdot2B_2O_3\cdot9H_2O$) from (1.5 to 5.5) %, and macallisterite ($MgO\cdot3B_2O_3\cdot7.5H_2O$) when the mass percentage of H_3BO_3 was higher than 5.5 %. The pH values of the equilibria liquid phases and the solubility data of the corresponding solid phases were determined, respectively. The mechanisms of the phase transformation of chloropinnoite in boric acid aqueous solution are proposed and discussed.

Introduction

A borate double salt $2MgO\cdot2B_2O_3\cdot MgCl_2\cdot14H_2O$ named chloropinnoite was obtained from the natural concentrated salt lake brine containing boron.[1] Gao et al.[2] investigated its crystallization kinetics. Xia et al.[3] and Liu et al.[4] studied the kinetics of dissolution and phase transformation of chloropinnoite in water. To find the forming relation between this double salt and magnesium borate minerals in the salt lakes, we studied the phase equilibria of the $2MgO\cdot2B_2O_3\cdot MgCl_2\cdot14H_2O$ + H_3BO_3 + H_2O system at 303 K.[5] This paper reports the equilibria data for this system at 273 K. The results obtained provide a physicochemical basis for preparation of borates, extraction of borate from salt lake brine containing boron, and explaining the formation of hydrated borate minerals in the salt lakes.

Experimental Section

Reagents and Apparatus. Analytical-grade H_3BO_3 (purity ≥ 99.5 %), $MgCl_2\cdot6H_2O$ (purity ≥ 99 %), and $Mg(OH)_2\cdot4MgCO_3\cdot6H_2O$ (purity ≥ 99 %) were produced by the Xi'an Chemical factory, China. Active MgO which dissolves in solution relatively quickly was obtained by thermal decomposition of $Mg(OH)_2\cdot4MgCO_3\cdot6H_2O$ in an electric furnace at 873 K for 3 h.

A Rigaku D/max-IIIC X-ray diffractometer (with Cu target (λ = 1.54178 Å) at 8°·min^{-1}), a Bruker Equinox 55 FT-IR spectrometer (recorded over the (400 to 4000) cm^{-1} region with KBr pellets at room temperature), and a Perkin-Elmer TGA7 (at a heating rate of 10 K·min^{-1} in flowing N_2) were used to analyze the solid samples obtained.

Procedure. Amounts of 0.9313 g of $2MgO\cdot2B_2O_3\cdot MgCl_2\cdot14H_2O$ (synthesized by the literature method[2]), 20.0 mL of redistilled water, and different masses of H_3BO_3 [mass percentage of $H_3BO_3 = m(H_3BO_3)/(0.9313 + m(H_3BO_3) + 20.0)$] were taken and placed in a three necked flask with a water sealed stirrer and set in an isothermal water bath at 273 K. After the mixture was stirred for 3 days, a 2.00 mL sample of solution was withdrawn with a syringe pipet carrying a filter cartridge for chemical analysis: EDTA titration for Mg^{2+}, $Hg(NO_3)_2$ standard solution for Cl^-, and NaOH standard solution in the presence of mannitol for total boron concentration (expressed as B_2O_3). After an additional day, a sample of the solution was taken again in the same way. When the concentrations of all the three ions remained constant, the equilibria liquid and solid phases were separated. The pH values of the liquid phases were determined with a PHSJ-4A pH meter (Shanghai, China). The solid phases were washed with absolute ethyl alcohol until there was almost no Cl^- in the mother liquor. Thereafter, the solids were washed again with absolute ether. The obtained solids were dried in a vacuum dryer to a constant mass at room temperature and were identified by IR spectra and XRD. The uncertainties in the measurements of the mass fraction of each species were estimated to be ± 0.2 %.

Table 1. Solubility Data of the $2MgO\cdot2B_2O_3\cdot MgCl_2\cdot14H_2O$ + H_3BO_3 + H_2O System at 273 K

	liquid phase				
mass of H_3BO_3 %	pH	$c(Cl^-)$ mol·L^{-1}	$c(Mg^{2+})$ mol·L^{-1}	$c(B_2O_3)$ mol·L^{-1}	solid phase[a]
0.00	9.76	0.171	0.102	0.0303	S1
0.25	9.29	0.166	0.101	0.0259	S1
0.50	9.21	0.168	0.102	0.0246	S1
0.75	9.09	0.167	0.101	0.0207	S1
1.00	8.47	0.169	0.0981	0.0259	S1
1.25	7.96	0.170	0.0961	0.0397	S1
1.50	7.78	0.172	0.0903	0.0448	S1 + S2
1.75	7.76	0.171	0.0937	0.0404	S2
2.00	7.75	0.169	0.0957	0.0562	S2
2.50	7.73	0.169	0.0970	0.0791	S2
3.00	7.29	0.171	0.0994	0.119	S2
4.00	7.14	0.172	0.107	0.226	S2
5.50	6.43	0.168	0.119	0.350	S2 + S3
5.89	6.41	0.175	0.112	0.302	S3
6.50	6.40	0.170	0.111	0.303	S3
8.00	6.39	0.174	0.109	0.304	S3
10.00	6.36	0.169	0.107	0.307	S3 + H_3BO_3

[a] S1, $2MgO\cdot3B_2O_3\cdot15H_2O$; S2, $MgO\cdot2B_2O_3\cdot9H_2O$; S3, $MgO\cdot3B_2O_3\cdot7.5H_2O$.

Results and Discussion

Final Transformation Products and Corresponding Solubility Data. In this system, the dissolution and phase transformation of the double salt $2MgO\cdot2B_2O_3\cdot MgCl_2\cdot14H_2O$

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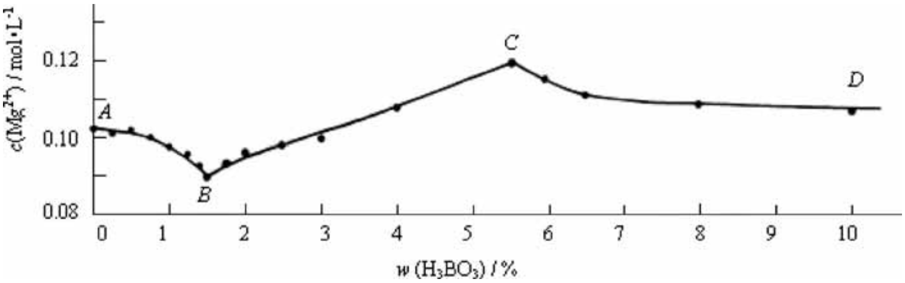

Figure 1. Solubility curve of the $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O + H_3BO_3 + H_2O$ system at 273 K.

in ($H_3BO_3 + H_2O$) solution would take place. Experimental results of the phase transformation of chloropinnoite in different concentrations of H_3BO_3 aqueous solution at 273 K are listed in Table 1.

The solid phases were identified by combining the recorded FT-IR spectra with those of ref 6. All data from the XRD of one product correspond with those of the JCPDS Card of file nos.11-583, 16-392, and 18-767, respectively. They were pure inderite ($2MgO\cdot 3B_2O_3\cdot 15H_2O$) when the mass percentage of H_3BO_3 was in the range from (0 to 1.5) %, hungtsaite ($MgO\cdot 2B_2O_3\cdot 9H_2O$) when the mass percentage of H_3BO_3 was in the range from (1.5 to 5.5) %, and macallisterite ($MgO\cdot 3B_2O_3\cdot 7.5H_2O$) when the mass percentage of H_3BO_3 was higher than 5.5 %, respectively. The solubility data of the corresponding equilibria solid phases are shown in curves *AB*, *BC*, and *CD* in Figure 1, respectively. When the mass percentage of H_3BO_3 was 10 %, the thermodynamic equilibrium solid phase identified by XRD contained a small amount of H_3BO_3 besides $MgO\cdot 3B_2O_3\cdot 7.5H_2O$, which means the end of the phase transformation of chloropinnoite in H_3BO_3 aqueous solution at 273 K.

As compared to the results in the literature,[5] the solid phase of kurnakovite ($2MgO\cdot 3B_2O_3\cdot 15H_2O$), which is the polymorph of inderite, disappeared in this system at 273 K, indicating that the kurnakovite is difficult to form at low temperature.

Mechanism of Phase Transformation. From the pH values of equilibrium solutions (the triborate anion in solution exists predominantly as the $[B_3O_3(OH)_4]^-$ ion at the lower pH value and exists as the $[B_3O_3(OH)_5]^{2-}$ ion at the higher pH value[7]) and the corresponding molecular structures of the equilibrium solid phases, and combining the structure of chloropinnoite which contains the $B_2O(OH)_6{}^{2-}$ group,[2] the following mechanism of phase transformation can be concluded.

When the mass percentage of $H_3BO_3 > 2.0$ %, chloropinnoite dissolved instantaneously to form clear solutions because of the relatively greater acidity of solution. After that, the $MgO\cdot 2B_2O_3\cdot 9H_2O$ and $MgO\cdot 3B_2O_3\cdot 7.5H_2O$ crystallized out from solutions with an increase of the concentration of boron according to the following reactions, respectively.

$$H_3BO_3 + 2H_2O \rightleftharpoons B(OH)_4{}^- + H_3O^+ \quad (1)$$

$$2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O \Leftrightarrow 2[MgB_2O(OH)_6\cdot H_2O]\cdot MgCl_2\cdot 6H_2O \xrightarrow{H_3O^+} 2B_2O(OH)_6{}^{2-} + 3Mg^{2+} + 2Cl^- + 8H_2O \quad (2)$$

$$2B(OH)_4{}^- \rightleftharpoons B_2O(OH)_6{}^{2-} + H_2O \quad (3)$$

$$B(OH)_4{}^- + B_2O(OH)_6{}^{2-} \rightleftharpoons B_3O_3(OH)_4{}^- + 2OH^- + 2H_2O \quad (4)$$

$$B_3O_3(OH)_4{}^- + B(OH)_4{}^- \rightleftharpoons B_4O_5(OH)_4{}^{2-} + 2H_2O \quad (5)$$

$$B_4O_5(OH)_4{}^{2-} + Mg^{2+} + 7H_2O \rightleftharpoons Mg[B_4O_5(OH)_4]\cdot 7H_2O\downarrow \quad (6)$$

$$B_4O_5(OH)_4{}^{2-} + B_2O(OH)_6{}^{2-} \rightleftharpoons B_6O_7(OH)_6{}^{2-} + 2OH^- + H_2O \quad (7)$$

$$B_6O_7(OH)_6{}^{2-} + Mg^{2+} + 4.5H_2O \rightleftharpoons Mg[B_6O_7(OH)_6]\cdot 4.5H_2O\downarrow \quad (8)$$

When the mass percentage of $H_3BO_3 \leqslant 2.0$ %, chloropinnoite dissolved incongruently because of the relatively small acidity of the solution, the same as that shown in the literature,[3] and led to the formation of a metastable phase of $[MgB_2O(OH)_6\cdot H_2O]$ as follows:

$$2[MgB_2O(OH)_6\cdot H_2O]\cdot MgCl_2\cdot 6H_2O \rightarrow 2[MgB_2O(OH)_6\cdot H_2O]\downarrow + Mg^{2+} + 2Cl^- + 6H_2O \quad (9)$$

$$[MgB_2O(OH)_6\cdot H_2O] \rightleftharpoons Mg^{2+} + B_2O(OH)_6{}^{2-} + H_2O \quad (10)$$

With an increase in concentration of $[B_2O(OH)_6]^{2-}$ in the solution, the following exothermic polymerization reaction 11 of $[B_2O(OH)_6]^{2-}$ would happen easily at the low temperature of 273 K, and then the metastable phase began to transform into the thermodynamic equilibrium solid phase, $2MgO\cdot 3B_2O_3\cdot 15H_2O$ or $MgO\cdot 2B_2O_3\cdot 9H_2O$ depending on the mass percentage of H_3BO_3, after a long time.

$$B_2O(OH)_6{}^{2-} + B(OH)_4{}^- \rightleftharpoons B_3O_3(OH)_5{}^{2-} + OH^- + 2H_2O \quad (11)$$

When the mass percentage of H_3BO_3 was in the range from (0.5 to 1.5) %, the metastable phase transformed into $2MgO\cdot 3B_2O_3\cdot 15H_2O$ as reaction 12 shows, which made the reactions 10 and 11 move to the right until the metastable phase disappeared.

$$B_3O_3(OH)_5{}^{2-} + Mg^{2+} + 5H_2O \rightleftharpoons Mg[B_3O_3(OH)_5]\cdot 5H_2O\downarrow \quad (12)$$

When the mass percentage of H_3BO_3 was in the range from (1.5 to 2.0) %, $B_3O_3(OH)_5{}^{2-}$ polymerized with $B(OH)_4{}^-$ to form $B_4O_5(OH)_4{}^{2-}$, as reaction 13, because of the increased concentration of H_3BO_3 in solution, and then the metastable phase transformed into $MgO\cdot 2B_2O_3\cdot 9H_2O$ as reaction 6 shows.

$$B_3O_3(OH)_5^{2-} + B(OH)_4^{-} \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H_2O + OH^{-} \tag{13}$$

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