EXPERIMENTAL STUDY OF TAKEDAITE SOLUBILITY AT 400°C AS A FUNCTION OF DENSITY OF AQUEOUS FLUID

Voronin M.V., Akinfiev N.N., Zotov A.V. (IGEM RAS)
voronin@igem.ru, Fax: +7(495) 230-21-79; Phone: +7(495) 230-82-31

Key words: experiment, takedaite, thermodynamic description, B $(OH)_{3,aq}$, equation of state, low-density fluid

Results of fluid inclusions investigation [1] give evidences on the fact of boron participation in numerous hydrothermal ore-forming processes. However, physical and chemical role of boron in these processes is not clear enough. This is substantially related to the absence of reliable thermodynamic description of aqueous boron hydroxide [$B(OH)_{3,aq}$] in super- and near-critical aqueous fluids. The similar problem is typical for plentiful neutral complexes of ore elements abundant in the low density natural hydrothermal solutions.

The purpose of the current study is to experimentally investigate and to obtain thermodynamic description of $B(OH)_{3,aq}$ in a wide range of aqueous solvent's density. Solubility of takedaite $Ca_3(BO_3)_2$ was investigated in a supercritical water fluid at H_2O density of $\rho_{H_2O} = 0.01 - 0.7$ g·cm^{-3}.

Experimental part

Experiments were carried out in titanium autoclaves (BT8 alloy) at temperature 400±1°C. Pressure within the limits of 100 – 1000 (±1.5) bars was specified by a degree of autoclave filling with distilled water. As a dissolving phase the calcium orthoborate (synthetic analogue of takedaite – $Ca_3(BO_3)_2$) was used. This last was synthesized using dry synthesis method of calcium hydroxide and a boric acid at 400°C. Equilibrium was attained during less than 24 hours. Boron content was analyzed by means of UV-Vis spectroscopy for pressure range of 300 – 1000 bar and by means of ISP-MS at pressures lower than 300 bar. Results of experiment are shown in the Fig. It is necessary to note smooth fall in $Ca_3(BO_3)_2$ solubility at pressure 1000 - 300 bar and its more steep decrease in low-density area.

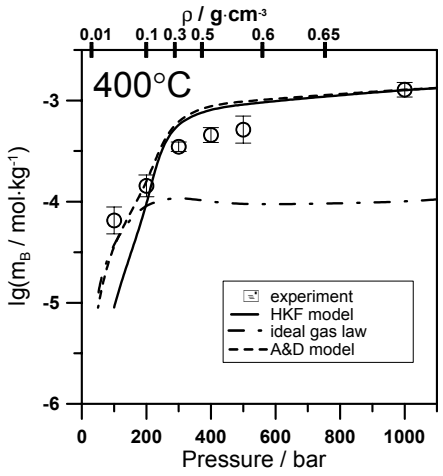

Fig. Pressure dependence of experimental takedaite solubility (symbols) and various equations of state predictions (lines) at 400°C

Thermodynamic description

For temperatures 0 - 350°C standard thermodynamic properties of $B(OH)_{3,aq}$ are determined quite reliably (see tab.). The widespread HKF equation of state [2] provides perfect description of B $(OH)_{3,aq}$ thermodynamic properties in the whole subcritical region of H_2O (0 – 350°C). However for supercritical conditions the appreciable divergence between experiment and HKF model description is observed [3], and this divergence increases while density of solvent reduces.

In our experiments solubility takedaite is specified by equilibrium of reaction:

$$1/2Ca_3(BO_3)_{2,cr.} + 3H_2O \Leftrightarrow 3/2Ca(OH)_{2,cr.}\downarrow + B(OH)_{3,aq} \quad (1)$$

at the presence of mineral assemblage of $Ca_3(BO_3)_{2,cr.}$ - $Ca(OH)_{2,cr.}$. As long as thermodynamics of solid phases is known, experimental data on takedaite solubility does directly assign thermodynamic

properties boron neutral hydrocomplex $B(OH)_{3,aq}$. Preliminary computation of boron speciation in aqueous fluid at 400ºC using the HKF model [2] indicated that even and 1000 bar (ρ_{H_2O} = 0.693 g·cm^{-3}) $B(OH)_{3,aq.}$ content exceeds 96 %, while at lower pressures its concentration tends to 100 %.

Table. Standard thermodynamic properties (298.15 K, 1 bar) and HKF- parameters of $B(OH)_{3,aq}$ [4]

$\Delta_f G°_{298}$ cal·mol^{-1}	$\Delta_f H°_{298}$ cal·mol^{-1}	$S°_{298}$ cal·(mol·K)$^{-1}$	$C_p°_{298}$ cal·(mol·K)$^{-1}$	$V°_{298}$ cm^3·mol^{-1}
-231540	-256292	38.790	25.50	39.43

$a_1 \cdot 10$ cal·(mol·bar)$^{-1}$	$a_2 \cdot 10^{-2}$ cal·mol^{-1}	a_3 cal·K·(mol·bar)$^{-1}$	$a_4 \cdot 10^{-4}$ cal·K·mol^{-1}	c_1 cal·(mol·K)$^{-1}$	$c_2 \cdot 10^{-4}$ cal·K·mol^{-1}	$\omega \cdot 10^{-5}$ cal·mol^{-1}
10.5116	3.4435	-8.7384	-2.0767	38.7980	-6.3554	0.0470

Strictly speaking, the HKF equation of state is inapplicable at fluid density lower, than 0.3 g·cm^{-3} [2]. However, if principles of the HKF approach should be expanded to the low-density area, its predictions result in essential disagreement with experiment (see fig., P <250 bar). At the same time the model of perfect gas behavior of $B(OH)_3$ is in fair accordance with experiment at low pressure limit (H_2O vapour at P ~ 100 bar), while at higher pressures it becomes inapplicable.

The available experimental data can be correctly described on the basis of equation of state proposed by the authors [5] for the whole range of solvent's density (0.01 – 1 g·cm^{-3}) (see fig.). This model empirical parameters have been estimated using thermodynamic properties of $B(OH)_{3,aq}$ at standard state conditions (25°C, 1 bar) solely.

This research was supported by grants of the Russian Foundation for Basic Research (04-05-65119 and 05-05-66811), NSERC-CRO "Gaseous transport of metals" and the Program on Leading Scientific Schools (№6722.2006.5)

References

1. *Prokof'ev V.Yu. Peretyazhko I.S. et al*. Boron and boric acids in endogenous ore-forming fluids. M.: PAS'VA, 2003. 192 p. (in Russian).
2. *Johnson J.W., Oelkers E.H., Helgeson H.C.* // Comp. Geosci., 1992. V. 18. PP. 899-947.
3. *Hnědkovsky L., Majer V., and Wood R.H.* // J. Chem. Thermodyn., 1995. V. 27. PP. 801-814.
4. *Akinfiev N.N., Voronin M.V., Zotov A.V., Prokof'ev V.Yu.* // Geochem. Int. 2006. (In press).
5. *Akinfiev N.N., Diamond L.W.* // Geochem. Cosmochim. Acta. 2003. V. 67. N. 4. PP. 613-627.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24)'2006
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/hydroterm-3e.pdf

Published on July, 1, 2006