Solubility of Trihydrogenboric Acid in Aqueous Solutions Containing Various Cations at Different pH Values

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Solubility of trihydrogenboric acid in aqueous solutions of sodium, potassium, calcium, and barium hydroxides at various pH values in the 5.5 to 12.5 range was investigated. Two solubility maxima in solutions of sodium or potassium hydroxides were found depending on the pH value. The first solubility maximum is in the neutral and the second one in the strongly basic pH range. The solubility of H_3BO_3 is in KOH solutions lower than in NaOH at the neutral reaction; in the basic pH range above the value of approximately 9 the solubility increases faster than in the presence of NaOH. Solubility of trihydrogenboric acid decreases monotonously in solutions containing calcium or barium hydroxides with the rise of the pH value. Solubility differences of H_3BO_3 in the presence of various cations and at different pH values are associated with the formation of polyborates and their different solubility. In systems with the highest solubility of trihydrogenboric acid sodium or potassium pentaborate (neutral region), or metaborates (basic region) are equilibrated with the saturated solutions.

Trihydrogenboric acid together with several inorganic and organic salts, containing prevalently sodium or potassium cations, are the main components of waste waters from nuclear power plants of the VVER type. These waters before being worked out into bitumenous or other matrices for a long-term storage are deposited in tanks where precipitation of a solid is unwanted. On the other hand, compounds produced in the solidification process have to be practically insoluble, must not react with water under enlargement of their volume and similar in order not to be leached from the matrices or to deform matrices due to volume differences of the fixed compounds during this long-term storage. Optimization of composition of waste waters for storage and also conditions for their solidification could not be solved on the basis of literature data only, because in our opinion no systemic necessary data are available. According to older literature [1] and also to newer one [2, 3] it is obvious that solutions of trihydrogenboric acid tend to form polyborates, preferentially penta- and tetraborates. These compounds crystallize from solutions almost at all conditions; at 0 °C also presence of metaborates [1] was identified in solid state. As follows, investigation of H_3BO_3 solubility constitutes at the same time examination of equilibrium reactions of its changes to polyborates. Importance of these changes follows explicitly from the study of equilibrium between the particular mono- and polynuclear particles present in solu-

tions [2]. Solubility of the system CaO—H_3BO_3—H_2O was investigated by several authors from the temperature point of view; they supposed that the equilibrated solid phases were composed of $CaO \cdot B_2O_3 \cdot 6H_2O$ or $2CaO \cdot B_2O_3 \cdot H_2O$ [4, 5]. In spite of the fact that literature reported the solubility data of H_3BO_3 at various temperatures and in the presence of some cations, it is our belief that systemic investigation of its solubility in the presence of various cations at different pH values has so far not been done. Therefore, we first of all paid attention to the study of the behaviour of trihydrogenboric acid in solutions simulating the composition of waste waters flowing out of the nuclear power plants of the VVER type.

EXPERIMENTAL

Buffer solutions K-21 (pH = 2.12), K-71 (pH = 7.06), K-91 (pH = 9.3), and K-113 (pH = 11.4) with maximum pH deviation ± 0.03 (Radelkis, Budapest), mannitol pure, and other chemicals of anal. grade (Lachema, Brno) were used. pH-Meter OP-201/2 with a pH-sensitive combined electrode OP-0808 P (Radelkis, Budapest), reproducibility ± 0.05 pH, was applied for measurements. Calibration was verified with a Polymetron buffer of pH 6.88. Ultrathermostat UH (MLX, Leipzig) with continuous circulation of tempered liquid was used. Goniometer DRON (Commonwealth of Indepen-

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dent States), radiation CuKα, Ni-filter was used for obtaining powder diffraction patterns; derivatograph OD-102 (MOM, Budapest) for thermal analysis; sample mass 100 mg, heating rate 5 K min^{-1}, maximum heating temperature 500 °C.

At the preparation of saturated solutions specified volume of volumetric solution of NaOH or KOH was added to the weighted amount of H_3BO_3 which was greater than the anticipated solubility of the product. The mixture was filled up to 50 cm^3 with redistilled water (20 °C). Solutions, containing Ca^{2+} or Ba^{2+} were obtained by adding the calculated amount of solid CaO, $Ba(OH)_2$ or solution of $Ba(OH)_2$ (c = 0.02 or 0.2 mol dm^{-3}) under nitrogen and the final solution was filled up to 50 cm^3. These solutions were transferred into glass-joint jacketed vessels equipped with a reflux condenser with a drying tube filled with KOH to prevent entering of CO_2. The systems were stirred, tempered and a part of them was after a predetermined time filtered off. The filtrate was analyzed for the content of H_3BO_3 and pH. This procedure was repeated till both values remained constant. Equilibrium in some systems was reached after 70 h.

Solid phases filtered off from these systems were dried over KOH at room temperature. Their composition was identified by the powder diffraction pattern method (data base Joint Committee on Powder Diffraction Standards) and thermal analysis.

The H_3BO_3 content in saturated solutions was determined titrimetrically after addition of mannitol with a volumetric NaOH solution, phenolphthalein being the indicator. The pH in alkaline solutions was prior to measurement adjusted by a volumetric HCl solution to the transition point of methyl orange. The adjustment of pH by the volumetric

HCl solution in cases when the pH of solution was lower than ≈ 9.5 led only to the back-titration of the added amount of HCl as in all the controls there was such a consumption of the volumetric HCl and NaOH solutions that after subtracting the NaOH consumption per nonadjusted solution the amount of substance ratio of NaOH and HCl was 1 : 1. Calculation of the equilibrium composition of the system H_3BO_3—H_2O—KOH showed that concentration of the tetrahydroxoborate anion $[B(OH)_4]^-$ is higher than the concentration of H_3BO_3 only at pH ≥ 10 [2]. Polyborates present in neutral and weakly basic solutions dissociate to H_3BO_3 after addition of mannitol due to formation of a complex; this was evidenced by the pH change of the solution from the originally basic to acidic one [6].

RESULTS AND DISCUSSION

Solubility of H_3BO_3 in aqueous NaOH (θ = 22 °C) at various $[H_3BO_3]$: $[NaOH]$ ratios and consequently, at different pH values in equilibrium systems is listed in Table 1. It is evident that the solubility of trihydrogenboric acid is maximal in the neutral region; further solubility maximum lies in the high pH value region (Fig. 1). Solid phases equilibrated with saturated solutions in the respective pH ranges were identified by the powder diffraction patterns as $Na[B_5O_6(OH)_4] \cdot 3H_2O$ (pH ≈ 7), a mixture of $Na[B_5O_6(OH)_4] \cdot 3H_2O$ and $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ (pH ≈ 8.6) and a mixture of

Table 1. Solubility of H_3BO_3 in Aqueous NaOH at Various Ratios of Their Concentrations and θ = 22 °C

$[H_3BO_3]$: $[NaOH]$	pH	$\dfrac{\rho(H_3BO_3)}{g\ dm^{-3}}$
1 : 0	3.05	55.53
1 : 0.011	5.10	59.73
1 : 0.044	5.90	68.44
1 : 0.045	6.50	96.80
1 : 0.181	6.95	193.31
1 : 0.187	7.05	226.93
1 : 0.248	7.45	190.60
1 : 0.297	8.20	111.06
1 : 0.377	8.60	59.13
1 : 0.66	11.06	45.01
a	11.98	114.46
a	12.04	118.22
b	12.25	194.70
b	12.52	228.52

The solutions were prepared from $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ by dissolving in 1 M-NaOH (a) or 2 M-NaOH (b).

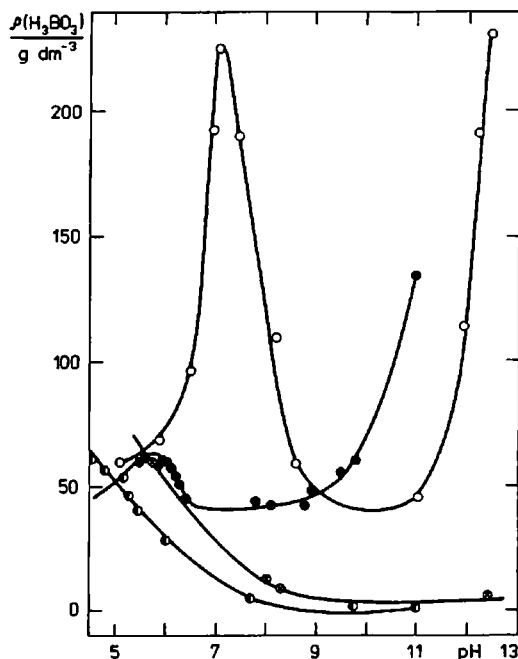**Fig. 1.** Dependence of the solubility of H_3BO_3 on the pH of the saturated solution in the presence of NaOH (O), KOH (●), CaO (⊗), and $Ba(OH)_2$ (◐).

Table 2. Powder Diffraction Patterns of Solid Phases Isolated from the System H_3BO_3—NaOH—H_2O at Different pH Values

pH						
6.95		8.60			12.04	
$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$	Assignment	$d/Å$	$I_r/\%$	Assignment
8.27	17	8.27	17	2	8.67	53	2
7.90	13	7.90	25		7.67	26	1
6.11	12				6.99	34	3
					5.94	37	1, 3
					5.83	36	3
		5.07	33	1	5.58	100	1
		4.80	50	1	5.26	28	3
4.53	47	4.55	83	2	4.93	34	
4.25	73	4.27	40	2	4.82	48	1, 2
4.10	27	4.10	50	2	4.67	39	3
					4.37	72	2
		3.90	15	1	3.93	14	1
3.75	20	3.75	33	2			
3.55	17	3.55	25	1, 2	3.56	20	1, 2, 3, 4
3.35	70			2	3.45	45	3
3.27	100			2	3.11	15	1, 4
3.19	77	3.19	83	1, 2	3.00	56	1, 2, 4
3.00	25	3.06	66	1, 2	2.93	77	2, 4, 5
2.92	25	2.92	75	2	2.86	82	2, 4, 5
2.89	17				2.84	71	1, 4
2.83	17	2.83	25	1, 2	2.76	17	3, 4
2.56	15	2.56	29	1, 2	2.65	10	1, 2, 3, 5
					2.59	32	3

Assignment: 1. $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$, 2. $Na[B_5O_6(OH)_4] \cdot 3H_2O$, 3. $Na[B_5O_6(OH)_4] \cdot 0.95H_2O$, 4. $Na_2B_2O_4 \cdot H_2O$, 5. $Na_4B_2O_5 \cdot 5H_2O$.

Table 3. Powder Diffraction Patterns of Some Sodium Polyborates according to JCPDS

1		2		3		4		5	
$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$
7.71	200	8.62	20	7.40	10	6.50	20	4.53	15
7.11	20	8.22	25	6.89	14	5.73	8	4.29	55
5.92	20	6.86	35	6.39	14	4.76	100	4.17	15
5.68	90	6.22	14	5.82	12	3.79	14	2.99	20
5.29	20	6.12	10	5.21	20	3.62	25	2.93	100
5.16	16	5.11	14	4.83	75	3.58	95	2.83	60
4.82	100	4.82	10	4.60	14	3.52	14	2.68	25
3.92	35	4.60	100	4.10	16	3.25	6	2.66	45
3.57	14	4.35	18	3.87	10	2.99	40	2.63	20
3.48	8	4.30	30	3.75	10	2.96	16	2.51	40
3.32	12	4.11	14	3.68	20	2.90	20	2.27	45
3.18	10	3.73	20	3.54	100	2.86	80		
2.97	40	3.56	40	3.36	10	2.84	20		
2.82	45	3.52	35	3.34	12	2.79	30		
2.66	10	3.35	16	3.30	14	2.76	25		
2.63	6	3.30	75	3.21	50	2.72	55		
2.56	65	3.20	75	2.92	20	2.52	16		
		3.13	10	2.91	18	2.43	14		
		3.04	18	2.78	18	2.41	40		
		2.95	16	2.66	12				
		2.93	18	2.605	14				
		2.87	18	2.455	8				
		2.68	18						
		2.57	40						
		2.41	10						

1. $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$, 2. $Na[B_5O_6(OH)_4] \cdot 3H_2O$, 3. $Na[B_5O_6(OH)_4] \cdot 0.95H_2O$, 4. $Na_2B_2O_4 \cdot H_2O$, 5. $Na_4B_2O_5 \cdot 5H_2O$. JCPDS (Joint Committee on Powder Diffraction Standards, Philadelphia, 1962, 1970, 1971, 1973, 1974), charts No. 12 – 258 (1), 24 – 1056 (2), 21 – 1023 (3), 20 – 1078 (4), 23 – 657 (5).

$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ with metaborates $Na_2B_2O_4 \cdot H_2O$ and $Na_4B_2O_5 \cdot 5H_2O$ (pH $\approx$ 12) (Tables 2 and 3). The latter composition was also corroborated by thermal analysis, when the loss of volatile components was lower than the content of water in pure borax on heating up to 500 °C (calculated mass percentage of water 47.20, found 40.3); this loss was, however, greater than the content of water in both metaborates (12.03 and 31.74 mass %, respectively).

Dependence of the solubility of H_3BO_3 on pH values displayed in the system H_3BO_3—KOH—H_2O also two maxima (Table 4). The maximum solubility in the first of them (pH = 6) is lower than in the system containing NaOH (Fig. 1). On the other hand, the solubility of trihydrogenboric acid increases more rapidly with the rising pH value, and already at pH $\approx$ 9 it is greater than in the system containing NaOH. The solid phase equilibrated with the saturated solutions containing KOH at pH $\approx$ 6 was identified as being $K[B_5O_6(OH)_4] \cdot 2H_2O$ (Table 5).

Solubility of H_3BO_3 in systems containing $Ca(OH)_2$ or $Ba(OH)_2$ decreases within the complete pH range under study (Table 6, Fig. 1).

Data concerning the solubility of H_3BO_3 (Tables 1, 4—6) stimulated us to examine the dependence between the pH values of solutions and the

Table 4. Solubility of H_3BO_3 in Aqueous KOH at Various Ratios of Their Concentrations and $\theta = 22$ °C

$[H_3BO_3]$: $[KOH]$	pH	$\dfrac{\rho(H_3BO_3)}{g\ dm^{-3}}$
1 : 0.01	4.98	52.81
1 : 0.04	5.62	61.42
1 : 0.08	5.90	62.40
1 : 0.10	5.76	64.20
1 : 0.12	6.07	59.80
1 : 0.15	5.90	59.15
1 : 0.18	6.00	59.11
1 : 0.20	5.91	61.15
1 : 0.22	6.12	57.72
1 : 0.25	6.16	56.73
1 : 0.26	6.18	53.68
1 : 0.28	6.38	49.60
1 : 0.29	6.40	45.60
1 : 0.30	8.80	47.27
1 : 0.32	8.87	49.60
1 : 0.39	9.90	67.58
1 : 0.54	10.68	135.80
1 : 0.60	11.25	139.50

Table 5. Solubility of H_3BO_3 in the System H_3BO_3—CaO—H_2O at Various Components Ratios and $\theta = 22\ °C$

$[H_3BO_3]$: [CaO]	pH	$\dfrac{\rho(H_3BO_3)}{g\ dm^{-3}}$
1 : 0.05	5.75	60.60
1 : 0.4	8.02	13.20
1 : 0.6	8.26	9.33
1 : 1	12.37	6.82

$[M(OH)_n]$: $[H_3BO_3]$ ratio (Fig. 2). These data make it clear that the added amounts of hydroxides were
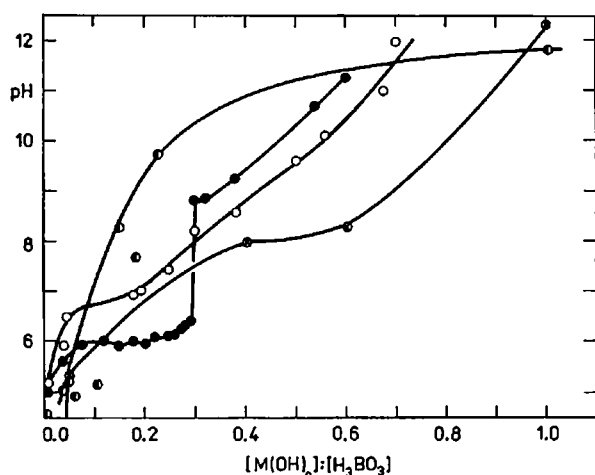
Fig. 2. Dependence of the pH value of the saturated solution on the $[M(OH)_n]$: $[H_3BO_3]$ ratio. M = Na (O), K (●), Ca (⊗), Ba (◐).

consumed also during formation of polyborates according to the equations

$$4\ H_3BO_3 + 2\ OH^- \rightleftarrows [B_4O_5(OH)_4]^{2-} + 5\ H_2O \quad (A)$$

$$5\ H_3BO_3 + OH^- \rightleftarrows [B_5O_6(OH)_4]^- + 6\ H_2O \quad (B)$$

Interval of the pH values within which these reactions proceed depends on the character of the cation M^{n+} and corresponds to regions where the particular systems behave as buffers. Our results

Table 6. Solubility of H_3BO_3 in the System H_3BO_3—Ba(OH)$_2$—H_2O at Various Components Ratios and $\theta = 22\ °C$

$[H_3BO_3]$: $[Ba(OH)_2]$	pH	$\dfrac{\rho(H_3BO_3)}{g\ dm^{-3}}$
1 : 0.005	4.82	57.34
1 : 0.10	5.15	47.43
1 : 0.11	5.45	40.61
1 : 0.12	6.00	27.88
1 : 0.18	7.73	5.4

disclose that the pH values remain approximately constant at the following $[M(OH)_n]$: $[H_3BO_3]$ ratios: 0.1 to 0.3 for M = K, 0.05 to 0.2 for Na and 0.4 to 0.6 for Ca. No similar interval appeared on the curve illustrating the dependence of pH on the $[Ba(OH)_2]$: $[H_3BO_3]$ ratio (Fig. 2).

Presuming that exclusively reaction (A) proceeded in the system containing KOH, the pH value should start to rise at the ratio [KOH] : $[H_3BO_3]$ = 0.5. Should the system obey eqn (B), the pH increase would start at the 0.2 ratio and at the ratios 0.22 and 0.3 the pH value of the solution should be 12.6 and 13.3, respectively. The experimental value of the [KOH] : $[H_3BO_3]$ ratio at which the pH began to rise was found to be 0.3; this corresponds to the following reaction leading to the triborate

$$3\ H_3BO_3 + OH^- \rightleftarrows [B_3O_3(OH)_4]^- + 3\ H_2O \quad (C)$$

in accordance with calculations [2]. Another possible rationalization is an enhancement of the tetraborate anion content according to the equation

$$4\ [B_5O_6(OH)_4]^- + 6\ OH^- \rightleftarrows 5\ [B_4O_5(OH)_4]^{2-} + H_2O \quad (D)$$
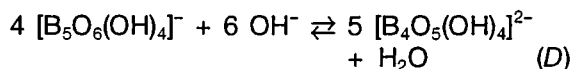
Taking these results into account it is necessary to correct the data in older literature [1] according to which tetra- and pentaborate anions are present only in concentrated borax solutions in sodium hydroxide, whereas all other solutions contain only H_3BO_3 molecules and anions $[B(OH)_4]^-$ originating in the reaction

Table 7. Powder Diffraction Patterns of Samples Isolated from the Systems H_3BO_3—KOH—H_2O at Different pH Values in Comparison with the $K[B_5O_6(OH)_4] \cdot 2H_2O$ Diffraction Pattern

pH				$K[B_5O_6(OH)_4] \cdot 2H_2O$	
6.40		8.80			
$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$	$d/Å$	$I_r/\%$
5.91	34	5.91	34	5.97	80
5.53	100	5.63	80	5.63	100
4.52	7	4.51	7	4.53	80
				3.94	30
3.50	94	3.51	95	3.50	100
3.34	100	3.34	100	3.36	100
3.28	28	3.28	26	3.27	80
2.96	16	2.96	13	2.97	60
2.91	10	2.91	10	2.91	60
2.81	17	2.81	17	2.81	60
2.76	47	2.76	39	2.77	100
2.57	8	2.58	7		
2.51	21	2.52	21	2.51	80
2.37	15	2.38	15	2.38	80
2.32	10	2.34	7	2.33	30
2.29	15	2.29	14	2.29	60
2.26	10	2.26	11	2.26	30
2.17	34	2.17	32	2.18	80
2.13	22	2.13	20	2.17	100

$$H_3BO_3 + OH^- \rightleftarrows [B(OH)_4]^- \qquad (E)$$

Provided only this reaction would proceed in this system, the pH value would have to be constant up to the ratio $[M(OH)_n] : [KOH] = 1$. Our results cannot exclude a concurrent course of reactions (A) to (D). Examination concerning composition of solutions of boric acid in aqueous KOH of various concentrations showed [2] that polyborates and the $[B(OH)_4]^-$ anion are present even at a low total content of H_3BO_3 ($c \approx 1$ mol dm^{-3}), and at pH values approximately 6, but concentration of $[B(OH)_4]^-$ approaches significant values already at pH ≥ 9.5. The fact that the sole solid phase isolated from the system in this pH region was $K[B_5O_6(OH)_4] \cdot 2H_2O$ (Table 7) can be due to the lowest solubility of compound among all potassium borates formed in these systems.

It can be concluded that the content of boric acid in its solutions depends on the pH value, but also on the cation present. Both factors influence both the polyborate types being formed in solutions and their solubility. The nuclear power plant waste waters should not contain cations of alkaline-earth metals when stored for a long time; in the presence of greater amounts of potassium their pH should be adjusted at least at 9.5. This pH region is, however, unfavourable for storage of solutions containing cations of sodium for a relatively low solubility of sodium tetraborate and therefore, the pH values should be greater than 11. Storage of strongly alkaline solutions is generally unfavourable and therefore, the content of potassium cations has to be kept at the lowest possible limit. As already mentioned, solubility of H_3BO_3 is influenced by further compounds appearing in waste waters from nuclear power plants of the VVER type; these results will be published elsewhere.

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