Phase Diagrams of the Ternary Systems $NaBH_4 + NaOH + H_2O$, $KBH_4 + KOH + H_2O$, $NaBO_2 + NaOH + H_2O$, and $KBO_2 + KOH + H_2O$ at −10 °C

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Concentrated water−alkaline solutions of sodium and potassium borohydrides are used as a fuel and as a hydrogen source in hydrogen power engineering, including low-temperature fuel cells, where borohydrides are converted into metaborates. The performance of such mixtures is determined by the solubility of their components, negative temperatures being especially critical. The solubility in the ternary systems $NaBH_4 + NaOH + H_2O$, $KBH_4 + KOH + H_2O$, $NaBO_2 + NaOH + H_2O$, and $KBO_2 + KOH + H_2O$ was studied by means of isothermal saturation at −10 °C. The compositions of the equilibrium solid phases and of mixtures corresponding to nonvariant equilibrium points were determined; the solubility diagrams of the systems were plotted. The presence of a range of homogeneous solutions and fields of crystallization of ice, anhydrous, and hydrated forms of the salts and hydroxides is characteristic of all four systems at the said temperature. The composition of crystalline hydrates depends on the ratio of the components in the mixture and on the cation nature. Of the borohydride systems, the best solubility was observed in that with $NaBH_4$, whereas in the metaborate systems it was that with KBO_2.

Introduction

Nowadays, much research in hydrogen power engineering and chemical power sources is devoted to the development of novel fuel cells (FCs).[1−4] One of the promising directions of research involves low-temperature FCs, in which salt-like borohydrides of alkaline metals, (Na, K)BH_4, are used as a source of hydrogen (fuel). From their characteristics, they are comparable with methanol-utilizing FCs.[4] In such devices, borohydrides are used in the form of suspensions or concentrated aqueous solutions with dissolved hydroxides, (Na, K)OH, as additives which stabilize the system by preventing borohydride ion (BH_4^-) hydrolysis as well as determining and controlling its chemical and electrochemical activity. During FC functioning, borohydrides are oxidized, releasing the contained hydrogen and being converted into soluble salts of boric acid, that is, metaborates, (Na, K)BO_2.

Thus, the initial fuel belongs by its composition to the ternary systems $NaBH_4 + NaOH + H_2O$ or $KBH_4 + KOH + H_2O$, while the final product to the ternary systems $NaOH + NaBO_2 + H_2O$ or $KOH + KBO_2 + H_2O$. There are reports devoted to studying the aqueous solubility of NaOH, $NaBO_2$, $NaBH_4$, KOH, KBH_4, and KBO_2 both as individual substances and in various combinations. Some earlier papers dealt with the solubility polytherms of the binary alkaline systems $NaOH + H_2O$[5,6] and $KOH + H_2O$;[7] information is also available on the binary systems $NaBH_4 + H_2O$,[6] $KBH_4 + H_2O$,[7] $NaBO_2 + H_2O$, and $KBO_2 + H_2O$.[8−10]

Some information on the ternary-system solubility diagrams under consideration is presented in refs 6 to 8, 11, and 12. In ref 11, the solubility isotherms of the purely alkaline ternary system $NaOH + KOH + H_2O$ were studied within a temperature range of (0 to 20) °C. Crystalline hydrates were shown to be in equilibrium with the solution, while anhydrous NaOH and KOH existed only under water deficiency (mixtures with mass fractions of alkali $w > 0.75$). The isotherms of the ternary systems $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ within (0 to 50) °C were investigated by Mikheyeva et al.[6,7,12] and also in ref 13. Some general regularities of the behavior of those systems were noted; in particular, alkali and borohydride were shown to lower the solubility of each other, but the total concentration of the saturated solution increased. Solid phases exist as crystalline hydrates of various compositions. Increasing the temperature is accompanied by growth of the solubility of all solid phases, the solubility of borohydride increasing more rapidly than that of the alkali. Simultaneously, dehydration of crystalline hydrates occurs with the appearance and growth of an anhydrous salt field, so that at 50 °C the solid phases are represented by the anhydrous compounds $NaBH_4$, NaOH, KBH_4, and KOH.

It can be seen that the early studies have been performed within the temperature range from (0 to 50) °C, whereas the expected functionality of borohydride FCs covers the range below 0 °C as well. The performance of fuel mixtures are determined by concentrations of the dissolved components, negative temperatures being especially critical. Decreasing temperature may result in the formation of additional solid phases, a solubility decrease, and shrinkage of the homogeneous liquid state field. No literature data have been found on the solubilities in the ternary systems $NaOH + NaBO_2 + H_2O$ and $KOH + KBO_2 + H_2O$.

Therefore, studying the aforementioned systems to obtain more complete information about the character of component solubility in the alkali + borohydride + water and alkali + metaborate + water mixtures is of both fundamental and practical importance. In the present work, the ternary systems $NaBH_4 + NaOH + H_2O$, $KBH_4 + KOH + H_2O$, $NaOH + NaBO_2 + H_2O$, and $KOH + KBO_2 + H_2O$ have been studied

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by means of isothermal saturation at −10 °C. For these systems, the compositions of the solid phases and mixtures corresponding to nonvariant equilibrium points have been determined and solubility isotherms plotted on the composition triangles, and the results obtained are analyzed and compared with the relevant literature data.

Experimental Section

Solubilities were measured in special glass vessels with a mechanical stirrer, glycerol seal to prevent gas exchange with the atmosphere, and a thermostatted sampling tube.[14] The composition of the loaded mixture was calculated considering the crystallization water in the reagents. The following chemicals ("reagent grade" quality) were used: $NaBO_2 \cdot 4H_2O$ and $KBO_2 \cdot 1.25H_2O$ (Vekton, Russian Federation); NaOH and KOH (ECROS, Russian Federation); $NaBH_4$ and KBH_4 (Aviabor, Russian Federation); distilled water with no dissolved carbon dioxide. The amount of the loaded mixture was (35 to 40) g per experiment; weighing with an uncertainty of ± 1 mg was carried out with a VLT 150P laboratory electronic balance. The saturation of solutions was performed in a PolySciens "AlexRedCTD" programmed thermostat at a fixed temperature [(−10 ± 0.01) °C].

After filling the vessel with the mixture studied, it was thermostatted under continuous stirring. The equilibration time in each system was estimated by sampling the saturated solution and analyzing its chemical composition. Equilibrium was established in ca. (2 to 3) h of stirring. After mixture settling, three samples of the saturated solution and two to three samples of the precipitate were taken. The sampling of the liquid was implemented by its replacement through a cotton wool filter. For sampling the solid phase, the saturated suspension was displaced, which then was filtered through a Schott glass filter under vacuum, separating the precipitate from the mother liquor and then pressing it between sheets of filter paper. The fact that the precipitate inevitably contained some mother liquor was insignificant, since the composition of the solid phase was determined by Schreinemakers' method. In this method, the straight line drawn through the compositions of the liquid phase and the corresponding wet solids passes through the composition of pure solid phase on the phase diagram; thus, the composition of the pure solid phase is obtained from the intersection of lines drawn through several such pairs.

The composition of the saturated solution and the solid phase was determined by quantitative chemical analysis. For the systems containing a mixture of alkali and borate, an acid−base titration was employed. For this purpose, a sample of liquid solution of (0.2 to 0.5) g or that of precipitate of (0.3 to 0.6) g was quantitatively transferred to a glass for titration, with further diluting with distilled water up to 50 mL. The titration was done with a 1 $mol \cdot L^{-1}$ HCl solution. Titration curves (Figure 1a) were processed by computer fitting of experimental and calculated titration curves.

The compositions of the equilibrium phases in the systems containing alkali and borohydride were analyzed by means of two different techniques. The alkali content was determined by acid−base titration. For borohydride analysis, an iodometric titration was used (Figure 1b). A liquid sample [(0.2 to 0.5) g] or that of the precipitate [(0.3 to 0.6) g] was quantitatively transferred to a 100 mL flask and brought to the mark with a 1 $mol \cdot L^{-1}$ NaOH solution. Then, a 5 mL aliquot was sampled, transferred to a glass for titration, and brought to 50 mL with a 1 $mol \cdot L^{-1}$ NaOH solution with further titration using a 0.1 $mol \cdot L^{-1}$ standard iodine solution.

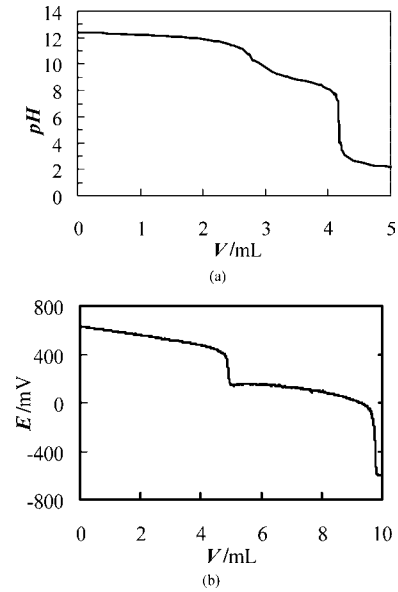

Figure 1. Typical curves of (a) acid−base titration and (b) iodometric titration of the solutions under study. Consecutive titrating steps correspond to (a) the titration of the hydroxide ion and the borate ion or to (b) the complex mechanism of the interaction $I_2 + BH_4^-$.

Table 1. Equilibrium Data for the $NaBH_4$ + NaOH + H_2O System at −10 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			equilibrium crystalline phases
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	
23.4	0.0	76.6				$NaBH_4 \cdot 2H_2O$
18.9	0.0	81.1				ice
18.3	27.3	54.4	51.3	7.7	41.0	$NaBH_4$ + $NaBH_4 \cdot 2H_2O$ (*p*1)
17.0	23.1	59.9	38.2	6.9	54.9	ice
16.1	8.2	75.7	42.3	4.6	53.1	$NaBH_4 \cdot 2H_2O$
14.6	32.7	52.7	82.2	7.0	10.8	$NaBH_4$
14.4	14.1	71.5	38.6	6.3	55.1	$NaBH_4 \cdot 2H_2O$
14.0	18.5	67.5	42.1	3.8	54.1	$NaBH_4 \cdot 2H_2O$
13.8	4.4	81.8	11.7	3.7	84.6	ice
12.2	38.2	49.6	74.5	10.6	14.9	$NaBH_4$
10.5	42.6	46.9	12.6	54.0	33.4	$NaBH_4$ + $NaOH \cdot H_2O$ (*e*1)
9.3	37.1	53.6	3.2	55.9	40.9	$NaOH \cdot H_2O$
8.3	33.5	58.2	1.8	60.1	38.1	$NaOH \cdot H_2O$
7.6	8.4	84.0	6.7	7.2	86.1	ice
6.2	31.3	62.5	2.6	52.6	44.8	$NaOH \cdot H_2O$
3.2	29.6	67.2	1.7	41.8	56.5	$NaOH \cdot H_2O$ + $NaOH \cdot 4H_2O$ (*p*2)
2.6	10.6	86.8	1.7	6.7	91.6	ice
1.6	26.4	72.0	0.9	31.1	68.0	$NaOH \cdot 4H_2O$
0.0	26.7	73.3				$NaOH \cdot 4H_2O$
0.0	9.8	90.2				ice

[a] Compositions and the equilibrium crystalline phases of peritonic points (*p*1, *p*2) and eutonic point (*e*1) are underlined.

The results of our experiments are presented as Gibbs−Roseboom triangles, the vertices of which correspond to pure components, the points on the sides to the compositions of the binary systems, and the points inside the triangles characterize the compositions of ternary mixtures. For each system under study, no less than 20 points were obtained; the liquidus lines and crystallization fields of solid phases were determined.

Results and Discussion

The results of the determination of the solubility and composition of equilibrium solid phases in the $NaBH_4$ + NaOH + H_2O system are presented in Table 1 and Figure 2. The area of liquid phase *l* is limited by the crystallization lines of five solid phases. One of them cuts off the ice crystallization area adjacent to the H_2O vertex; the others limit the crystallization areas of alkali and metaborate.

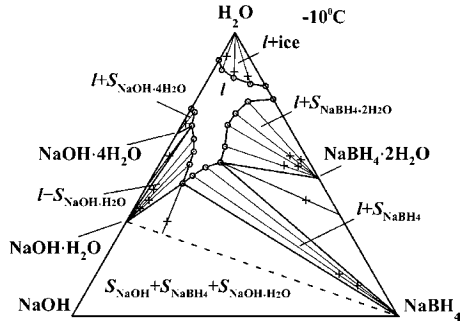

Figure 2. Phase diagram for the $NaBH_4$ + NaOH + H_2O system at −10 °C. *l* and *S* are liquid and solid phases, respectively. Compositions of the equilibrium liquid phase (○) and wet solid phase (+) are listed in Table 1. Thin lines are tie-lines between coexisting phases, and thick solid and dashed lines are the bounds among monophase, two-phase, and three-phase areas.

Let us analyze the course of solubility and phase ratios, considering the diagram from the right to the left. The range of homogeneous liquid solution in the $NaBH_4$ + H_2O system is *w* = (0.189 to 0.234) at −10 °C. Solutions with lower $NaBH_4$ concentrations contain ice crystals. Increasing the borohydride concentration results in the onset of the equilibrium "liquid + solid $NaBH_4 \cdot 2H_2O$" in the system. Our data agree well with the results of earlier work,[6] except for the borders of the homogeneous solution in the binary $NaBH_4$ + H_2O system. According to ref 6, a homogeneous liquid solution at −10 °C exists at $NaBH_4$ fractions $w \approx$ (0.09 to 0.26).

The ice crystallization range (l + ice) is located at the water vertex of the triangle. This area is cut off by the upper liquidus line, connecting the triangle's sides at mass fractions of 0.189 for borohydride and 0.106 for alkali. The liquid solution *l* area is limited by the lower liquidus line, consisting of four sections connected by one eutonic point *e*1 and two peritonic points *p*1 and *p*2; their compositions are given in Table 1. The eutonic $l + S_{NaBH_4} + S_{NaOH \cdot H_2O}$ triangle is characterized by equilibrium between the phases of the saturated solution, anhydrous borohydride, and alkali monohydrate. On the right side of the eutonic triangle there are two borohydride crystallization fields corresponding to the anhydrous salt ($l + S_{NaBH_4}$) and monohydrate ($l + S_{NaBH_4 \cdot 2H_2O}$).

On the left of the eutonic triangle there are alkali crystallization fields. In the $l + S_{NaOH \cdot H_2O}$ area there exists $NaOH \cdot H_2O$, the $l + S_{NaOH \cdot 4H_2O}$ range corresponds to $NaOH \cdot 4H_2O$, and the presence of the latter is characteristic of this system. References 6 and 15 to 17 have revealed no existence of the tetrahydrate $NaOH \cdot 4H_2O$ in the $NaBH_4$ + NaOH + H_2O system within (0 to 50) °C. This tetrahydrate, according to the NaOH + H_2O solubility polytherms,[5] crystallizes at negative temperatures and alkali fractions within (0.25 to 0.35). Three-phase peritonic equilibria correspond to the $NaBH_4 \cdot 2H_2O \leftrightarrow NaBH_4$ (*p*1) and $NaOH \cdot 4H_2O \leftrightarrow NaOH \cdot H_2O$ (*p*2) transitions. The solid NaOH + $NaOH \cdot H_2O$ + $NaBH_4$ mixture exists at the bottom part of the diagram.

Analyzing the mutual component solubility in a similar potassium system, the solubility data are given in Table 2 and Figure 3. First, note an essentially lower solubility of potassium borohydride as compared with that of sodium borohydride, which is extremely important from a practical viewpoint. The maximum KBH_4 solubility at −10 °C is $w = 0.113$ (*e*2 point); it is reached in pure water (this value agrees well with the polythermal data of the binary KBH_4 + H_2O system[7]). The introduction of alkali into the system sharply reduces the KBH_4 solubility, which falls down to $w < 0.01$ in concentrated alkaline solutions. Therefore, the major part of the triangle's area is occupied by the crystallization fields of KOH, KBH_4, and their hydrates. The main field corresponds to the crystallization of monohydrate $l + S_{KBH_4 \cdot H_2O}$. Below is the eutonic $l + S_{KBH_4 \cdot H_2O} + S_{KOH \cdot H_2O}$ triangle; the eutonic solution *e*3 is mainly formed by KOH. In the water vertex of the diagram, an ice crystallization field (l + ice) is located. The peritonic point *p*3 ($l + S_{KBH_4 \cdot 3H_2O} + S_{KBH_4 \cdot H_2O}$ equilibrium) can only be found with difficulty.

The phase diagram KBH_4 + KOH + H_2O also contains two very narrow heterogeneous fields, namely: (i) that of trihydrate $KBH_4 \cdot 3H_2O$ crystallization, the $l + S_{KBH_4 \cdot 3H_2O}$ field adjoining the borohydride side of the diagram; (ii) that of monohydrate $KOH \cdot H_2O$ crystallization, the $l + S_{KOH \cdot H_2O}$ field adjoining the alkali side. The trapezoid region at the bottom of the diagram corresponds to the existence of a solid mixture of anhydrous components and their crystalline hydrates. However, we did not investigate the region of solid mixtures; therefore, phase equilibria are not shown.

As was noted above, there is little solubility data in the literature for the binary systems metaborate + water and no systematic reports on the ternary systems alkali + metaborate

Table 2. Equilibrium Data for the KBH_4 + KOH + H_2O System at −10 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			equilibrium crystalline phases
KBH_4	KOH	H_2O	KBH_4	KOH	H_2O	
11.3	0.0	88.7				ice + $KBH_4 \cdot 3H_2O$ (*e*2)
11.1	0.7	88.2	29.2	0.3	70.5	$KBH_4 \cdot 3H_2O$
10.6	2.1	87.3	34.7	1.2	64.1	$KBH_4 \cdot 3H_2O$ + $KBH_4 \cdot H_2O$ (*p*3)
9.5	1.8	88.7	6.5	1.2	92.3	ice
9.1	3.5	87.4	58.7	1.1	40.2	$KBH_4 \cdot H_2O$
7.6	5.8	86.6	53.7	2.2	44.1	$KBH_4 \cdot H_2O$
6.1	5.8	88.1	5.0	4.5	90.5	ice
5.3	9.3	85.4	45.4	7.2	47.4	$KBH_4 \cdot H_2O$
3.1	14.9	82.0	31.1	7.4	61.5	$KBH_4 \cdot H_2O$
3.0	12.9	84.1	38.3	9.1	52.6	$KBH_4 \cdot H_2O$
1.7	11.3	87.0	1.1	6.3	92.6	ice
1.6	21.0	77.4	47.8	7.2	45.0	$KBH_4 \cdot H_2O$
0.8	44.1	55.1	53.9	12.5	33.6	$KBH_4 \cdot H_2O$
0.8	34.4	64.8	45.5	13.5	41.0	$KBH_4 \cdot H_2O$
0.7	11.7	87.6	43.5	11.3	45.2	$KBH_4 \cdot H_2O$
0.7	48.0	51.3	8.8	46.8	44.4	$KOH \cdot H_2O$ + $KBH_4 \cdot H_2O$ (*e*3)
0.6	38.1	61.3	42.5	16.5	41.0	$KBH_4 \cdot H_2O$
0.2	47.0	52.8				$KOH \cdot H_2O$
0.0	48.8	51.2				$KOH \cdot H_2O$
0.0	12.1	87.9				ice

[a] Compositions and the equilibrium crystalline phases of peritonic point (*p*3) and eutonic points (*e*2, *e*3) are underlined.

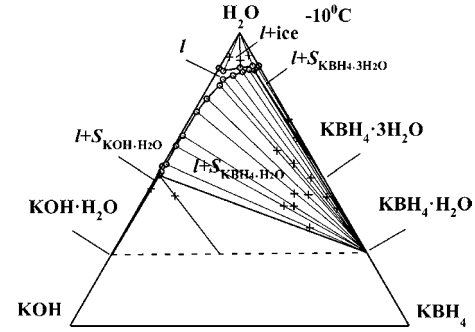

Figure 3. Phase diagram for the KBH_4 + KOH + H_2O system at −10 °C. *l* and *S* are liquid and solid phases, respectively. Compositions of the saturated liquid solution (○) and wet solid phase (+) are listed in Table 2. Thin lines are tie-lines between coexisting phases, and thick solid and dashed lines are the bounds among monophase, two-phase, and three-phase areas.

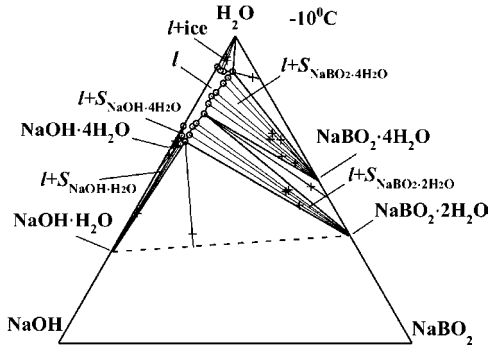

Figure 4. Phase diagram for the $NaBO_2$ + NaOH + H_2O system at −10 °C. *l* and *S* are liquid and solid phases, respectively. Compositions of the saturated liquid solution (○) and wet solid phase (+) are listed in Table 3. Thin lines are tie-lines between coexisting phases, and thick solid and dashed lines are the bounds among monophase, two-phase, and three-phase areas.

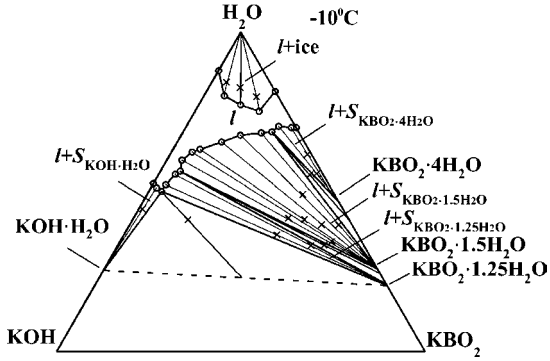

Figure 5. Phase diagram for the KBO_2 + KOH + H_2O system at −10 °C. *l* and *S* are liquid and solid phases, respectively. Compositions of the saturated liquid solution (○) and wet solid phase (+) are listed in Table 4. Thin lines are tie-lines between coexisting phases, and thick solid and dashed lines are the bounds among monophase, two-phase, and three-phase areas.

+ water. For instance, in refs 8 to 10, the solubility polytherms of the $NaBO_2$ + H_2O and KBO_2 + H_2O systems were studied in different temperature ranges. It has been shown that the eutectic in the KBO_2 + H_2O system lies at −20 °C, and a homogeneous solution exists within $w \approx$ (0.24 to 0.32) of KBO_2 at −10 °C.[10] The system $NaBO_2$ + H_2O has not been studied at −10 °C.

Figures 4 and 5 show the isothermal phase diagrams of the ternary borate + alkali systems, and Tables 3 and 4 contain the coordinates of the experimental points. The diagram of the $NaBO_2$ + NaOH + H_2O system at −10 °C is rather complex (Figure 4) and is characterized by the presence of two eutonic points *e*4 and *e*5, two peritonic points *p*4 and *p*5, and five crystallization fields. The crystallization fields of ice (*l* + ice) and $NaBO_2 \cdot 4H_2O$ ($l + S_{NaBO_2 \cdot 4H_2O}$) adjoin the eutonic triangle with vertex *e*4, while fields $l + S_{NaBO_2 \cdot 2H_2O}$ and $l + S_{NaOH \cdot H_2O}$ adjoin the eutonic triangle with vertex *e*5. The solubility of sodium metaborate is low and generally decreases with increasing NaOH content, while the total solubility grows.

The tetrahydrate $NaBO_2 \cdot 4H_2O$ precipitates at low alkali contents and loses crystallization water with increasing NaOH concentration in the system, resulting in the formation of the $NaBO_2 \cdot 4H_2O$ + $NaBO_2 \cdot 2H_2O$ peritonic point *p*4. As to the NaOH crystallization field, the peritonic decomposition at increasing alkalinity of the system occurs as well: $NaOH \cdot 4H_2O$ decomposes into $NaOH \cdot H_2O$ and water. The bottom part of the diagram corresponds to a mixture of solid components.

Table 3. Equilibrium Data for the $NaBO_2$ + NaOH + H_2O System at −10 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			equilibrium crystalline phases
$NaBO_2$	NaOH	H_2O	$NaBO_2$	NaOH	H_2O	
5.1	6.6	88.3	11.7	1.8	86.5	ice + $NaBO_2 \cdot 4H_2O$ (*e*4)
4.8	8.9	86.3	29.8	4.1	66.1	$NaBO_2 \cdot 4H_2O$
4.3	11.1	84.6	26.3	5.4	68.3	$NaBO_2 \cdot 4H_2O$
3.8	21.5	74.7	46.3	3.0	50.7	$NaBO_2 \cdot 2H_2O$ + $NaBO_2 \cdot 4H_2O$ (*p*4)
3.8	14.7	81.5	26.7	7.0	66.3	$NaBO_2 \cdot 4H_2O$
3.5	18.6	77.9	32.8	6.4	60.8	$NaBO_2 \cdot 4H_2O$
3.2	25.2	71.6	40.1	10.1	49.8	$NaBO_2 \cdot 2H_2O$
3.1	29.1	67.8	45.6	9.4	45.0	$NaBO_2 \cdot 2H_2O$
3.1	16.5	80.4	37.6	3.7	58.7	$NaBO_2 \cdot 4H_2O$
3.0	31.4	65.6	20.2	44.3	35.5	$NaOH \cdot H_2O$ + $NaBO_2 \cdot 2H_2O$ (*e*5)
2.7	26.9	70.4	39.5	11.0	49.5	$NaBO_2 \cdot 2H_2O$
2.5	9.1	88.4	1.6	6.4	92.0	ice
2.1	33.1	64.8	1.1	56.5	42.4	ice
1.6	33.9	64.5	0.7	38.3	61.0	$NaOH \cdot H_2O$ + $NaOH \cdot 4H_2O$ (*p*5)
1.4	9.8	88.8	1.0	6.0	93.0	ice
1.2	33.1	65.7	0.5	35.5	64.0	$NaOH \cdot 4H_2O$
1.1	31.3	67.6	0.3	34.0	65.7	$NaOH \cdot 4H_2O$
0.0	10.1	89.9				ice
0.0	29.3	70.7				$NaOH \cdot 4H_2O$

[a] Compositions and the equilibrium crystalline phases of peritonic points (*p*4, *p*5) and eutonic points (*e*4, *e*5) are underlined.

Table 4. Equilibrium Data for the KBO_2 + KOH + H_2O System at −10 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			equilibrium crystalline phases
KBO_2	KOH	H_2O	KBO_2	KOH	H_2O	
30.0	0.0	70.0				$KBO_2 \cdot 4H_2O$
28.7	1.3	70.0	37.4	1.1	61.5	$KBO_2 \cdot 4H_2O$
25.0	4.5	70.5	42.9	1.6	55.5	$KBO_2 \cdot 4H_2O$
24.1	7.2	68.7	41.2	3.7	55.1	$KBO_2 \cdot 4H_2O$ + $KBO_2 \cdot 1.5H_2O$ (*p*6)
21.4	10.3	68.3	56.8	3.6	39.6	$KBO_2 \cdot 1.5H_2O$
18.6	0.0	81.4				ice
17.4	7.5	75.1	14.5	5.8	79.7	ice
16.0	16.3	67.7	42.3	8.6	49.1	$KBO_2 \cdot 1.5H_2O$
12.0	22.5	65.5	52.2	8.2	39.6	$KBO_2 \cdot 1.5H_2O$
11.3	11.5	77.2	8.7	8.8	82.5	ice
7.3	29.5	63.2	46.7	12.1	41.2	$KBO_2 \cdot 1.5H_2O$
5.6	32.1	62.3	57.6	8.1	34.3	$KBO_2 \cdot 1.5H_2O$
5.4	14.5	80.1	4.1	11.7	84.2	ice
5.3	38.3	56.4	56.0	10.7	33.3	$KBO_2 \cdot 1.5H_2O$ + $KBO_2 \cdot 1.25H_2O$ (*p*7)
4.5	40.1	55.4	52.5	14.4	33.1	$KBO_2 \cdot 1.25H_2O$
4.1	36.1	59.8	42.1	16.2	41.7	$KBO_2 \cdot 1.5H_2O$
3.5	44.3	52.2	41.6	21.9	36.5	$KBO_2 \cdot 1.25H_2O$
3.5	46.5	50.0	15.0	43.7	41.3	$KBO_2 \cdot 1.25H_2O$ + $KOH \cdot H_2O$ (*e*6)
1.5	47.3	51.2	1.1	54.3	44.6	$KOH \cdot H_2O$
0.0	47.5	52.5				$KOH \cdot H_2O$
0.0	12.1	87.0				ice

[a] Compositions and the equilibrium crystalline phases of peritonic points (*p*6, *p*7) and eutonic point (*e*6) are underlined.

The solubility diagram of the system KBO_2 + KOH + H_2O at −10 °C (Figure 5, the coordinates of experimental points are given in Table 4) turns out to be no less sophisticated. Crystallization fields of seven solid phases were found in the system, including ice, anhydrous KOH, anhydrous KBO_2, and the crystalline hydrates $KBO_2 \cdot 4H_2O$, $KBO_2 \cdot 1.5H_2O$, $KBO_2 \cdot 1.25H_2O$, and $KOH \cdot H_2O$. The KBO_2 solubility in pure water is $w = 0.300$ at −10 °C, which is close to the literature data ($w = 0.320$).[9] At the water vertex, there is an ice crystallization field *l* + ice. On increasing alkali content, metaborate is displaced from the solution, precipitating as, first, $KBO_2 \cdot 4H_2O$ (the $l + S_{KBO_2 \cdot 4H_2O}$ field), which loses crystallization water at increasing alkali content, converting into $KBO_2 \cdot 1.5H_2O$ (the *l*

+ $S_{KBO_2 \cdot 1.5H_2O}$ field) and, further, into $KBO_2 \cdot 1.25H_2O$ (the l + $S_{KBO_2 \cdot 1.25H_2O}$ field). At KOH introduction into the system, about the same amount of KBO_2 is removed from the solution, while the crystalline phase composition changes. Then the total solubility rapidly grows owing to KOH, reaching its maximum at the eutonic point $e6$. The points $p6$ and $p7$ are associated with the peritonic transitions $KBO_2 \cdot 4H_2O \leftrightarrow KBO_2 \cdot 1.5H_2O$ and $KBO_2 \cdot 1.5H_2O \leftrightarrow KBO_2 \cdot 1.25H_2O$, respectively. The bottom part of the diagram corresponds to a mixture of solid components.

Analyzing the solubility in the four ternary systems under study, the opposite influence of the alkali cation nature has been observed. Indeed, in the borohydride ternary systems, the sodium salt has the best solubility, while the corresponding potassium salt is much less soluble. Sodium borohydride dissolves well both in pure water (0.234 of $NaBH_4$ against 0.113 of KBH_4 at −10 °C) and in strongly alkaline solutions: a solution containing 0.105 of $NaBH_4$ and 0.426 of NaOH is in equilibrium with the precipitate at the eutonic point $e1$! On the contrary, potassium borohydride is almost insoluble in water−alkali mixtures even at relatively low KOH concentrations.

In the borate systems the situation is the opposite. Potassium metaborate forms a highly concentrated aqueous solution at −10 °C, whereas sodium metaborate is generally insoluble (it forms a solid mixture with ice). Introducing a sufficient amount of NaOH into the system results in transferring part of sodium metaborate to the solution; nevertheless, at all ratios the $NaBO_2$ concentration in the saturated solution is within w = (0.027 to 0.051) only. KBO_2 is much more soluble; its concentration at an increasing alkalinity gradually decreases from $w = 0.300$ in pure water down to $w = 0.035$ at the eutonic point $e6$. Thus, the KBO_2 solubility remains above $w \approx 0.1$ in the practically important concentration range. The phase diagrams of the $NaBH_4$ + NaOH + H_2O and KOH + KBO_2 + H_2O systems have the largest area of the homogeneous-liquid state l, and the KBH_4 + KOH + H_2O and NaOH + $NaBO_2$ + H_2O systems have the least.

Thus, according to our study, the systems with sodium and potassium ions considerably differ by the solubility of both the initial fuel components and the products of FC discharge. These data have essential importance for the development of FCs with the borohydride fuel. The high concentration of the borohydride ion BH_4^- in solution is extremely important from the viewpoint of electrochemistry, kinetics, and power engineering of borohydride utilization in a FC. The high solubility of the BO_2^- ion is significant from the viewpoint of avoiding accumulation of the discharge products in the porous structure of FC electrodes. The optimum choice of the components ratio is possible by means of joint use of our phase diagrams.

Conclusions

A critical analysis of the scientific literature shows that there are many reports on studies of the aqueous solubility of NaOH, $NaBO_2$, $NaBH_4$, KOH, KBH_4, and KBO_2 both individually and in various double mixtures. However, from a fundamental and practical point of view, of greater interest are ternary systems in which the solubility of the components can strongly differ from the individual solubility of each component. The ternary systems $NaBH_4$−NaOH−H_2O, KBH_4−KOH−H_2O, NaOH−$NaBO_2$−H_2O, and KOH−KBO_2−H_2O are of special interest. Mixtures belonging to the first two systems are used as a fuel and as a hydrogen source in hydrogen power engineering, including low-temperature FCs. In the course of their oxidation, borohydrides are converted into metaborates. Hence, mixtures belonging to the last two systems represent the discharged product of hydrogen power engineering. The performance of such mixtures is determined by the solubility of their components, negative temperatures being especially critical. Therefore, in the present work we investigated the aforementioned ternary systems at −10 °C. The compositions of the equilibrium liquid and solid phases and the compositions of the eutonic and peritonic equilibria have been determined for all four systems by the method of isothermal saturation. The coordinates of the homogeneous solution ranges in the solubility diagrams have been defined for all four systems as well. The best solubility of the solid components at −10 °C is characteristic of the systems $NaBH_4$−NaOH−H_2O and KOH−KBO_2−H_2O.

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