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Temperature-Induced Transformation of the Phase Diagrams of Ternary Systems $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$

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ABSTRACT: Concentrated water−alkaline solutions of sodium and potassium borohydrides are used as a fuel and hydrogen source in hydrogen power engineering, including low-temperature fuel cells; borohydrides convert into metaborates. The performance of fuel mixtures is determined by their solubility in water. A general analysis of the solubility in the ternary systems $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ within the range (−10 to 50) °C is done, and regularities and features of the temperature-induced transformation of the phase diagrams of the systems are revealed. The systems with sodium and potassium ions are different in relation to the temperature influence on the solubility of the solid components. The presence of a range of homogeneous solutions and fields of crystallization of hydrated and anhydrous forms of the borohydrides and hydroxides is characteristic for both systems. The composition of crystalline hydrates depends on the component ratio in the mixture and the cation nature.

INTRODUCTION

Now, borohydrides of alkaline metals are of interest for researchers and technical designers. The possibility to use borohydrides as a high-energy fuel in fuel cells (FC) requires intense studies of their physicochemical properties. In particular, there are a number of papers on electrochemical processes in FCs using water−alkaline borohydride mixtures as fuel.[1−3] As the basic current-producing reaction of the electrochemical oxidation of borohydride ions proceeds in the liquid phase, the solubility of components essentially influences the power characteristics of FC. Therefore, studies of borohydride solubility in water−alkaline media are rather urgent.

The present work continues our previous research[4,5] of the solubility in the ternary systems borohydride + alkali + water and metaborate + alkali + water. Our study[4] of isotherms in the phase diagrams of $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ at −10 °C is supplemented with literature data on the behavior of these systems at higher temperatures, (0 to 50) °C. A general analysis of all of the data found is done, and regularities and features of the temperature-induced transformation of the phase diagrams of the ternary $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ systems are revealed.

EXPERIMENTAL SECTION

The method of isothermal saturation of solutions is the optimum one for exploring the solubility of various solid substances in water. The quantitative chemical analysis of isothermally selected samples of both liquid and solid phases follows, with the subsequent graphic construction of a saturated solution line (liquidus), a line of complete insolubility (solidus), and all phase fields. Phase equilibria in mixtures of the components of the ternary $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ systems were studied by thermal saturation of solutions according to the experimental technique described earlier.[4,5] The chemical compositions of solutions and the solid precipitation were determined by acid−basic and iodometric titrations; the technique of analysis is also described in detail in refs 4 and 5. The true composition of the solid phase was determined by Schreinemakers's method of wet residues. The accuracy of the chemical analysis corresponded to the uncertainty of the point positions in the phase diagrams $\delta w = 0.001$. The results of our experiments are presented as Gibbs−Roseboom's concentration triangles, whose vertices, points on the sides, and points inside the triangle correspond to the individual components, binary systems, and ternary mixtures, respectively.

RESULTS AND DISCUSSION

Our solubility study of the isothermal (at −10 °C) $NaBH_4 + NaOH + H_2O$ system has shown that it is characterized by the presence of the range of homogeneous solution l and five crystallization phases S_i (ice and the crystalline hydrates $NaBH_4 \cdot 2H_2O$, $NaBH_4$, $NaOH \cdot H_2O$, and $NaOH \cdot 4H_2O$).[4] The existence of all of these phases at the specified temperature was also proven by reference data on the solubility polytherms of the binary $NaOH + H_2O$ and $NaBH_4 + H_2O$ systems.[6] Refs 7 and 8 give the solubility data for the $NaBH_4 + NaOH + H_2O$ system at (0, 18, 30, and 50) °C. The analysis of these data shows that an increase in temperature up to 0 °C results in natural changes in the phase diagram; namely, the homogeneous solution range extends, and the solid phases (ice and tetrahydrate $NaOH \cdot 4H_2O$) disappear. Though the decomposition temperature of $NaOH \cdot 4H_2O$ is about 5.4 °C,[6] in the ternary system this crystalline hydrate is not detected at 0 °C.

The solubility diagram of the $NaBH_4 + NaOH + H_2O$ system at 0 °C (Figure 1) shows that to the left of the eutectic point $e1$ the alkali crystallizes as monohydrate $NaOH \cdot H_2O$, and to the right of it various forms of sodium borohydride crystallize. From

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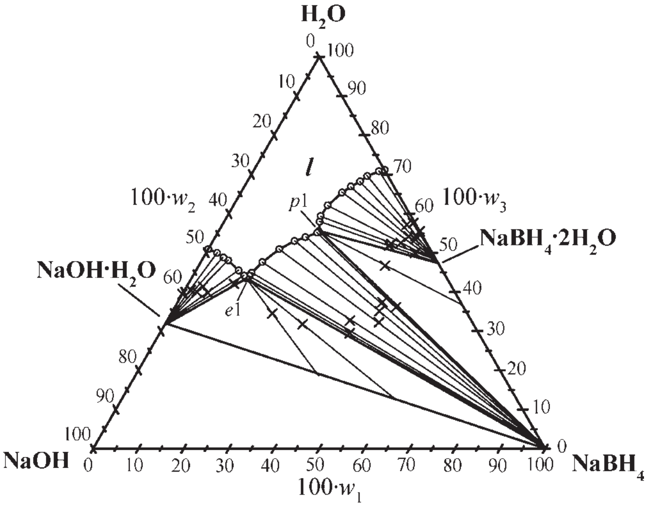

Figure 1. Phase diagram for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system at 0 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 1. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

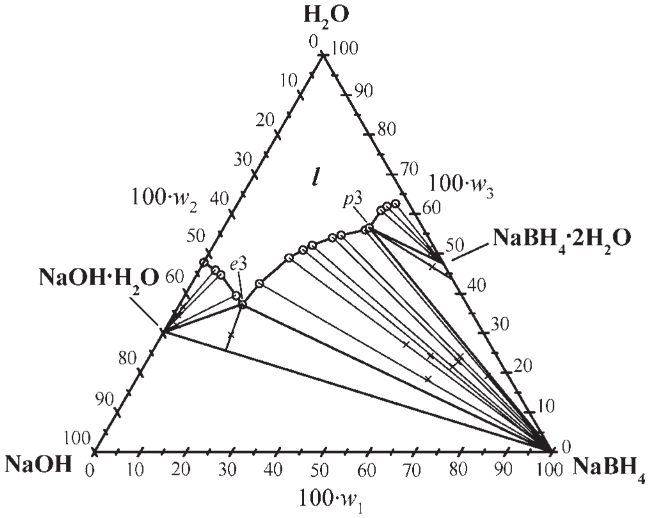

Figure 3. Phase diagram for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system at 25 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 3. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

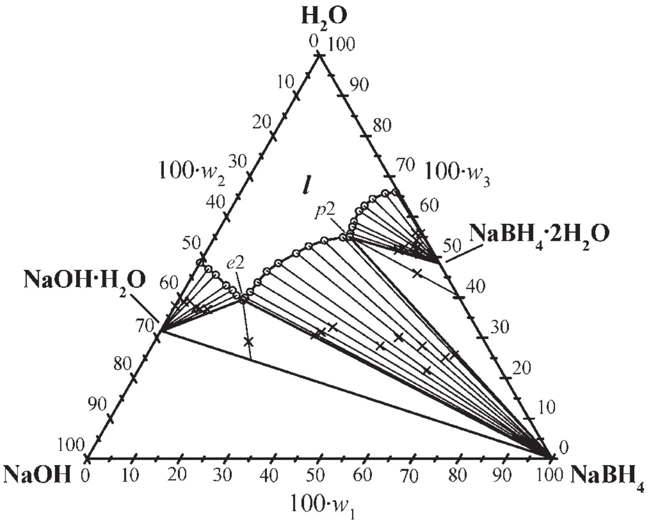

Figure 2. Phase diagram for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system at 18 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 2. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

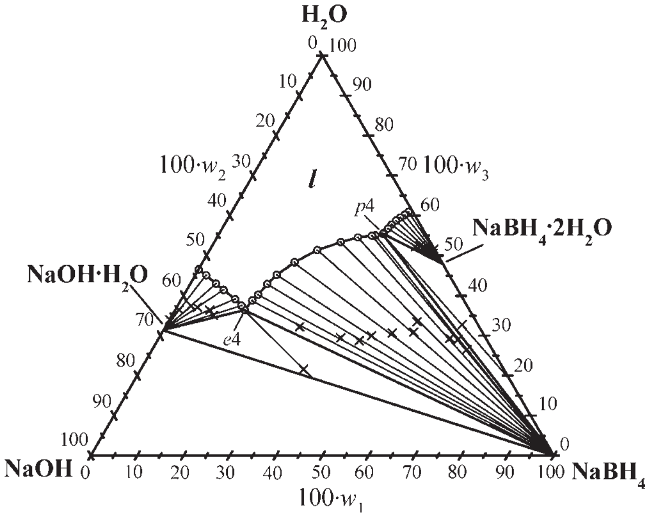

Figure 4. Phase diagram for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system at 30 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 4. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

an aqueous sodium-borohydride-saturated solution, as the alkali is introduced, dihydrate $NaBH_4 \cdot 2H_2O$ crystallizes first, and after the peritectic point $p1$, the anhydrous $NaBH_4$ crystallizes. Except for $NaBH_4 \cdot 2H_2O$, $NaBH_4$, and $NaOH \cdot H_2O$, no other solid phases have been revealed in the system.

Let us consider the transformations of the phase diagram of the $NaBH_4$ + NaOH + H_2O system at the temperature transition 0 °C → 18 °C → 25 °C → 30 °C (Figures 1 to 4); the compositions of the equilibrium liquid and wet solid phases are given in Tables 1 to 4. The set of crystallizing solid phases is the same for all the four temperatures, namely, $NaBH_4 \cdot 2H_2O$, $NaBH_4$, and $NaOH \cdot H_2O$. The data given in few early sources[7−9] speak for a natural increase in the solubility of the components in the system at changing temperature from 0 °C up to 30 °C. The expansion of the homogeneous solution range l is accompanied by the appropriate moving of the solubility line. The crystallization fields of $NaOH \cdot H_2O$ and $NaBH_4 \cdot 2H_2O$ hydrates reduce, and the crystallization field of anhydrous $NaBH_4$ extends. This is the most typical transformation of the phase diagrams when increasing temperature makes

Table 1. Equilibrium Data of the $NaBH_4 + NaOH + H_2O$ System at 0 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	equilibrium crystalline phase[7,8]
28.9	0	71.1	44.5	0	55.5	$NaBH_4 \cdot 2H_2O$
27.8	1.4	70.8	42	0.4	57.6	$NaBH_4 \cdot 2H_2O$
25.8	4.6	69.6	40.8	2	57.2	$NaBH_4 \cdot 2H_2O$
24.9	6.9	68.2	44.2	1.5	54.3	$NaBH_4 \cdot 2H_2O$
23.5	9.6	66.9	44.6	2	53.4	$NaBH_4 \cdot 2H_2O$
22.3	12.3	65.4	42.7	3.1	54.2	$NaBH_4 \cdot 2H_2O$
20.8	17.1	62.1	46.3	3.8	49.9	$NaBH_4 \cdot 2H_2O$
20.6	20	59.4	41.8	5.7	52.5	$NaBH_4 \cdot 2H_2O$
21.1	21	57.9	39.8	7.9	52.3	$NaBH_4 \cdot 2H_2O$
22.1	22.4	55.5	39.5	8.6	51.9	$NaBH_4 \cdot 2H_2O$
22.3	22.5	55.2	41.2	12.1	46.7	$NaBH_4 \cdot 2H_2O + NaBH_4$ (*p*1)
22	22.9	55.1	48.9	15	36.1	$NaBH_4$
19.9	26.1	54	45.3	17.3	37.4	$NaBH_4$
18	29	53	45.8	19.1	35.1	$NaBH_4$
15.7	33.4	50.9	47.1	20.6	32.3	$NaBH_4$
13.6	38.8	47.6	40.4	26.9	32.7	$NaBH_4$
12.6	42.5	44.9	30.4	37.8	31.8	$NaBH_4$
12.5	43.4	44.1	42	28.5	29.5	$NaBH_4$
12.13	44.4	43.47	22.4	43.1	34.5	$NaBH_4 + NaOH \cdot H_2O$ (*e*1)
11.3	44.5	44.2	10.1	47.8	42.1	$NaOH \cdot H_2O$
9.4	45.1	45.5	5.5	54.7	39.8	$NaOH \cdot H_2O$
5.8	46.1	48.1	3.6	55	41.4	$NaOH \cdot H_2O$
4.4	46.8	48.8	2.8	57.1	40.1	$NaOH \cdot H_2O$
2.4	47.6	50	1.4	58.1	40.5	$NaOH \cdot H_2O$
0	49.1	50.9	0	60.5	39.5	$NaOH \cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic point (*p*1) and eutectic point (*e*1) are underlined.

less-hydrated forms of the solid compounds more and more stable, up to anhydrous crystals. In our case, this corresponds to the transitions $NaOH \cdot 4H_2O \rightarrow NaOH \cdot H_2O \rightarrow NaOH$ (though no formation of anhydrous alkali is achieved within the temperature range used) and $NaBH_4 \cdot 2H_2O \rightarrow NaBH_4$. The change of the equilibrium stability constant of $NaBH_4 \cdot 2H_2O \leftrightarrow NaBH_4 + 2H_2O$ is reflected in the phase diagram by moving of the peritectic point $p1 \rightarrow p2 \rightarrow p3 \rightarrow p4$ toward the $H_2O - NaBH_4$ side. This peritectic point reaches this triangle side at the temperature $t > 30$ °C and disappears, being not detected at 50 °C (Figure 5).

For the isotherms $t = 0$ °C and $t = 18$ °C, an original course of the solubility line in immediate proximity of the dehydration points *p*1 and *p*2 is observed: contrary to the law of mass action, an increase in the $NaBH_4 \cdot 2H_2O$ solubility is observed at increasing the alkali concentration. At higher temperatures (25 °C and more) such an effect in the $NaBH_4 + NaOH + H_2O$ system does not manifest itself.

An increase of temperature up to 50 °C results in a simplification of the phase diagram of the $NaBH_4 + NaOH + H_2O$ system because of the disappearance of dihydrate $NaBH_4 \cdot 2H_2O$ and its crystallization field (Figure 5, Table 5). A simple diagram appears with one eutectic point *e*5 formed by saturated solution and the solid $NaBH_4$ and $NaOH \cdot H_2O$ phases.

Considering the overall picture of solubility (Figure 6) in the isothermal $NaBH_4 + NaOH + H_2O$ system within (−10 to 50) °C, one can note that sodium borohydride is a typical salt-like compound by nature; its behavior in aqueous solutions is not distinguishing from that of other inorganic salts. The solutions of NaOH dehydrate the crystalline hydrate $NaBH_4 \cdot 2H_2O$; the lower the temperature is, the higher the alkali concentration in solution necessary for the dehydration. An increase in temperature of the system also results in a gradual loss of crystallization water by $NaBH_4 \cdot 2H_2O$ down to the complete dehydration. The maximum total solubility of the components in the system corresponding to the eutectic points (*e*1 to *e*5) regularly increases as well (Tables 1 to 5). Judging by Figure 6, a ternary eutectic point should exist approximately at the center of the homogeneous field *l*, corresponding to the minimum temperature of existence of a liquid in this system; approximate coordinates of the ternary eutectic point are $w_{NaBH_4} \approx 0.1$; $w_{NaOH} \approx 0.25$; $w_{H_2O} \approx 0.65$. Also from Figure 6 follows that the anhydrous salt $NaBH_4$ is characterized by a lower temperature coefficient of solubility than the dihydrate $NaBH_4 \cdot 2H_2O$ whose crystallizing field extends very quickly at decreasing temperature.

On the whole, the temperature-induced transformation of the phase diagram of the $NaBH_4 + NaOH + H_2O$ system is rather favorable for its usage in the hydrogen power engineering and the low-temperature FCs. An extensive range of homogeneous liquid solution with a high concentration of dissolved borohydride exists at both room and increased temperature, and it is preserved at the lower temperatures. However, the low solubility of metaborate $NaBO_2$,[5] which is a product of borohydride oxidation, can have a negative effect for the FC application.

Table 2. Equilibrium Data of the $NaBH_4 + NaOH + H_2O$ System at 18 °C[a]

composition of liquid phase (100 w)			composition of wet solid phase (100 w)			
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	equilibrium crystalline phase[7]
33.3	0.6	66.1	43.8	0.3	55.9	$NaBH_4\cdot 2H_2O$
31.2	3	65.8	42.6	1.4	56	$NaBH_4\cdot 2H_2O$
29.2	6.4	64.4	43.8	2.1	54.1	$NaBH_4\cdot 2H_2O$
28.3	9	62.7	44.9	2.6	52.5	$NaBH_4\cdot 2H_2O$
27.8	10.8	61.4	43.8	3.6	52.6	$NaBH_4\cdot 2H_2O$
28	13.2	58.8	46.2	3	50.8	$NaBH_4\cdot 2H_2O$
28.3	14.2	57.5	42	5.8	52.2	$NaBH_4\cdot 2H_2O$
28.7	15.5	55.8	41.1	7.2	51.7	$NaBH_4\cdot 2H_2O$
29	16	55	48.1	6	45.9	$NaBH_4\cdot 2H_2O + NaBH_4$($p$2)
27.6	17.5	54.9	66.1	8.2	25.7	$NaBH_4$
24	21.9	54.1	64.5	10.4	25.1	$NaBH_4$
21.3	26	52.7	58.1	13.9	28	$NaBH_4$
19.5	29.6	50.9	51.9	18	30.1	$NaBH_4$
16.9	34.6	48.5	62	16.1	21.9	$NaBH_4$
15.4	38.1	46.5	49	23	28	$NaBH_4$
14.8	41.5	43.7	36.5	30.9	32.6	$NaBH_4$
14.4	44.2	41.4	34.6	34	31.4	$NaBH_4$
14	46.1	39.9	33.6	35.7	30.7	$NaBH_4$
13.9	46.8	39.3	20.2	50.8	29	$NaBH_4 + NaOH\cdot H_2O$ (e2)
11.9	47.6	40.5	7.4	55.6	37	$NaOH\cdot H_2O$
10.4	47.8	41.8	5.7	57.1	37.2	$NaOH\cdot H_2O$
8.4	48.6	43	4.7	57.8	37.5	$NaOH\cdot H_2O$
4.9	49.5	45.6	2.6	58.4	39	$NaOH\cdot H_2O$
2.6	50.4	47	1.4	59.7	38.9	$NaOH\cdot H_2O$
0	51.4	48.6	0	62.1	37.9	$NaOH\cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic point (p2) and eutectic point (e3) are underlined.

Table 3. Equilibrium Data of the $NaBH_4 + NaOH + H_2O$ System at 25 °C[a]

composition of liquid phase (100 w)			composition of wet solid phase (100 w)			
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	equilibrium crystalline phase[9]
34.5	2.9	62.6	47.5	1.2	51.3	$NaBH_4\cdot 2H_2O$
32.9	5.1	62	49.4	1	49.6	$NaBH_4\cdot 2H_2O$
32.1	6.9	61	48.3	1.7	50	$NaBH_4\cdot 2H_2O$
31.8	11.7	56.6	50.4	2.9	46.7	$NaBH_4 + NaBH_4\cdot 2H_2O$ (p3)
31.2	12.9	55.9	76.3	4.5	19.2	$NaBH_4$
26.5	18.8	54.7	67.9	8	24.1	$NaBH_4$
25	20.9	54.1	68	9.3	22.7	$NaBH_4$
21.5	26.3	52.2	67.6	10.9	21.5	$NaBH_4$
20.1	28.9	51	61.3	14.5	24.2	$NaBH_4$
18	33	49	54.5	18.3	27.2	$NaBH_4$
14.8	42.6	42.6	63.7	17.9	18.4	$NaBH_4$
13.7	49.1	37.2	15.1	55.4	29.5	$NaOH\cdot H_2O + NaBH_4$(e3)
11.2	49.3	39.5	2.1	66	31.9	$NaOH\cdot H_2O$
5.2	50	44.8	1	64.4	34.6	$NaOH\cdot H_2O$
3.5	50.6	45.9	0.9	62.3	36.8	$NaOH\cdot H_2O$
0	52.2	47.8	-	-	-	$NaOH\cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic point (p3) and eutectic point (e3) are underlined.

Let us note that all of the presented phase diagram isotherms of the ternary system $NaBH_4 + NaOH + H_2O$ contain no points peculiar to the binary $NaBH_4 + H_2O$ system (that is $w_{NaOH} = 0$). Figure 5 expresses most brightly this fact: the solubility line does

Table 4. Equilibrium Data of the $NaBH_4 + NaOH + H_2O$ System at 30 °C[a]

composition of liquid phase (100 w)			composition of wet solid phase (100 w)			equilibrium crystalline phase[7]
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	
38.1	0.9	61	48.3	0.1	51.6	$NaBH_4 \cdot 2H_2O$
37.7	2.1	60.2	48.7	0.8	50.5	$NaBH_4 \cdot 2H_2O$
37	3.4	59.6	46.5	1.2	52.3	$NaBH_4 \cdot 2H_2O$
36.5	4.7	58.8	47.1	1.3	51.6	$NaBH_4 \cdot 2H_2O$
36.1	6.1	57.8	44.9	2.5	52.6	$NaBH_4 \cdot 2H_2O$
35.8	7.4	56.8	46	2.3	51.7	$NaBH_4 \cdot 2H_2O$
35.4	8.9	55.7	44	3.9	52.1	$NaBH_4 \cdot 2H_2O$
35.4	9.1	55.5	63.8	3.4	32.8	$NaBH_4 + NaBH_4 \cdot 2H_2O$ ($p4$)
33.9	11	55.1	68	5.5	26.5	$NaBH_4$
33.2	11.8	55	64.8	6.1	29.1	$NaBH_4$
30.4	15	54.6	62.9	7.8	29.3	$NaBH_4$
27.3	19.3	53.4	53.7	12.8	33.5	$NaBH_4$
23.2	25.4	51.4	54.3	14.8	30.9	$NaBH_4$
19.8	31.8	48.4	49.8	19.5	30.7	$NaBH_4$
17.5	37.2	45.3	45.6	24.4	30	$NaBH_4$
16.6	40.4	43	43.6	27.7	28.7	$NaBH_4$
16	43.7	40.3	39.2	31.3	29.5	$NaBH_4$
15.4	45.7	38.9	29	38.8	32.2	$NaBH_4$
15	48.5	36.5	35.1	43.3	21.6	$NaOH \cdot H_2O + NaBH_4$($e4$)
13.7	48.7	37.6	8.9	56	35.1	$NaOH \cdot H_2O$
11.6	49.2	39.2	7.5	56.1	36.4	$NaOH \cdot H_2O$
7.9	50.6	41.5	4.4	58.5	37.1	$NaOH \cdot H_2O$
5.5	51.4	43.1	2.9	59.6	37.5	$NaOH \cdot H_2O$
2.3	52.5	45.2	0.8	62.7	36.5	$NaOH \cdot H_2O$
0	53.4	46.6	0	66	34	$NaOH \cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic point ($p4$) and eutectic point ($e4$) are underlined.

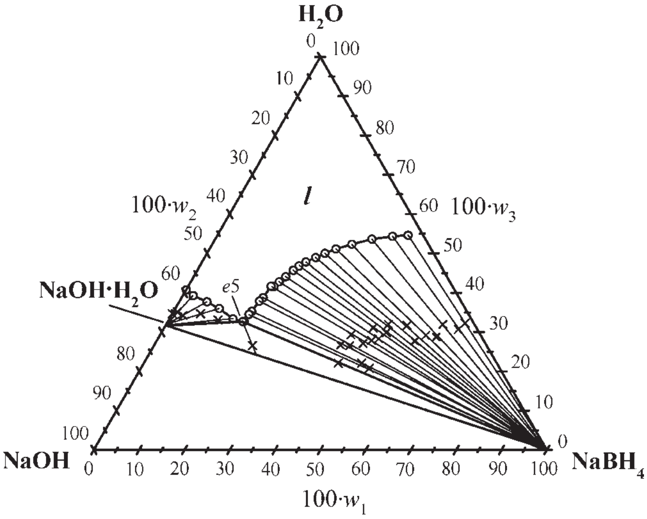

Figure 5. Phase diagram for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system at 50 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 5. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

not reach the lateral side of the triangle. This is caused by the high concentration of the dissolved BH_4^- ion and its chemical instability (hydrolysis) in the absence of alkali. Therefore, the concentration measurements in the binary $NaBH_4 + H_2O$ system are unreliable. The rate of the hydrolysis reaction $BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$ exponentially grows with increasing temperature and lower pH.[12]

Let us proceed to considering temperature-induced transformations of the solubility diagrams for a similar potassium system. The results of an early solubility study of the binary $KBH_4 + H_2O$ system definitely point to the existence of three stable solid phases, namely, anhydrous KBH_4, monohydrate $KBH_4 \cdot H_2O$, and trihydrate $KBH_4 \cdot 3H_2O$.[10] The authors did not exclude a possible formation of other phases enriched with crystallization water, for example, $KBH_4 \cdot 4H_2O$ or $KBH_4 \cdot 8H_2O$. In ref 4, we described the solubility in the isothermal $KBH_4 + KOH + H_2O$ system at −10 °C. It turned out that this system is characterized by the presence of an extremely narrow range of homogeneous solution l, while the other area of the triangle is occupied by four crystallization fields, namely, ice, trihydrate $KBH_4 \cdot 3H_2O$, monohydrate $KBH_4 \cdot H_2O$, and monohydrate $KOH \cdot H_2O$. No other solid phases were revealed. The anhydrous KBH_4 and KOH do not crystallize from a saturated solution at the given temperature. Refs 10 and 11 present the results of a solubility study of the $KBH_4 + KOH + H_2O$ system at (0, 20, and 25) °C. Let us analyze, in general, the regularities of changes of the solubility diagram of the ternary system when temperature varies from −10 °C up to 25 °C.

Figures 7 to 9 show the isothermal diagrams of the ternary $KBH_4 + KOH + H_2O$ system at (0, 20, and 25) °C, respectively; the compositions of the liquid and solid equilibrium phases are given in Tables 6 to 8. These diagrams are very similar to the corresponding one[4] at $t = -10$ °C, only differing by the absence of the ice crystallization field at the top corner. Besides, the authors of refs 10 and 11 could not precisely establish the composition of the phases forming eutectics, having assumed that KOH crystallizes at 0 °C and dihydrate $KOH \cdot 2H_2O$ does at (20 and 25) °C. This is quite difficult for determination, as the crystallization field of solid alkali is extremely narrow. However, the suggested scheme contradicts the phase diagram of the binary $KOH + H_2O$ system drawn by the same authors,[10] and it contradicts a general trend of phase transformations, according to which

Table 5. Equilibrium Data of the $NaBH_4$ + NaOH + H_2O System at 50 °C[a]

composition of liquid phase (100 w)			composition of wet solid phase (100 w)			equilibrium crystalline phase[7]
$NaBH_4$	NaOH	H_2O	$NaBH_4$	NaOH	H_2O	
42.1	3.3	54.6	65.8	1.9	32.3	$NaBH_4$
38.8	6.9	54.3	65.1	4.2	30.7	$NaBH_4$
34.6	11.8	53.6	61.1	6.9	32	$NaBH_4$
30.8	16.9	52.3	61.2	10	28.8	$NaBH_4$
27.9	21	51.1	58.7	12.1	29.2	$NaBH_4$
26	24	50	53.3	15	31.7	$NaBH_4$
24.5	26.6	48.9	57	15.3	27.7	$NaBH_4$
22.9	29.3	47.8	49	19	3	$NaBH_4$
21.9	31.3	46.8	49.6	20.5	29.9	$NaBH_4$
21.2	33.1	45.7	46.1	22.8	31.1	$NaBH_4$
20.3	35.6	44.1	48.7	23	28.3	$NaBH_4$
19.5	37.7	42.8	47.4	24.7	27.9	$NaBH_4$
19	39.4	41.6	42.1	28.6	29.3	$NaBH_4$
18.3	40	41.7	45.9	27	27.1	$NaBH_4$
18	43.2	38.8	43.2	30.3	26.5	$NaBH_4$
17.6	44.5	37.9	41.1	32.2	26.7	$NaBH_4$
17.2	47.5	35.3	48.1	29.8	22.1	$NaBH_4$
17	48.5	34.5	50.4	28.8	20.8	$NaBH_4$
16.8	50.4	32.8	42.9	35	22.1	$NaBH_4$
16.5	50.8	32.7	21.7	51.7	26.6	$NaBH_4 + NaOH\cdot H_2O$ (e5)
14	52.6	33.4	10.9	56	33.1	$NaOH\cdot H_2O$
9.7	54.3	36	6.2	59.1	34.7	$NaOH\cdot H_2O$
6.1	56.2	37.7	2.6	63.2	34.2	$NaOH\cdot H_2O$
2.3	58.4	39.3	0.8	64	35.2	$NaOH\cdot H_2O$
0	59.2	40.8	0	65.3	34.7	$NaOH\cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of eutectic point (e5) are underlined.

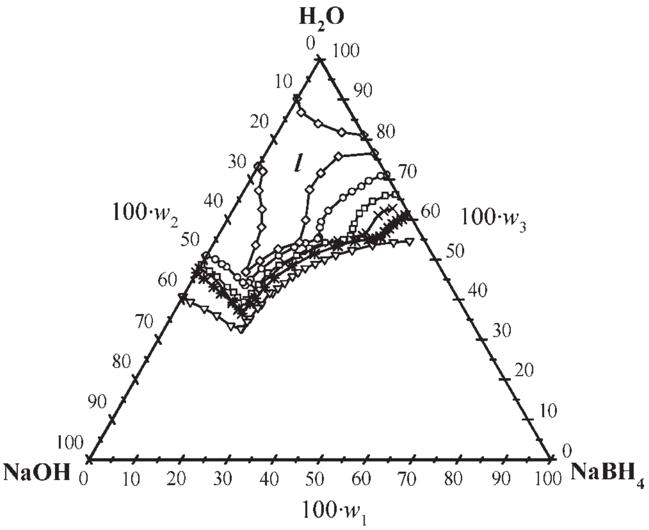

Figure 6. Temperature-induced movement of solubility line for the $NaBH_4$ (1) + NaOH (2) + H_2O (3) system: ◇, $t = -10$ °C; ○, $t = 0$ °C; □, $t = 18$ °C; ×, $t = 25$ °C; ∗, $t = 30$ °C; ▽, $t = 50$ °C. Compositions of equilibrium liquid phase are listed in Tables 1 to 5 and in refs 4, 7, 8, and 9.

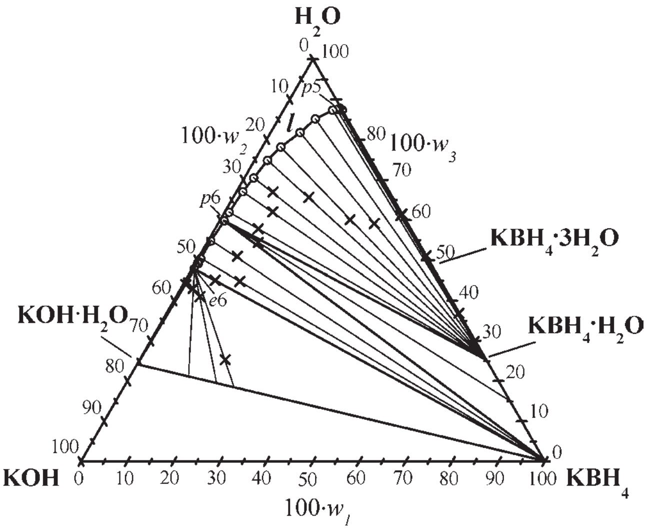

Figure 7. Phase diagram for the KBH_4 (1) + KOH (2) + H_2O (3) system at 0 °C (l is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 6. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

an increase in temperature could be accompanied by dehydration but not vice versa. $KOH\cdot H_2O$ is the sole stable crystalline hydrate in the KOH + H_2O system, which melts at 150 °C without decomposition, whereas other crystalline hydrates $KOH\cdot 2H_2O$, $KOH\cdot 4H_2O$, and $KOH\cdot 5H_2O$ are unstable; they

Table 6. Equilibrium Data of the $KBH_4 + KOH + H_2O$ System at 0 °C[a]

composition of liquid phase (100 w)			composition of wet solid phase (100 w)			
KBH_4	KOH	H_2O	KBH_4	KOH	H_2O	equilibrium crystalline phase[10]
12.7	0	87.3	38.5	0	61.5	$KBH_4 \cdot 3H_2O$
11.9	0.3	87.8	48.9	0	51.1	$KBH_4 \cdot 3H_2O$
11.2	1.2	87.6	38.5	0.4	61.1	$KBH_4 \cdot 3H_2O$
10.6	2	87.4	63.1	0.1	36.8	$KBH_4 \cdot 3H_2O + KBH_4 \cdot H_2O$ ($p5$)
8	6.9	85.1	69.8	0.3	29.9	$KBH_4 \cdot H_2O$
6.4	11.9	81.7	33.7	7.2	59.1	$KBH_4 \cdot H_2O$
4	17.8	78.2	28	11.9	60.1	$KBH_4 \cdot H_2O$
2.8	22.4	74.8	16.4	18	65.6	$KBH_4 \cdot H_2O$
2	27.5	70.5	8	25	67	$KBH_4 \cdot H_2O$
1.4	31.6	67	10.4	27.6	62	$KBH_4 \cdot H_2O$
1	37	62	9.3	32.8	57.9	$KBH_4 \cdot H_2O$
1	39.2	59.8	11	34.5	54.5	$KBH_4 \cdot H_2O + KBH_4$($p6$)
0.6	44.6	54.8	8.3	40.7	51	KBH_4
0.6	49	50.4	11.9	43.3	44.8	KBH_4
0.6	50.2	49.2	2.7	54.3	43	$KBH_4 + KOH \cdot H_2O$ ($e6$)
0.5	51.7	47.8	6.4	48.5	45.1	$KOH \cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic points ($p5$, $p6$) and eutectic point ($e6$) are underlined.

melt with decomposition and exist in a narrow concentration—temperature range. The anhydrous KOH exists only with suitably low amounts of water. Therefore, it should be assumed (and our measurements have confirmed it) that just $KOH \cdot H_2O$ crystallizes to the left of the eutectic points in the ternary $KBH_4 + KOH + H_2O$ system.

Let us consider Figure 7 in more detail. A narrow sector of trihydrate $KBH_4 \cdot 3H_2O$ crystallization adjoins to the right side of the triangle, ending by the point $p5$ of incongruent decomposition $KBH_4 \cdot 3H_2O \leftrightarrow KBH_4 \cdot H_2O + 2H_2O$ with the corresponding peritectic triangle $l + S_{KBH_4 \cdot 3H_2O} + S_{KBH_4 \cdot H_2O}$. At movement along the liquidus from the right to the left, the total solubility of the components grows considerably, but the borohydride content in the saturated solution is reduced. On achievement of the second peritectic point $p6$, further dehydration of the monohydrate $KBH_4 \cdot H_2O$ occurs to form the anhydrous salt KBH_4. This feature of the system is well-shown in the diagram. The eutectic is formed by the $l + S_{KBH_4} + S_{KOH \cdot H_2O}$ phases, and the saturated eutectic solution $e6$ contains very little of the dissolved borohydride ($w_{KBH_4} = 0.006$; Table 6).

A rise in temperature up to 20 °C and further up to 25 °C (Figures 8 and 9) results in quantitative and qualitative changes of the phase diagram. These changes are caused by two factors, namely, the general growth of solubility and changes of the stability constants of the equilibria $KBH_4 \cdot 3H_2O \leftrightarrow KBH_4 \cdot H_2O + 2H_2O \leftrightarrow KBH_4 + 3H_2O$. The equilibrium shift is reflected by moving of the peritectic points in the phase diagram along the solubility line toward the lateral $KBH_4 + H_2O$ side of the triangle. The peritectic point $p5$ reaches the side of the triangle when $t > 0$ °C, and it disappears, not being found at 20 °C. This is caused by the low stability of the trihydrate $KBH_4 \cdot 3H_2O$: it melts incongruently at 7.3 °C, as a study on the binary $KBH_4 + H_2O$ system shows.[10] So, the top temperature border of $KBH_4 \cdot 3H_2O$ existence should be even lower in the presence of the dehydrating reagent KOH in the ternary mixture. Nevertheless, the authors of ref 10 have not excluded the possibility of its presence in the ternary system at 20 °C, though it contradicts their own data.

The data seem to show there may be a peritectic point $p8$ at 25 °C. There seems to be a distinct change in slope of the saturated solution line as very small amounts of KOH are added. This agrees as well with the data on the $KBH_4 + H_2O$ system, according to which crystalline monohydrate $KBH_4 \cdot H_2O$ exists within (7.3 to 39) °C in the binary mixture.[10] However Schreinemakers' method of wet residues does not confirm this assumption. All rays are directed to the "anhydrous KBH_4" angle and water content in the wet residuals (two right outermost points in Figure 9; two top lines in Table 8) is equal accordingly $w_{H_2O} = 0.117$ and $w_{H_2O} = 0.142$. It is much less than the water content in monohydrate $KBH_4 \cdot H_2O$ ($w_{H_2O} = 0.250$). Therefore, we think that the second peritectic point actually reaches the side of the triangle and disappears within the temperature interval (20 to 25) °C that corresponds to the disappearance of the $KBH_4 \cdot H_2O \leftrightarrow KBH_4 + H_2O$ equilibrium in the system. The moving of the second peritectic point along the solubility line can be reflected as $p6$ (0 °C) → $p7$ (20 °C) → × (25 °C). As a result, the phase diagram at 25 °C essentially simplifies (Figure 9) to one with one eutectic point $e8$ formed by saturated solution and the solid phases KBH_4 and $KOH \cdot H_2O$.

A fast change in the basic crystallizing phase is one of the results of these transformations; while the saturated solution in the equilibrium with $KBH_4 \cdot H_2O$ exists on the diagrams at (−10 and 0) °C,[4] the anhydrous KBH_4 becomes the basic phase on the diagrams at (20 and 25) °C. The liquid homogeneity region l remains small, as shown in Figure 10, where the solubility lines are constructed at four temperatures. All of the isotherms are characterized by sharp reduction of the KBH_4 solubility in response to KOH introduction into the system. The minimum of the potassium borohydride solubility is reached at the eutectic points, being $w_{KBH_4} = 0.007$ ($t = -10$ °C); 0.006 ($t = 0$ °C); 0.008 ($t = 20$ °C); 0.004 ($t = 25$ °C), respectively.

On the whole, the temperature-induced transformation of the $KBH_4 + KOH + H_2O$ phase diagram does not favor the usage of the system in the hydrogen power engineering and in the

Table 7. Equilibrium Data of the $KBH_4 + KOH + H_2O$ System at 20 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			
KBH_4	KOH	H_2O	KBH_4	KOH	H_2O	equilibrium crystalline phase[10]
15.8	0.9	83.4	40.5	0	59.5	$KBH_4 \cdot H_2O$
15.6	1	83.4	43.8	0	56.2	$KBH_4 \cdot H_2O$
14.4	2.8	82.8	56.1	0.9	43	$KBH_4 \cdot H_2O$
14	3.5	82.5	49.8	1.9	48.3	$KBH_4 \cdot H_2O$
12.7	5.5	81.8	51.3	2.5	46.2	$KBH_4 \cdot H_2O$
11.1	8.5	80.4	45.6	4	50.4	$KBH_4 \cdot H_2O$
9.1	11.9	79	58.5	5	36.5	$KBH_4 \cdot H_2O + KBH_4$ (*p*7)
8.9	12.5	78.6	48.2	6.8	45	KBH_4
8.7	12.6	78.7	49.5	6.4	44.1	KBH_4
6.6	17.1	76.3	45.7	9.6	44.7	KBH_4
6	18.9	75.1	39.7	11.8	48.5	KBH_4
5	21.7	73.3	41	13.6	45.4	KBH_4
3.3	27.6	69.1	52.2	13.1	34.7	KBH_4
2.9	29.9	67.2	55.9	13.3	30.8	KBH_4
1.6	37.5	60.9	43.4	20.8	35.8	KBH_4
1.4	40.3	58.3	33	27.1	39.9	KBH_4
1	46	53	28.5	32.9	38.6	KBH_4
0.9	50.5	48.6	28.2	36.4	35.4	KBH_4
0.8	54.9	44.3	28	39.6	32.4	KBH_4
0.8	55.1	44.1	3.9	56.4	39.7	$KBH_4 + KOH \cdot H_2O$ (*e*7)
0.8	55.1	44.1	18.1	49.2	32.7	$KOH \cdot H_2O$
0.9	55.2	43.9	11.5	58.3	30.2	$KOH \cdot H_2O$
0.9	55.3	43.8	0.6	58.2	41.2	$KOH \cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of peritectic point (*p*7) and eutectic point (*e*7) are underlined.

Table 8. Equilibrium Data of the $KBH_4 + KOH + H_2O$ System at 25 °C[a]

composition of liquid phase (100 *w*)			composition of wet solid phase (100 *w*)			
KBH_4	KOH	H_2O	KBH_4	KOH	H_2O	equilibrium crystalline phase[11]
16.3	0.8	82.9	88.3	–	11.7	KBH_4
16.1	0	83.9	85.8	0	14.2	KBH_4
8.9	12.2	78.9	77.9	3.2	18.9	KBH_4
6	17.6	76.4	77.8	3.6	18.6	KBH_4
3.7	24	72.3	78.3	5.7	16	KBH_4
3.1	27.9	69.1	70.6	8.9	20.5	KBH_4
1.9	32.2	65.9	60.4	12.3	27.3	KBH_4
1.1	39.6	59.3	59.8	16	24.2	KBH_4
0.9	43.9	55.3	76.7	9.9	13.4	KBH_4
0.6	48.9	50.5	70.8	14	15.2	KBH_4
0.4	54	45.6	12	49.2	38.8	$KBH_4 + KOH \cdot H_2O$ (*e*8)
0	54.2	45.8	0	58.1	41.9	$KOH \cdot H_2O$

[a] Compositions and the equilibrium crystalline phases of eutectic point (*e*8) are underlined.

low-temperature FCs. The small range of homogeneous liquid solution with the low concentration of the dissolved BH_4^- ion exists only when $t > 0$ °C and is quickly reduced at lower temperatures. The largest part of the phase diagram is covered with the crystallization fields of various solid phases.

Considering the general transformation course of the diagrams of the ternary $NaBH_4 + NaOH + H_2O$ and $KBH_4 + KOH + H_2O$ systems at the temperature transition −10 °C → 0 °C → 20 °C → 25 °C, it is possible to conclude that it is quite similar as a whole. In both systems the solubility of all the solid components increases at increasing temperature; it occurs, in particular, due to a consecutive loss of stability of the crystalline hydrates and transition to the anhydrous salts as a bottom phase. A picture of the dehydrating action of NaOH and KOH alkalis on the crystalline hydrates of borohydrides is similar; the difference is consistent with the various hydrates' stability.

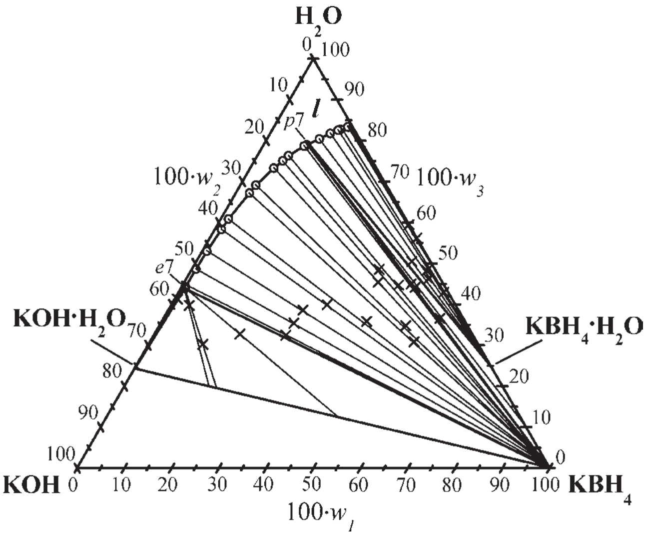

Figure 8. Phase diagram for the KBH_4 (1) + KOH (2) + H_2O (3) system at 20 °C (*l* is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 7. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

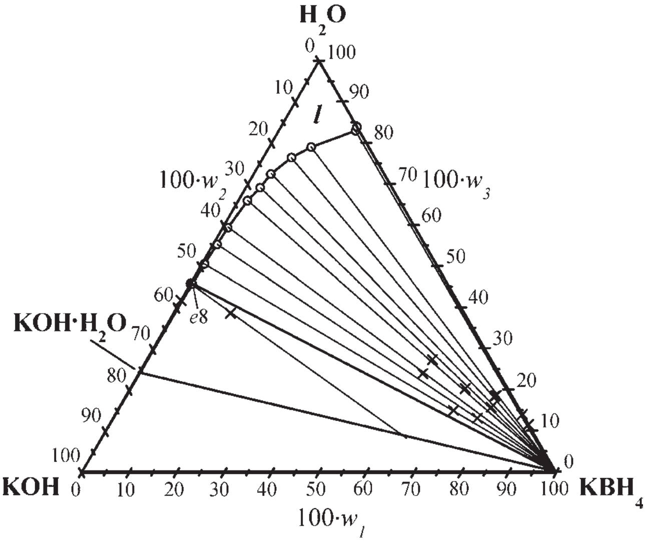

Figure 9. Phase diagram for the KBH_4 (1) + KOH (2) + H_2O (3) system at 25 °C (*l* is the area of the liquid phase). Compositions of the equilibrium liquid phase (○) and wet solid phase (×) are listed in Table 8. Thin lines are tie-lines between coexisting phases; thick solid lines are the bounds among monophase, two-phase, and three-phase areas.

The dihydrate $NaBH_4 \cdot 2H_2O$ formed in the sodium system is rather stable and loses crystallization water at 36.4 °C.[7] The hydrates of potassium borohydride are less stable. The shape of the solubility lines also speaks for the various hydrates' stability. Its smooth course in the KBH_4 + KOH + H_2O phase diagram points to no formation of strong compounds. Simultaneously, the sharp breaks of the liquidus in the $NaBH_4$ + NaOH + H_2O phase diagram testify to the strength of the formed compound $NaBH_4 \cdot 2H_2O$.

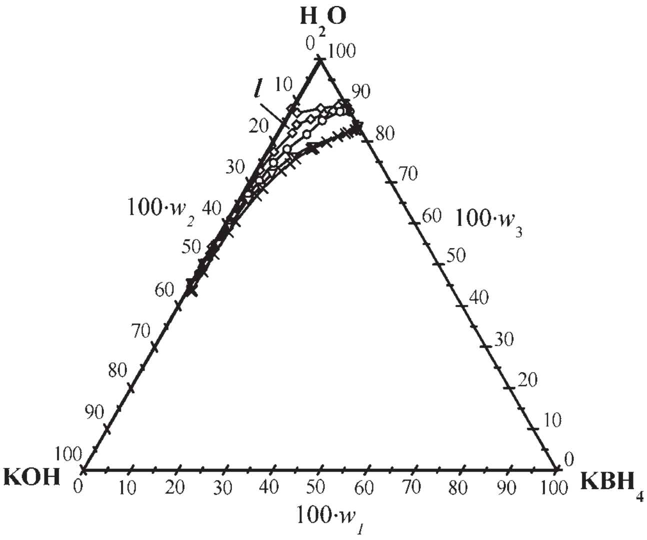

Figure 10. Temperature-induced movement of solubility line for the KBH_4 (1) + KOH (2) + H_2O (3) system: ◇, $t = -10$ °C; ○, $t = 0$ °C; ×, $t = 20$ °C; ▽, $t = 25$ °C. Compositions of equilibrium liquid phase are listed in Tables 6 to 8 and in refs 4, 10, and 11.

CONCLUSION

Concentrated water−alkaline solutions of sodium and potassium borohydrides are used as a fuel and hydrogen source in hydrogen power engineering, including low-temperature FCs; borohydrides convert into metaborates. The performance of fuel mixtures is determined by their solubility in water. A general analysis of the solubility in the ternary systems $NaBH_4$ + NaOH + H_2O and KBH_4 + KOH + H_2O within the range (−10 to 50) °C is done, and regularities and features of the temperature-induced transformation of the phase diagrams are revealed. Five crystallization phases (ice, $NaBH_4 \cdot 2H_2O$, $NaBH_4$, $NaOH \cdot H_2O$, and $NaOH \cdot 4H_2O$) exist in the $NaBH_4$ + NaOH + H_2O system, and five crystallization phases (ice, $KBH_4 \cdot 3H_2O$, $KBH_4 \cdot H_2O$, KBH_4, and $KOH \cdot H_2O$) exist in the KBH_4 + KOH + H_2O system.

Sodium and potassium borohydrides are the typical salt-like compounds by nature; their behavior in aqueous solutions is not distinguishing in principle from that of other inorganic salts. The alkaline solutions dehydrate the crystalline hydrates $NaBH_4 \cdot 2H_2O$ and $KBH_4 \cdot 3H_2O$; the lower the temperature is, the higher the alkali solution concentration is necessary for the dehydration. An increase in temperature of the system also results in a gradual loss of crystallization water down to the complete dehydration. As a result, the consecutive phase transformations $NaBH_4 \cdot 2H_2O \leftrightarrow NaBH_4 + 2H_2O$ and $KBH_4 \cdot 3H_2O \leftrightarrow KBH_4 \cdot H_2O + 2H_2O \leftrightarrow KBH_4 + 3H_2O$ take place in the systems.

On the whole, the temperature-induced transformation of the phase diagram of the $NaBH_4$ + NaOH + H_2O system is rather favorable for its usage in the hydrogen power engineering and the low-temperature FCs. An extensive range of homogeneous liquid solution with a high concentration of dissolved borohydride exists at both room and increased temperature, and it is preserved at the lower temperatures. On the contrary, the KBH_4 + KOH + H_2O phase diagram has the small area of homogeneous liquid solution with the low concentration of the dissolved BH_4^- ion.

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