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Solubility and related equilibria in the $\text{KBO}_2 - \text{H}_2\text{O}$ and $\text{KBO}_2 - \text{H}_2\text{O} - \text{KOH}$ systems

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Abstract

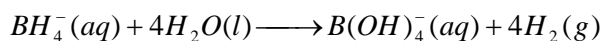
Potassium borohydride KBH_4 is an attractive chemical hydride for H_2 generation and storage in portable fuel cell applications. Nevertheless, the control of the by-products, in terms of stability and solubility in aqueous solutions, is one of the limiting steps of the hydrolysis reaction of H_2 release. We report here some physicochemical properties of concentrated KBO_2 aqueous solutions: solubility and gravimetric density are measured as function of temperature between 10 to 80°C . The stability of hydrated metaborates $\text{KBO}_2 \cdot x\text{H}_2\text{O}$ solid phases (with $x = 4/3$ and 4) in alkaline aqueous solutions is also evaluated at 20°C .

Keywords:

Potassium metaborate, solubility in water, phase diagram

1 INTRODUCTION

Alkali borohydride, $\text{M}(\text{BH}_4)$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) could be promising compounds to store hydrogen as a serious alternative to fossil fuel resources. Hydrolysis of these compounds, in the presence of a catalyst, leads to generate hydrogen on demand and alkali metaborates following the reaction:



In order to avoid the self hydrolysis of the borohydride aqueous solution, alkali hydroxide is added and stable concentrated solutions are obtained. One limiting step of this way of storage will be the precipitation of metaborate hydrates, $\text{MBO}_2 \cdot x\text{H}_2\text{O}$, precluding the elimination of the products and leading to stop the hydrolysis reaction.

The general work aims to a better understanding of alkali borohydride hydrolysis and more particularly for $\text{M} = \text{K}$, in order to improve the hydrogen production in terms of feasibility. This paper is focused on the aqueous solubility of the hydrolysis by-products potassium metaborates into the hydrogen generation conditions that is to say near the ambient temperature and in alkaline medium.

Potassium metaborates (with $\text{K/B} = 1$) are known for a long time and several hydrated compounds are proposed with a large uncertainty concerning their hydration degree. Previously, the ternary phase diagram $\text{H}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3$ was studied by Dukelski and al. [1] at 30°C and the existence of the hydrate $\text{KBO}_2 \cdot 5/4\text{H}_2\text{O}$ has been demonstrated. Toledano and al. [2] focused on the binary phase diagram $\text{KBO}_2 - \text{H}_2\text{O}$. Under pressure (until 4 bars), thermal analyses lead to determine temperatures and the existence domain for the three stable metaborate hydrates estimated by the authors for this system: $\text{KBO}_2 \cdot 4\text{H}_2\text{O}$ (at low

temperature), $\text{KBO}_2 \cdot 5/4\text{H}_2\text{O}$ and $\text{KBO}_2 \cdot 1/4\text{H}_2\text{O}$ (at sub-ambient temperature). The solubility of KBO_2 in water has been also determined from -70 to 300°C and will be compared with our results. Therefore some ambiguities remain as regards the hydration degree of these phases and the compounds $\text{KBO}_2 \cdot 4/3\text{H}_2\text{O}$ and $\text{KBO}_2 \cdot 1/3\text{H}_2\text{O}$ seem more probable [3]. More recently these two stoichiometries were confirmed by structural determination [4] and thermogravimetric analysis [5]. The more hydrated metaborate, estimated by Toledano from thermal analysis at temperature lower than ambience has never been confirmed by other authors.

The purpose of this study was the determination of the aqueous solubility of each hydrated potassium metaborate solid phase as the function of temperature under atmospheric pressure and the influence of potassium hydroxide in the ternary system $\text{KBO}_2-\text{KOH}-\text{H}_2\text{O}$.

2 EXPERIMENTAL DETERMINATION OF SOLUBILITY

The classical methods of solubility measurements consist of removing a small quantity of the saturated solution and then to carry out the chemical analysis of the sample. These methods are not really suited to the aqueous metaborate solutions, which are difficult to analyse chemically. This is the reason why we have chosen a method of the isoplethic type [6], fitting well with the multiconstituted and polyphased systems and without needing systematic chemical analyses. By definition, these methods consist to linearly modify the global composition of a mixture, at constant pressure and temperature, and to follow the evolution of an intensive physical property (conductivity [7], pH, density [8] ...) of the monophasic solution or of the liquid phase in equilibrium with one or more solid phases.

In a system of c independent constituents A_i , the molar or massic composition vector \vec{A} of a mixture A satisfies the relation:

$$(1) \quad a\vec{A} = \sum_i^c (a_i \vec{A}_i) \quad \text{since} \quad a = \sum_i^c a_i$$

where a and a_i are molar or massic quantities of the mixture A and the constituents A_i . In the general case, the small modifications of the quantities da_i of the different constituents can be written as:

$$(2) \quad da\vec{A} + a d\vec{A} = \sum_i^c (a_i d\vec{A}_i) + \sum_i^c (da_i \vec{A}_i)$$

But if just a small quantity da_j of the constituent A_j is added to the mixture A, \vec{A} becomes \vec{A}' , and according to the isobarycentric transformations, this relation is simpler and becomes:

$$(3) \quad (a + da_j)\vec{A}' = a\vec{A} + da_j \vec{A}_j \quad \text{or}$$

$$(4) \quad \vec{AA}' = [da_j / (a + da_j)] \vec{AA}_j$$

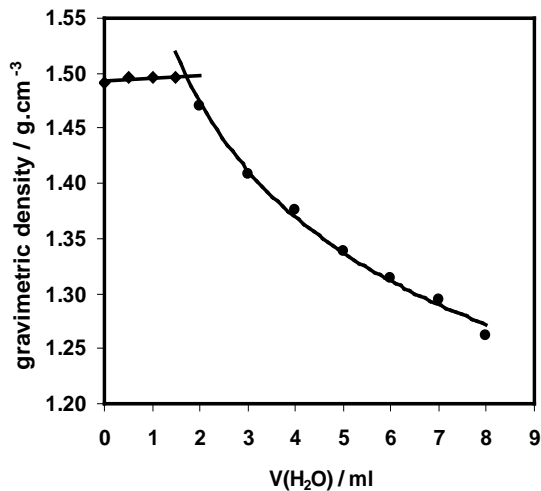
Finally, it is established that the representative points of all the new mixtures A' are co-linear with both the points A and A_j , and then that the experimental study is isoplethic.

In the special case of aqueous solutions of salt systems, water acts towards a polyphased medium as a common solvent, relatively easy to introduce quantitatively in the mixture and the numerical values measured can be represented versus the added water volume. The curves obtained follow proper laws, which are specific of the analysed equilibrium and each change in the nature of one of the phase means in one change of the variation law. The exploitation of the angular points of the curves allows, in principle, to determine the thermodynamics stability domains of the different phases: liquidus, diphased equilibria and invariant equilibrium domains, as the three phases equilibrium triangles, for instance, in the ternary systems. Whatever the chosen intensive physical variable, the invariance of the system depicts a plateau corresponding to constant measured values and this

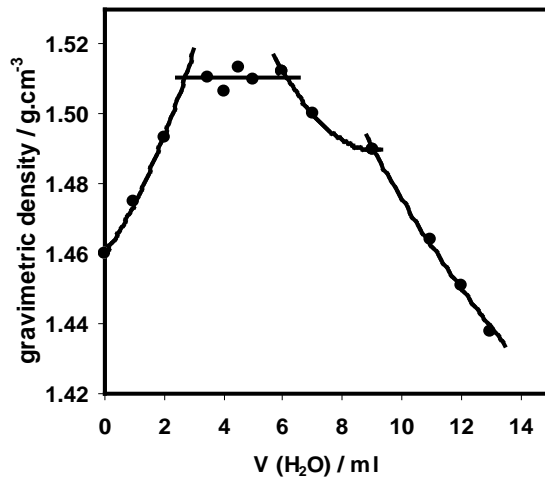
phenomenon allows having a better identification of the concerned phase equilibrium.

The selected experimental technique was the measurement of the gravimetric density. This thermodynamic property is especially interesting because of the relatively easiness to realise this experiment. From this technique, the « Isoplethic Densimetry Analysis », or « IDA », allows furthermore the calculation of partial molar volumes, as well as the calculation of the volumetric composition variables (molarities) from the mass composition variables (molar or mass fractions), and reciprocally.

Commercial hydrated KBO_2 (Fluka, purity>98%), potassium hydroxide pellets (Sigma-Aldrich) and deionised water were used as starting materials. The commercial metaborate, with a stoichiometry near to the ratio $H_2O/KBO_2 = 1.5$, was previously dehydrated by a thermal treatment at $300^\circ C$ during 5 days under argon atmosphere, until the final product was identified as anhydrous KBO_2 by X-ray diffraction analysis (ICCD file n° 01-072-0612). Study of the solid-liquid equilibrium in the binary and ternary system between KBO_2 , water and KOH have been carried out under atmospheric pressure for a temperature range from 10 to $80^\circ C$ in a closed reactor with a thermostatic double jacket. Temperature was support with an accuracy of $\pm 0.2^\circ C$. After weighing of the constituents, the mixtures were magnetically stirred for several hours to reach the equilibrium state. The gravimetric density of the liquid phase is then followed as function of the added solvent quantity. Each equilibrium domain has a corresponding specific variation law, allowing the determination of phase transformation. In isotherm-isobar conditions, the typical curves obtained are presented in figure 1 for binary KBO_2 - H_2O system and ternary system with KOH when a volume of pure water is added. In the case of binary mixture (figure 1a), two parts are distinguished : the first plateau results from the gravimetric density of the invariant liquid phase in equilibrium with a solid phase, and after dissolution the decreasing corresponds to the dilution of a non-ideal solution. For a ternary mixture (figure 1b), a plateau of invariance is observed for a triphased domain (one liquid and two solid phases), and then the solubility of each solid phase is indicated by a break in the curve. The results of the solubility experiments for binary and ternary systems are given in table 1, including the gravimetric density value.



(a)



(b)

Figure 1: Typical IDA curves for (a) binary system and (b) ternary system.

Saturated solutions in the binary system			Saturated solutions in the ternary system at 20°C		
T (°C)	x _{KBO₂}	gravimetric density (g.cm ⁻³)	x _{KBO₂}	x _{KOH}	gravimetric density (g.cm ⁻³)
10	0.1447	1.494	0.1485	0.00	1.483
15	0.1455	1.497	0.1414	0.0090	1.497
20	0.1483	1.483	0.1319	0.0202	1.499
25	0.1512	1.512	0.1260	0.0236	1.509
35	0.1531	1.494	0.1300	0.0294	1.522
40	0.1545	1.488	0.1173	0.0377	1.493
50	0.1566	1.476	0.0975	0.0665	1.467
60	0.1587	1.493	0.0966	0.0715	1.445
80	0.1672	1.449	0.0850	0.0850	-
			0.0715	0.1184	1.431
			0.0505	0.1257	1.423
			0.0514	0.1328	-
			0.0383	0.1539	1.427
			0.0270	0.1763	1.448
			0.0211	0.1933	1.448
			0.0162	0.2073	-

Table 1: Experimental results of solubility as a function of temperature for the KBO₂-H₂O binary system, and for the isotherm 20°C of the KBO₂-H₂O-KOH ternary system.

3 RESULTS AND DISCUSSION

3.1 Analysis of the unsaturated solutions

Figure 2 shows the variation of the experimental gravimetric density of solutions containing 0.06 to 0.14 mol fraction of KBO₂ in the temperature range 10-80°C. For a given temperature, the gravimetric density increase with the molar fraction *x* according to a quadratic relation, as expected for non ideal solutions:

$$(5) \quad \rho = ax^2 + bx + c$$

In the temperature range studied, the coefficients *a*, *b* and *c* vary linearly with the temperature and the gravimetric density becomes as function of *x* and *T*:

$$(6) \quad \rho = (\alpha T + \alpha_o)x^2 + (\beta T + \beta_o)x + \gamma T + \gamma_o$$

The linear coefficients, calculated with a least square method, have the following values when the gravimetric density is expressed in g.cm⁻³ and temperature in °C:

$$\begin{aligned} \alpha &= -0.1811 & \alpha_o &= -0.4760 \\ \beta &= 0.0470 & \beta_o &= 3.0044 \\ \gamma &= -0.0038 & \gamma_o &= 1.0835 \end{aligned}$$

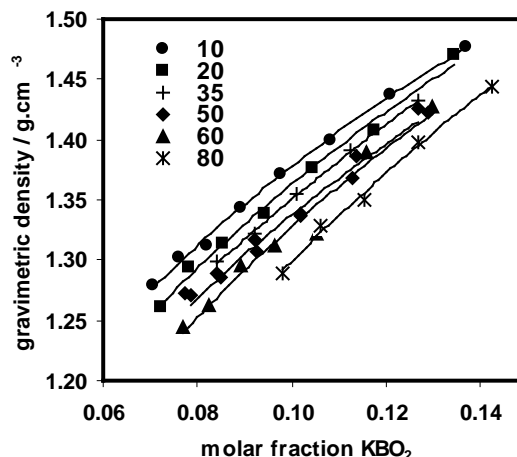


Figure 2: Variation of the gravimetric density of unsaturated aqueous solutions of KBO₂ at different temperatures.

3.2 Solubility in the KBO₂-H₂O binary system

The variation of the liquidus curve as a function of the temperature between 10 to 80°C is shown in figure 3 and compared with few values taken from the literature. At 25 ± 0.2°C, the results of solubility, expressed in molar fraction of KBO₂, are in a very good agreement: 0.1512 (this work), 0.1480 [2] and 0.1438 [9]. The aqueous solubility doesn't

vary very much with temperature, from 0.1447 at 10°C until 0.1672 at 80°C. However, two parts are clearly observed in the liquidus curve: the upper curve corresponds to the solubility of $\langle \text{KBO}_2 \cdot 4/3\text{H}_2\text{O} \rangle$ (according to the structural determination [4]). The lower one is attributed to the crystallization of another solid phase; this phase is not yet identified and could correspond to the more hydrated metaborate $\langle \text{KBO}_2 \cdot 4\text{H}_2\text{O} \rangle$ proposed by Toledano [2].

Under this consideration, the intersection of the two liquidus branches at 27°C can be attributed to the peritectic decomposition of the solid phase $\langle \text{KBO}_2 \cdot 4\text{H}_2\text{O} \rangle$ measured by thermal analysis at the temperature 24°C [2] according to the reaction (7). The liquid in equilibrium with the two solid phases at 27°C contains 0.1520 mol fraction of KBO_2 .

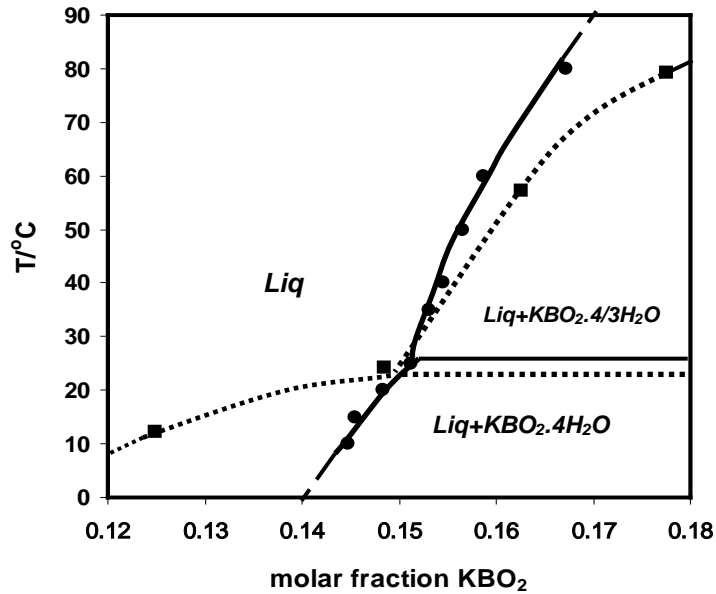
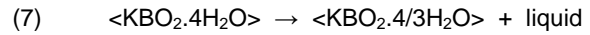
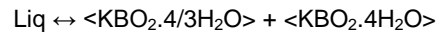


Figure 3: Solubility of KBO_2 in water as a function of temperature (● this work, ■ [2]).

3.3 Solubility in the $\text{KBO}_2\text{-H}_2\text{O-KOH}$ ternary system

In order to evaluate the solubility of KBO_2 in potassium hydroxide medium, series of isoplethic sections have been determined in the $\text{KBO}_2\text{-H}_2\text{O-KOH}$ ternary system as a function of the temperature. Each isoplethic section is defined by the constant mass ratio $m(\text{KOH}) / m(\text{KBO}_2) = 2, 5$ or 10% . The experimental results, reported in figure 4, are compared with the mixture without KOH . These results confirm the phenomena previously established in the system limit $\text{KBO}_2\text{-H}_2\text{O}$. In the area rich in potassium

metaborate, the crystallisation fields of the solid phases $\langle \text{KBO}_2 \cdot 4/3\text{H}_2\text{O} \rangle$ and $\langle \text{KBO}_2 \cdot 4\text{H}_2\text{O} \rangle$ are separated by the invariant line corresponding to the equilibrium:



Furthermore the solubility increases slowly with temperature and decreases weakly with the addition of potassium hydroxide, according to the common ion effect, but in all cases the solid phase $\langle \text{KBO}_2 \cdot 4/3\text{H}_2\text{O} \rangle$ is stabilized with regard to the upper hydrate.

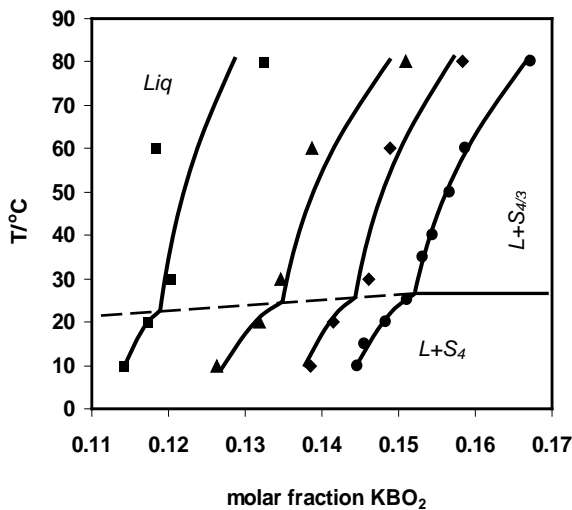


Figure 4: Variation of KBO_2 solubility when KOH is added (● 0w%, ◆ 2w%, ▲ 5w%, ■ 10w%).

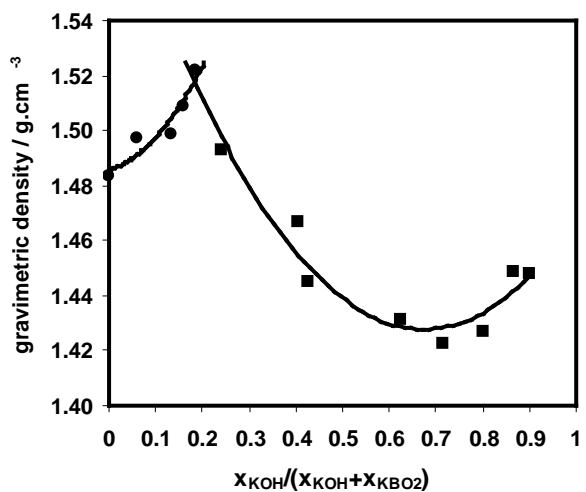


Figure 5: Variation of the gravimetric density of alkaline saturated solutions at 20°C.

The solid-liquid equilibria of the system $\text{KBO}_2\text{-H}_2\text{O-KOH}$ have been systematically studied by using the IDA method, at 20°C . At this temperature, the dihydrated potassium hydroxide and the tetrahydrated potassium metaborate only need to have a stable crystallisation field in the ternary system. But in fact, the liquidus curves of the two hydrates of KBO_2 could be observed: in the binary system $\text{H}_2\text{O-KBO}_2$, at 20°C , the solubilities of the compounds $\langle\text{KBO}_2\cdot 4\text{H}_2\text{O}\rangle$ and $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$ are much closed and, moreover, the solid phase $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$ is stabilized by addition of potassium hydroxide. The composition of the invariant isobar-isotherm solution in equilibrium with the two hydrated potassium metaborates has been determined by the analysis of the gravimetric density measurements of the saturated ternary solutions. Figure 5 shows the variation of this density as a function of the molar ratio: $r = x_{\text{KOH}} / [x_{\text{KOH}} + x_{\text{KBO}_2}]$. Two curves can be clearly distinguished and their intersection leads to the coordinates of the invariant point, so called liquid I. In the area rich in potassium hydroxide, a second invariant point, separating the liquidus curves of solid phases

$\langle\text{KOH}\cdot 2\text{H}_2\text{O}\rangle$ and $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$, is observed. The composition of the corresponding saturated solution (liquid J) is estimated by extrapolation of the liquidus curve of $\text{KBO}_2\cdot 4/3\text{H}_2\text{O}$:

Composition of liquid I: $x_{\text{KBO}_2} = 0.117$, $x_{\text{KOH}} = 0.030$
 Composition of liquid J: $x_{\text{KBO}_2} = 0.010$, $x_{\text{KOH}} = 0.250$

Finally the isotherm 20°C has been completely established. All the experimental results are gathered in figure 6. Three solid phases present equilibria with the liquid phase: $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$, $\langle\text{KBO}_2\cdot 4\text{H}_2\text{O}\rangle$ and $\langle\text{KOH}\cdot 2\text{H}_2\text{O}\rangle$. The three corresponding liquidus curves are characterized by the existence of two isobar isotherm invariant equilibria:

Liquid I $\leftrightarrow \langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle + \langle\text{KBO}_2\cdot 4\text{H}_2\text{O}\rangle$
 Liquid J $\leftrightarrow \langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle + \langle\text{KOH}\cdot 2\text{H}_2\text{O}\rangle$

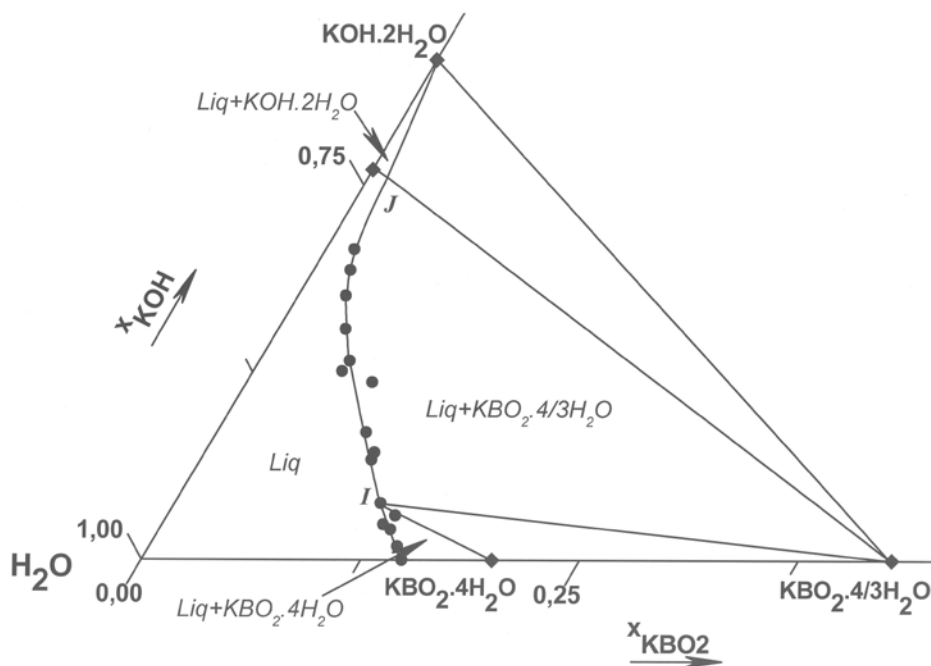


Figure 6: Crystallization domains in the ternary system $\text{KBO}_2\text{-H}_2\text{O-KOH}$ - Isotherm 20°C .

4 CONCLUSION

The experimental results presented in this paper concern the solubility and stability of hydrated potassium metaborates produced by the hydrolysis of KBH_4 . The aqueous solubility has been measured by Isoplethic Densimetry Analysis (IDA) and the exploitation of the gravimetric density curves has been demonstrated to determine the thermodynamics stability domains of the different phases: liquidus, diphased equilibria and invariant equilibrium domains.

In the $\text{KBO}_2\text{-H}_2\text{O}$ binary system, the crystallization field of the two solid phases $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$ and $\langle\text{KBO}_2\cdot 4\text{H}_2\text{O}\rangle$

was determined as a function of temperature. The addition of potassium hydroxide affects the solubility of each solid phase: whatever the temperature the solubility decreases when KOH is added, but in all cases the compound with $4/3$ molecules of H_2O is stabilized.

The isotherm 20°C of the ternary system $\text{KBO}_2\text{-H}_2\text{O-KOH}$ has been completely studied. No double salt appears in this conditions but a large domain of crystallization of the hydrate $\langle\text{KBO}_2\cdot 4/3\text{H}_2\text{O}\rangle$ is observed. The others solid phases in equilibrium with the liquid phase are $\langle\text{KBO}_2\cdot 4\text{H}_2\text{O}\rangle$ and $\langle\text{KOH}\cdot 2\text{H}_2\text{O}\rangle$.

5 ACKNOWLEDGMENT

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