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SOLUBILITY ISOTHERMS AT 0°C IN THE TERNARY SYSTEMS

$NaBH_4$–NaCl–H_2O and $NaBH_4$–NaBr–H_2O

(Presented by Academician I. I. Chernyaev, September 5, 1960)

The solubility isotherms of the ternary system $NaBH_4$–NaOH–H_2O, which underlies all aqueous-salt systems involving sodium borohydride, are characterized by crystallization of pure sodium borohydride dihydrate, anhydrous sodium borohydride, and sodium hydroxide monohydrate ([1],[2]). In the present work we studied the solubility at 0°C in the ternary systems $NaBH_4$–NaCl–H_2O and $NaBH_4$–NaBr–H_2O.

The study of these systems is of interest for establishing the conditions and forms of separation of sodium borohydride from aqueous solutions containing sodium halides, for the possibility of obtaining new solid phases involving sodium borohydride, and for further characterization of the physicochemical properties of sodium borohydride and the borohydride ion.

To prevent hydrolysis of sodium borohydride, the solubility study was carried out in a 1% aqueous NaOH solution; that is, in essence, we studied isoconcentrates with 1% NaOH of the quaternary systems $NaBH_4$–NaCl–NaOH–H_2O and $NaBH_4$–NaBr–NaOH–H_2O, which, however, practically coincide with the lateral ternary systems $NaBH_4$–NaCl–H_2O and $NaBH_4$–NaBr–H_2O.

In the literature we found no information on the study of the above-mentioned systems. Only in the work of Stockmayer et al. ([3]), devoted to the thermodynamic properties of sodium borohydride, is there an indication of the formation of solid solutions between $NaBH_4 \cdot 2H_2O$ and the compounds $NaBr \cdot 2H_2O$ and $NaJ \cdot 2H_2O$. At a temperature of 0°C, both sodium borohydride and sodium chloride and bromide separate from aqueous solutions as dihydrates, $NaBH_4 \cdot 2H_2O$, $NaCl \cdot 2H_2O$, and $NaBr \cdot 2H_2O$. Above +36.4°, +0.15°, and +50.7°, respectively, anhydrous $NaBH_4$, NaCl, and NaBr crystallize ([4],[5]).

In the work, sodium borohydride containing 99.0–99.4% $NaBH_4$ (according to analysis for active hydrogen) was used; it was obtained from the technical product by recrystallization from aqueous solution followed by extraction with liquid ammonia. Sodium chloride and sodium bromide of chemically pure grade were used; the water was freshly distilled. The solubility study was carried out under isothermal conditions; the composition of the solid phase was determined by the Schreinemakers method ([6]) and checked microscopically. The content of sodium borohydride in the liquid phase and in the solid "residue" was determined by

Fig. 1. Solubility isotherm of the $NaBH_4$–NaCl–H_2O system at 0°C

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titration ([1],[2]). The content of NaCl and NaBr was determined by titration with 0.1 N $AgNO_3$ solution by the Mohr method. To verify the absence of hydrolysis of sodium borohydride in aqueous solutions of sodium halides, the $NaBH_4$ content in the liquid phase was also determined in parallel by the iodate method ([7]), and the H/B ratio was calculated. As the concentration of halides in the solution increased, this ratio remained constant, which confirmed the absence of hydrolysis of $NaBH_4$ during the work.

The 0° solubility isotherm of the ternary system $NaBH_4$–NaCl–H_2O (Fig. 1) consists of two branches intersecting at the eutonic point

B (25.5 wt.% $NaBH_4$, 4.3 wt.% NaCl, 70.2 wt.% H_2O). The main part of the diagram is occupied by the crystallization field of anhydrous NaCl, which indicates the high salting-out capacity of sodium borohydride with respect to sodium chloride. If the Schreinemakers rays corresponding to the crystallization of anhydrous NaCl converge well at one point (Fig. 1), then the rays corresponding to the crystallization of another solid phase diverge; consequently, the second branch of the solubility isotherm AB (from 0 to 4.3 wt.% NaCl) corresponds to the crystallization of solid solutions based on sodium borohydride dihydrate, apparently of composition: $Na(BH_4, Cl) \cdot 2H_2O$.

Fig. 1. Solubility isotherm of the $NaBH_4$–NaCl–H_2O system at 0°C

The solubility isotherm at 0°C of the ternary system $NaBH_4$–NaBr–H_2O (Fig. 2) indicates the crystallization of only one solid phase–a continuous solid solution between $NaBH_4 \cdot 2H_2O$ and $NaBr \cdot 2H_2O$. The solubility of this solid solution decreases uniformly (almost in a straight line) from 28.3 wt.% $NaBH_4$ (point A) to 44.6 wt.% NaBr (point B). The composition of the solid phase correspondingly changes gradually from pure $NaBH_4 \cdot 2H_2O$ (point C) to pure $NaBr \cdot 2H_2O$ (point D).

The results obtained confirm the closeness of the physicochemical properties of the borohydride ion and the halide ions, as indicated by Stockmayer et al. ([3]). Our data are also in agreement with the general regularities of solid-solution formation from the standpoint of the magnitude of the ionic radii and the polarizability coefficients of the corresponding ions.

The ionic radii for the BH_4^-, Cl^-, and Br^- ions are 2.03 Å ([9]), 1.81 Å and 1.96 Å ([9]), respectively, and the polarizability coefficients are 3.94 $Å^3$ ([10]), 3.05 $Å^3$ and 4.17 $Å^3$ ([11]). From a comparison of the crystallochemical radii and polarizability coefficients it is evident that, in its properties, the borohydride ion is closer to the bromide ion than to the chloride ion. This also explains why, between $NaBH_4 \cdot 2H_2O$ and $NaBr \cdot 2H_2O$ at 0°C, a continuous series of solid solutions is formed, whereas between $NaBH_4 \cdot 2H_2O$ and $NaCl \cdot 2H_2O$ the solid

Fig. 2. Solubility isotherm of the system $NaBH_4$–NaBr–H_2O at 0°C

Figure 2: Fig. 2. Solubility isotherm of the system $NaBH_4$–NaBr–H_2O at 0°C

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solutions are formed only on the side of $NaBH_4 \cdot 2H_2O$, in a narrow concentration interval (from 0 to ~ 8 wt.% NaCl).

The present work, together with the preceding one[1,2], shows that systems involving the borohydride ion are subject to the general regularities

Fig. 2. Solubility isotherm of the system $NaBH_4$—NaBr—H_2O at 0°C

governing the formation of the principal types of state diagrams in accordance with the physicochemical properties of the crystallizing salts.

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Note: Figure translations are in progress. See original paper for figures.