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Abstract

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SOLUBILITY ISOTHERM OF SODIUM BOROHYDRIDE AND SODIUM HYDROXIDE HYDRATE IN WATER AT 0°C

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Sodium borohydride, $NaBH_4$, although it was first obtained only in 1946, has in recent years already found wide application as a selective reducing agent, an intermediate product in the preparation of high-calorie fuels, a source of diborane, and a compact hydrogen carrier ([1]). Sodium borohydride dissolves readily in water, undergoing only slight hydrolysis. By adding alkalis, the hydrolysis of aqueous sodium borohydride solutions can be reduced to an insignificant degree, even at temperatures above room temperature ([2]). The solubility of $NaBH_4$ in a $0.1\,N$ aqueous solution of NaOH as a function of temperature (from 0 to $-50°$) was studied by Jensen ([3]). According to his data, at temperatures below 36.4°, the dihydrate $NaBH_4 \cdot 2H_2O$ is in equilibrium with a saturated solution of sodium borohydride, and above this temperature—anhydrous $NaBH_4$. The temperature 36.4° at a pressure of 1 atm corresponds to the equilibrium of a saturated solution with two solid phases: $NaBH_4 \cdot 2H_2O$ and $NaBH_4$.

We have for the first time studied the complete solubility isotherm of $NaBH_4$–$NaOH$–H_2O at 0°, which is of considerable interest for establishing the conditions for stabilization of aqueous sodium borohydride solutions and for studying the conditions for isolation of its crystalline hydrates.

In the work, sodium borohydride containing 99.8% $NaBH_4$, obtained by double extraction with liquid ammonia of a technical product containing 85% $NaBH_4$, sodium hydroxide hydrate in the form of a 50% aqueous solution of chemically pure NaOH ([4]), and freshly distilled water were used. The investigation was carried out by determining the joint solubility of $NaBH_4$ and NaOH in water under isothermal conditions, with simultaneous chemical analysis of the solid phase by Schreinemakers' method ([6]) and microscopic control. Glass vessels equipped with a stirrer with an oil seal and a side opening for taking samples were placed in a thermostat in which a mixture of distilled water and ice maintained a temperature of 0° with an accuracy of ±0.1°. The time required to establish equilibrium, according to chemical analysis data, was 2–3 hours. Separation of the solid and liquid phases was carried out by filtration under isothermal conditions through a porous filter.

Fig. 1. Solubility isotherm of NaBH4 and NaOH in water at 0°

Figure 1: Fig. 1. Solubility isotherm of NaBH4 and NaOH in water at 0°

Chemical analysis of the liquid phase and of the solid residue was carried out by titration with 0.1 N HCl using methyl red to determine total alkalinity and by subsequent titration with 0.1 N NaOH, in the presence of mannitol, using phenolphthalein ([5]) to determine the content of boric acid formed as a result of complete hydrolysis of sodium borohydride. The $NaBH_4$ content was calculated from the boron analysis data, and the NaOH content—by difference.

The solubility diagram of the ternary system $NaBH_4$–NaOH–H_2O at 0° (Fig. 1) shows that from an aqueous solution saturated with sodium borohydride, A (28.9% $NaBH_4$), as the NaOH content increases, the dihydrate $NaBH_4 \cdot 2H_2O$ crystallizes up to the composition corresponding to point B (22.3% $NaBH_4$, 22.5% NaOH), then anhydrous sodium borohydride, and, beginning with the composition corresponding to point C (12.3% $NaBH_4$, 44.4% NaOH),

monohydrate of sodium hydroxide hydrate, $NaOH \cdot H_2O$. Apart from $NaBH_4 \cdot 2H_2O$, $NaBH_4$, and $NaOH \cdot H_2O$, no other solid phases in equilibrium with the saturated aqueous solution were found.

The portion of the crystallization curve of $NaBH_4 \cdot 2H_2O$ adjacent to the dehydration point B deserves attention. Upon addition of sodium hydroxide hydrate to a saturated solution of $NaBH_4$, according to the law of mass action one would expect a successive decrease in the solubility of the dihydrate. However, the latter is observed only at the beginning of the curve; then the solubility

Fig. 1. Solubility isotherm of $NaBH_4$ and NaOH in water at 0°

of $NaBH_4 \cdot 2H_2O$ increases noticeably with increasing concentration of NaOH in the solution, which is possibly connected with the formation, between the components, of a complex compound stable only in solution.

The obtained solubility isotherm of sodium borohydride and sodium hydroxide hydrate in water at 0°, the first among diagrams of water-salt systems involving the borohydride anion, along with characterizing the composition of saturated solutions and the conditions for separation of the crystalline hydrate forms of sodium borohydride and sodium hydroxide hydrate, indicates the crystallization (at certain NaOH contents) of anhydrous sodium borohydride. The sufficiently broad concentration region corresponding to crystallization of anhydrous $NaBH_4$ determines the possibility of refining technical sodium borohydride by recrystallizing it from aqueous solutions of sodium hydroxide hydrate.

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