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Abstract

Full Text

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On the Solubility of Sodium Borohydride in Pyridine

(Presented by Academician I. I. Chernyaev, 21 XI 1962)

Despite the use of sodium borohydride in laboratory practice as a reducing agent and as a source of hydrogen and diborane, its behavior toward various solvents has still been insufficiently studied. Over a more or less wide temperature range, the solubility of sodium borohydride has been studied only in diglyme ([1]) and liquid ammonia ([2]). As a solvent for sodium borohydride we studied pyridine—a relatively accessible and readily dehydrated solvent, compatible at the same time with the borohydride anion.

Information on the solubility of sodium borohydride in pyridine is limited only to an indication of the solubility at two temperatures—0 and 75°, amounting respectively to 3.1 and 3.4 g of $NaBH_4$ per 100 g of pyridine ([3]). To study the solubility in pyridine, a preparation containing 99% $NaBH_4$ was used, obtained by recrystallizing the technical product from a 1*N* NaOH solution, followed by dehydration and double extraction with liquid ammonia. "Pure" grade pyridine was kept for 5-6 days over calcium hydride and distilled. The fraction boiling at 114.4-114.8° (748 mm), with a melting point of −41.7° and a refractive index of 1.5090, was collected.

Fig. 1. Polytherm of solubility of $NaBH_4$—pyridine. *a*—data of the visual-polythermal method, *b*—data of the isothermal method

The solubility in the temperature region below −10° was determined by the visual-polythermal method ([4]) using double-walled glass vessels equipped with a platinum stirrer with a hydraulic seal. The temperature was measured with a chromel-copel thermocouple connected to a PP-type potentiometer. The accuracy of measurement was ±0.5°.

In the temperature interval −10-+75°, the solubility was determined by the isothermal method ([4]) using special vessels equipped with a stirrer, an oil seal, and a side outlet for sampling. Thermostating was carried out with an accuracy of ±0.1°. The time required to establish equilibrium was determined from the constancy of the composition of the liquid phase; in the region corresponding to the maximum solubility of sodium borohydride, it was the longest, reaching 7-9 hours. The liquid phase was sampled under isothermal conditions with the aid of a glass pipette with a porous filter. The composition of the solid phase was established by analysis of samples separated from the liquid phase by centrifugation under isothermal conditions, followed by purging with dry cooled nitrogen. For deter-

To determine the sodium borohydride content, both the iodometric (5) and gasometric (6) methods were used.

The solubility polytherm of sodium borohydride in pyridine that we studied (Fig. 1) covers the temperature range from −44.5° to +75°. The melting point of pyridine is appreciably lowered by the addition of sodium borohydride, and the crystallization line of pure pyridine ends at the eutectic point e at −44.5° and a concentration of about 1.0 wt. % $NaBH_4$.

Beyond the eutectic follows the crystallization line of sodium borohydride tripyridinate, $NaBH_4 \cdot 3Py$, which ends at the nonvariant point p_1 at −4.7° and a concentration of 6.8 wt. % $NaBH_4$, corresponding to the reaction

$$NaBH_4 \cdot 3Py \rightleftarrows NaBH_4 \cdot 2.5Py + \text{solution}. \tag{1}$$

The crystallization line of the solvate $NaBH_4 \cdot 2.5Py$, in turn, ends at the nonvariant point p_2 at +5.0° and a concentration of 8.1 wt. % $NaBH_4$, corresponding to the peritectic reaction

$$NaBH_4 \cdot 2.5Py \rightleftarrows NaBH_4 + \text{solution}. \tag{2}$$

Above the latter nonvariant point, unsolvated $NaBH_4$ crystallizes from the saturated solution. Its solubility in pyridine decreases sharply with increasing temperature, falling to 2.3 wt. % $NaBH_4$ at +75°.

Thus the maximum solubility of sodium borohydride in pyridine—8.1 wt. % $NaBH_4$—corresponds to a temperature of +5.0°.

The nonvariant equilibria at −4.7° and +5.0° are confirmed by thermographic study of the solvates. On slow heating of crystals of the compound $NaBH_4 \cdot 3Py$, a clearly expressed endothermic effect is observed, associated with the release of part of the pyridine into the liquid phase, and at about +5.0° an effect associated with crystallization of unsolvated $NaBH_4$. The low thermal stability of both solvates, resulting from the incongruent character of their melting, is confirmed by their easy decomposition under vacuum-treatment conditions even at −10 to −20°.

Attention is drawn to the complex form of the solubility curve, characterized by a clearly expressed maximum in the sodium borohydride content at about

+5.0°. The increase in the solubility of sodium borohydride in pyridine in the region corresponding to crystallization of the solvate $NaBH_4 \cdot 3Py$ is replaced by a slower increase in solubility with increasing temperature: when the saturated solution is in contact with the solvate $NaBH_4 \cdot 2.5Py$, and above +5°, a sharp decrease in solubility is observed, associated with the simultaneous crystallization from the solution of unsolvated $NaBH_4$.

The same course of solubility change with temperature has been established for the diglyme–sodium borohydride system (1), as well as for a number of water-salt systems, for example, water–Na_2SO_4, water–Na_2CO_3, water–Li_2SO_4 (7). This testifies to the unity of the causes responsible for such an anomalous course of solubility change with increasing temperature in both aqueous and nonaqueous solutions. The anomalous course of the solubility curve is apparently associated with solvation of the molecules of the dissolved substance within a certain narrow temperature interval and with the destruction of solvates as the temperature is further raised.

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CITED LITERATURE

1. H. C. Brown, E. V. Mead et al., *J. Am. Chem. Soc.*, **77**, 6209 (1955).
2. G. A. Egorenko, Ya. I. Babel' , I. S. Antonov, *ZhNKh*, **7**, issue 10, 2419 (1962).
3. H. J. Schlesinger, H. C. Brown et al., *J. Am. Chem. Soc.*, **75**, 199 (1953).
4. A. G. Bergman, N. P. Luzhnaya, *Physicochemical Principles of the Study and Use of the Salt Metrology of the Chloride-Sulfate Type*, Moscow, 1951, p. 24.
5. D. A. Lyttle, E. H. Jensen, W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).
6. V. I. Mikheeva, V. B. Breits, *ZhNKh*, **5**, issue 11, 2553 (1960).
7. *Handbook on the Solubility of Salt Systems*, **3**, 1961.

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