586 *J. Chem. Eng. Data* **1996,** *41,* 586−588

Solubility of Sodium Perborate Tetrahydrate in Water and Sodium Metaborate Solutions

G. Yildiz Yüksel, Sibel Titiz, and A. Nusret Bulutcu*

Department of Chemical Engineering, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey

The solubilities of sodium perborate tetrahydrate were measured in water and sodium metaborate solutions as a function of the temperature. The results obtained in the temperature range (11 to 30) °C in the solutions containing sodium metaborate at concentrations up to 5 mass % were compared with previous work.

Introduction

Sodium perborate is a solid peroxygen compound used in bleaching formulations. It is commercially obtained in the tetrahydrate form with reaction crystallization between aqueous solutions of sodium metaborate and hydrogen peroxide:

$$NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3{\cdot}4H_2O \qquad (1)$$

In the present technology, sodium perborate tetrahydrate is used directly or converted to monohydrate to add to detergents. In both cases, the strength of the crystals should be increased so as not to cause breakage during the handling and dehydration process. The strength can be altered by changing the crystal growth habit and size. Changing the operating conditions causes change. An excess of one of the reactants and some additives are used to modify the crystallization kinetics and hence the characteristics of the sodium perborate tetrahydrate crystals. An excess of the theoretical requirement of sodium metaborate is frequently used as a crystal modifier.

During the measurements of crystal growth and the width of the metastable region, solubilities of sodium perborate tetrahydrate at different impurity levels should be known, since these solubility values are one of the parameters in the determination of supersaturation levels. Some impurities have no effect on the solubility of sodium perborate tetrahydrate. Frances et al. (1993) found that $MgSO_4$, $Al_2(SO_4)_3$, Na_2SO_4, NaCl (in the range of (0 to 500) mg/L), cetyltrimethylammonium bromide, sodium dodecyl sulfate, and betaine (in the range of (0 to 100) mg/L) did not affect the solubility of sodium perborate tetrahydrate in water. In spite of this, an excess of sodium metaborate had a pronounced effect on the solubility of sodium perborate tetrahydrate. The solubility of sodium perborate tetrahydrate as a function of sodium metaborate concentration is given by Frances et al. (1993) at 20 °C and Chianese et al. (1986) at (20 and 25) °C. Smith (1962) also gave the solubilities at (18, 25, 29, and 32) °C, but the results are not directly comparable since the concentrations of both components are given on a g/L basis. Chianese et al. (1986) measured the solubility of sodium perborate tetrahydrate at 4.5 mass % sodium metaborate medium as a function of temperature between (15 and 35) °C. Gelder (1958) studied the ternary system of sodium metaborate + sodium perborate + water at (18, 25, 37.5, and 50) °C. Solubilities of sodium perborate tetrahydrate in water as a function of temperature are given by Chianese et al. (1986), Livk et al. (1993), and Gelder (1956).

All the previous works gave the solubility values either at some fixed level of sodium metaborate concentration in which they are interested, as a function of temperature, or at the temperature in which they are interested, as a function of sodium metaborate concentration.

The aim of this work is to construct a solubility diagram of sodium perborate tetrahydrate as a function of sodium metaborate concentration and temperature and to compare the results with previous measurements.

Experimental Section

Materials and Analysis. Pure sodium perborate tetrahydrate crystals (Riedel-de Haën 11621) were used in all measurements. Pure sodium metaborate tetrahydrate was prepared from industrial grade borax pentahydrate and sodium hydroxide, purified by twice recrystallization and checked for the most frequently encountered impurities such as calcium and heavy metals. Calcium analysis by atomic absorption spectrometry gave less than 0.005 mass % of calcium. Heavy metal analysis was performed on 10 mass % sodium metaborate solution. The solution which was acidified with acetic acid was saturated with H_2S and the resulting dark color compared with that of equally treated standard lead solutions. The heavy metal content was less than 0.002 mass %.

Concentrations of sodium perborate and sodium metaborate were calculated from the determinations of boron and active oxygen content of the solutions and controlled by the determination of alkalinity content. Alkalinity was determined on (5 to 10) g of solution depending on the concentration by titration with standardized 0.1 N HCl in the presence of methyl red indicator (Lowenheim, 1973). The same sample was used to determine the boron content. The slightly acidified solution boiled for (3 to 5) minutes to expel carbon dioxide and cooled to room temperature, and the excess acid was titrated with 0.1 N NaOH to the methyl red end point. After approximately 5 g of mannitol was added, the solution was titrated with standardized 0.1 N NaOH to the phenolphthalein end point. The volume of titrant used from the methyl red to the phenolphthalein end point was used to compute the boron content present (Braman, 1968). The active oxygen content was determined on approximately 10 g of solution by adding 3 cm^3 of 6 M H_2SO_4 and 2 drops of 5 mass % manganous sulfate solution and titrating with standardized 0.1 N $KMnO_4$ solution to the first pink color (Mathre, 1971).

Procedures. Two different methods were used in the solubility measurements. In the first method, equilibrium was attained in the presence of solid sodium perborate tetrahydrate in the solution saturated with respect to

0021-9568/96/1741-0586$12.00/0

Table 1. Solubilities of Sodium Perborate at Different Temperatures and Sodium Metaborate Concentrations

	c/(g of $NaBO_3 \cdot 4H_2O$/ 100 g of solution)							
	mass % $NaBO_2$							
t/°C	0	0.1	1.0	2.2	2.5	2.9	4.4	5.5
11.2	1.81	1.66	0.98	0.78	0.76	0.78	0.94	1.09
14.2	1.94	1.89	1.12	0.92	0.90	0.93	1.07	1.24
15.7	2.09	2.01	1.20	0.99	0.99	1.00	1.16	1.34
17.5	2.29	2.14	1.32	1.10	1.11	1.11	1.27	1.49
19.6	2.50	2.36	1.48	1.24	1.26	1.26	1.43	1.68
21.5	2.78	2.51	1.64	1.39	1.41	1.42	1.60	1.86
23.4	3.04	2.82	1.82	1.57	1.57	1.60	1.78	2.05
25.0	3.28	3.06	1.99	1.74	1.71	1.77	1.96	2.22
27.0	3.59	3.37	2.22	1.97	1.91	1.99	2.19	2.45
30.0	4.05	3.93	2.61	2.30	2.27	2.26	2.56	2.91

sodium perborate and containing a predetermined amount of sodium metaborate. A screwthread Erlenmeyer flask containing the saturated solution and excess solid phase of sodium perborate tetrahydrate was put into a thermostatically controlled shaker bath having a temperature stability better than ±0.1 K, and it was shaken for 5 h to attain equilibrium. The saturated solution was quickly separated from the solid phase at the same temperature using a glass filter having the maximum pore size of (10 to 16) μm (porosity No. 4).

In the second method, the polythermal method described by Nyvlt (1977) was used. Samples obtained from the first method were put into a jacketed glass reactor in a 30 cm^3 active volume. The solution was stirred magnetically and cooled by means of cold water passing from the jacket of the reactor until nucleation of sodium perborate tetrahydrate was observed. Then the solution was heated to a temperature 0.5 K below its saturation point, and heating is continued with a heating rate of 0.2 K/h. The saturation temperature was taken as the temperature at which the disappearance of last of the solid phase was observed visually. After the experiment was finished, the solution was analyzed to determine if there was any decomposition. No decomposition was detected in any experiment.

In the second method the saturation temperature was found to be determined somewhat higher than that determined in the first method, in the range of (0.5 to 1.0) K. When the solution temperature is kept constant at the equilibrium temperature determined in the first method, the same saturation temperature is obtained in (4 to 5) h. Therefore it was decided that the polythermal method gives erroneous results when it is directly applied. The reason for these erroneous results comes from the very slow dissolution rate of sodium perborate tetrahydrate in the vicinity of the saturation point. Therefore results of the first method only are given.

In the experiments three samples were taken for the analysis. Analytical results showed that differences in the individual measurements were always less than ±0.01% with respect to the $NaBO_3 \cdot 4H_2O$ mass % of the solution.

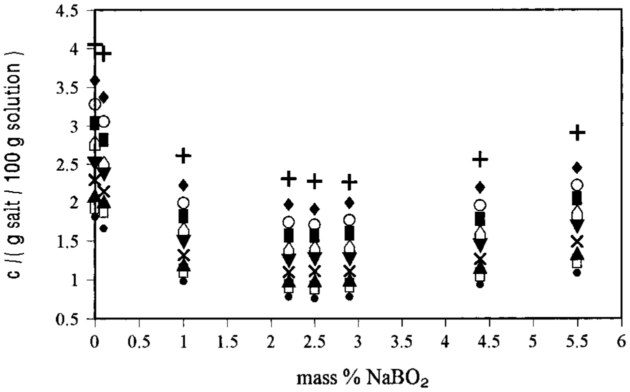

Figure 1. Dependence of solubility of sodium perborate tetrahydrate on sodium metaborate concentration. t/°C: (●) 11.2; (□) 14.2; (▲) 15.7; (×) 17.5; (▼) 19.6; (⌂) 21.5; (■) 23.4; (○) 25, (♦) 27, (+) 30.

Results and Discussion

The equilibrium time in the first method was determined by using a solution containing 2.5 mass % sodium metaborate at 20.4 °C. Experiments were carried out up to 20 h, and samples are taken in 0.5 h intervals. It was determined that equilibrium was reached in 0.5 h and there was no more change with time. No decomposition was detected up to 20 h. Therefore in the foregoing experiments, samples were shaken in the thermostat for 5 h to be sure of equilibrium. The results are reported in Table 1. Figure 1 shows the solubility of sodium perborate tetrahydrate as a function of concentration of sodium metaborate at different temperatures. The solubility of sodium perborate tetrahydrate decreases in the presence of sodium metaborate, in the concentration range of (0 to 2) mass %. This is an expected result because of the common ion effect. Existence of (2 to 3) mass % of sodium metaborate has only a very slight effect on the solubility, and increasing the sodium metaborate concentration causes an increase in the sodium perborate concentration. This effect is explained by Chianese et al. (1986) as due to a sharp decrease of the activity coefficient.

Solubility values obtained in this work are in very good agreement with the values given by Gelder (1958) and slightly different than the values given by Chianese et al. (1986) and Frances et al. (1993). But the comparison can only be made for the limited range of temperature and sodium metaborate concentration, since in this work these functions are investigated in a broader range and in frequent intervals.

Conclusions

The solubility of sodium perborate tetrahydrate in the presence of sodium metaborate is investigated in the temperature range (11 to 30) °C in the solution containing sodium metaborate at concentrations up to 5.5 mass %. It is concluded that the polythermal method gives erroneous results because of a very slow dissolution rate in the vicinity of the saturation point.

Solubility of sodium perborate tetrahydrate in the presence of sodium metaborate shows the same behavior for all the temperatures up to 30 °C. A decrease of the sodium perborate concentration with an increase of the sodium metaborate concentration up to 2 mass %, followed by a very slight change in the (2 to 3) mass % sodium metaborate region, and then an increase in the solubility with increasing sodium metaborate concentration is the general character of the system.

Literature Cited

Braman, R. S. Boron Determination. In *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D., Hilton, C. L., Eds.; Interscience Publishers: New York, 1968; Vol. 7, p 405.

Chianese, A.; Contaldi A.; Mazzarota, B. Primary Nucleation of Sodium Perborate in Aqueous Solutions. *J. Cryst. Growth* **1986**, *78*, 279−290.

Frances, C.; Biscans, B.; Gabas, N.; Laguérie, C. Investigations of the Effects of Some Additives on the Crystallization of Tetrahydrate Sodium Perborate. *J. Cryst. Growth* **1993**, *128*, 1268−1272.

Gelder, D. W. A New Hydrate of Sodium Perborate. *Recl. Trav. Chim.* **1956**, *75*, 117−126.

Gelder, D. W. Equilibria in the Ternary System Sodium Metaborate-Sodium Perborate-Water. *Recl. Trav. Chim.* **1958**, *77*, 739−745.

Livk, I.; Smodis, M.; Golob, J.; Pohar, C. Crystallization Kinetics of Sodium Perborate. *Symp. Ind. Cryst., 12th* **1993**.

Lowenheim, F. A. Sodium. In *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D., Ettre, L. S., Eds.; Interscience Publishers: New York, 1973; Vol. 18, p 245.

Mathre, O. B. Hydrogen Peroxide. In *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D., Ettre, L. S., Eds.; Interscience Publishers: New York, 1971; Vol. 14, pp 432−433.

Nyvlt, J. *Solid-Liquid Phase Equilibria*; Elsevier Scientific: Amsterdam, 1977.

Smith, J. Improvements in or Relating to the Preparation of Sodium Perborate. *Brit. Pat.* 911, 664, **1962**.

Received for review October 24, 1995. Accepted February 26, 1996.⊗

JE950267R

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.