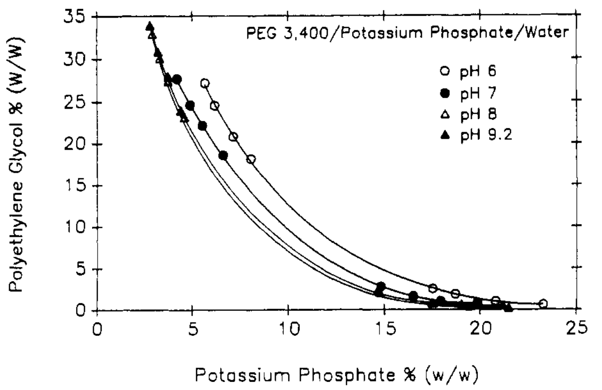

Figure 2. Binodial curves for PEG 3400/potassium phosphate/water over the pH range 6–9.2 at 4 °C.

A pasteur pipet was used to collect the top phase, while the lower phase was drained from the polypropylene tube by piercing a hole at its bottom.

Potassium phosphate concentration, which includes quantification of both potassium and phosphate, was determined to a precision of ±0.02% (w/v) by ion exchange chromatography and titration, as described in detail by Svehla (*3*). The column was filled with Dowex-50 cation exchange resin (8% cross-linked), while titration was performed with 0.1 N sodium hydroxide and bromocresol green as the indicator. The concentrations obtained on a weight per volume basis were converted to weight per weight by density measurements using pycnometry. The precision of the density was ±0.001 g/mL. In order to determine water content, samples of about 2–3 g from each phase were weighed into 20-mL polypropylene tubes, diluted with 5–7 mL of water, and freeze-dried for 24–72 h. In order to verify that no PEG was lost during the freeze-drying process, samples of PEG aqueous solutions were freeze-dried, and the weights before and after the drying were found to be the same. Therefore, no PEG was lost during the process. The precision of the water concentration was ±0.02% (w/w). Having determined the potassium phosphate and water concentrations, the PEG content was obtained by subtraction.

Materials

ACS reagent grade monobasic and dibasic potassium phosphate were obtained from Aldrich Chemical Co., Milwaukee, WI. Poly(ethylene glycol) of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000 was also obtained from Aldrich.

The Dowex 50-w cation exchange resin was purchased from Sigma Chemical Co., St. Louis, MO.

Results and Discussion

Phase diagrams have been obtained at 4 °C for PEG/potassium phosphate/water systems at pH 7 by utilizing PEG of molecular weight 400, 600, 1000, 1500, 3400, 8000, and 20 000. Phase equilibrium data have also been obtained for the PEG 3400/potassium phosphate/water system at pH 6, 7, 8, and 9.2. The phase compositions for the systems with varying PEG molecular weight and pH are presented in Tables I and II, respectively. Similarly, the phase diagrams for the two sets of systems are presented in Figures 1 and 2, respectively.

Analysis of binodial curves of systems A–G in Figure 1 reveals the effect of PEG molecular weight on phase separation. As the molecular weight is increased, the binodial curve shifts to lower PEG and phosphate concentrations. This trend is in agreement with the experimental results of Albertsson (*1*).

Examination of the binodial curves in Figure 2 demonstrates the effect of pH on phase separation at constant PEG molecular weight. As the system becomes more basic, the binodials shift to lower PEG and phosphate concentrations, as was observed for the molecular weight effect. The difference in position between the binodials begins to diminish at high pH, with the binodials for pH 8 and 9.2 being almost identical.

Acknowledgment

We give special thanks to Kanokrot Phalakornkul, a summer student from Princeton University, and Ge Zhang from the Beijing Specialty Gas Research Institute, China, for laboratory help with titration and freeze-drying.

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Received for review August 17, 1989. Accepted June 15, 1990. This work was supported by National Science Foundation Grant Nos. EET-8708839 and CBT-8702912.

Some Physicochemical Data on Tetrahydrate Sodium Perborate in Aqueous Solutions

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The solubility of tetrahydrate sodium perborate as a function of temperature in aqueous solutions has been determined. The results can be expressed by an Arrhenius-type equation. Experiments have also been carried out with solutions containing sodium metaborate. The solubility is greatly affected by the presence of metaborate. The density, viscosity, and diffusivity as a function of concentration have also been reported. Some equations are proposed to correlate the experimental results. Measured data are compared with some available data of the literature.

Introduction

Sodium perborate $NaBO_3 \cdot 4H_2O$ is a bleaching agent used in detergents and washing powders. It is produced by the reaction between aqueous solutions of sodium metaborate and hydrogen peroxide.

$$NaBO_2 + H_2O_2 + 3H_2O \rightarrow NaBO_3 \cdot 4H_2O$$

Some experimental physicochemical data relative to tetrahydrate sodium perborate in aqueous solutions are reported here.

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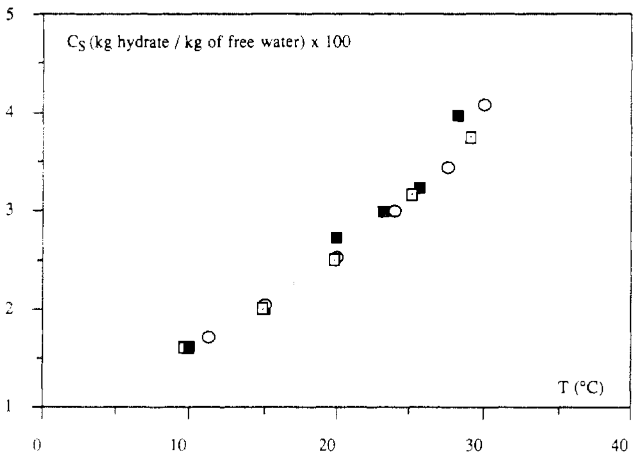

Figure 1. Solubility of tetrahydrate sodium perborate in aqueous solutions: (□) our data (industrial product); (○) Dugua's data (*1*); (■) Chianese's data (*2*).

Sodium perborate used in the present study has been produced by the Air Liquide Co. (Cité de Varennes; BP 111 - 71103 Chalon/Saone Cedex, France). Its purity is about 99.7% in weight.

Analyses of impurities have given the following results:

impurity	wt %	impurity	wt %
Cl^-	0.04	Ca^{2+}	0.006
PO_4^{3-}	0.02	K^+	0.02
SO_4^{3-}	0.1	Mg^{2+}	0.04
NO_3^-	0.003	Si^{4+}	0.03

Titration

Sodium perborate can be rewritten with the formula $^1/_2$-($Na_2O{\cdot}B_2O_3$)$\cdot H_2O_2{\cdot}3H_2O$. The concentration of sodium perborate in aqueous solutions is deduced from the Na_2O concentration, determined by reaction with HCl in the presence of helianthine (*1*).

Moreover, sodium perborate in aqueous solution is easily decomposed by heat, resulting in an escape of oxygen. For temperatures higher than 35 °C, thermal decomposition is no longer negligible and increases with increasing temperature (*2*). Nevertheless, decomposition can occur at temperatures less than 35 °C in special cases, with impurities or additives. So, before each run, hydrogen peroxide is titrated by potassium permanganate (*1*) to verify that no decomposition has taken place.

Solubility

A straightforward experimental method has been followed for the determination of the solubility. A stirred solution containing some excess of solid solute is maintained at a constant temperature (±0.1 °C) for 6 h at least. This time is necessary to reach an equilibrium between the salt and the solution. Then, the stirring is stopped and the remaining solid allowed to settle for about 1 h. A sample of the solution is withdrawn, filtered (through a filter with pores of diameter 0.45 μm), and analyzed. Some experiments have also been carried out with recrystallized sodium perborate. The results, expressed in kilograms of solute/kilogram of free water are presented in Table I. The estimated precision of this procedure is 0.7% in weight. Data of this study and those of other authors (*2*, *3*) reduced to the same units are reported in Figure 1.

Between 10 and 30 °C, experimental results can be correlated in the form

$$C_S = 5.423 \times 10^3 \exp(-29930/RT) \qquad (1)$$

in which C_S is expressed in kilograms of hydrate/kilogram of free water and T in Kelvin. The mean deviation between experiments and correlation is 1.5% and the maximum deviation is about 3.0%. Agreement with Dugua's data (*2*) is good, whereas the difference with Chianese's results (*3*) is more important. That discrepancy is probably due to the difference in the purity of the product used.

Table I. Solubility of Tetrahydrate Sodium Perborate in Aqueous Solution

industrial product		recrystallized product	
temp, °C	C, 100 kg of hydrate/kg of free water	temp, °C	C, 100 kg of hydrate/kg of free water
9.7	1.625	10.0	1.665
14.9	1.991	20.0	2.561
19.9	2.501		
25.1	3.165		
29.0	3.742		

Table II. Solubility of Tetrahydrate Sodium Perborate in Aqueous Solutions Containing Sodium Metaborate at 20 °C

amt of metaborate in soln, % in weight	solubility of perborate C_S, 100 kg of hydrate/kg of free water	amt of metaborate in soln, % in weight	solubility of perborate C_S, 100 kg of hydrate/kg of free water
0.39	1.975	2.77	1.307
1.18	1.495	3.60	1.317
1.57	1.408	5.00	1.432
1.98	1.349	10.00	2.117
2.36	1.300	15.00	3.567

Table III. Solubility of Tetrahydrate Sodium Perborate in Aqueous Solutions Containing Sodium Metaborate versus Temperature

3.6 wt % metaborate in solution		4.5 wt % metaborate in solution	
temp, °C	C, 100 kg of hydrate/kg of free water	temp, °C	C, 100 kg of hydrate/kg of free water
9.7	0.735	9.7	0.764
14.9	1.065	14.9	1.143
19.9	1.317	19.9	1.384
25.1	1.846	25.1	2.010
29.0	2.514	29.0	2.704

In order to determine the influence of the presence of sodium metaborate on the solubility of sodium perborate, experiments have also been performed at 20 °C with different concentrations of sodium metaborate in solution. The results expressed as solubility of sodium perborate versus concentration of sodium metaborate are presented in Table II.

As the concentration of metaborate is increased up to about 15%, the solubility of perborate decreases in a first stage and then increases because of the effect of the common ion Na^+ (*4*).

$$Na^+ + BO_3^- + 4H_2O \rightarrow NaBO_3{\cdot}4H_2O \qquad \text{(ppt)}$$

The variations of solubility, with 4.5% and 3.6% in weight of sodium metaborate, versus temperature are presented in Table III.

Density

The density of the solutions has been determined at 20 and 25 °C by means of a pycnometer. Solutions were prepared by dissolving a known amount of salt in a weighed quantity of distilled water. The accuracy of this procedure is about 5×10^{-3} kg/m^3 on the determination of density and about 2×10^{-6} kg/kg on the concentration. The data are presented in Table IV and shown in Figure 2. They are correlated according to the equations

$$\text{at 20 °C} \quad 1/\rho = 1.00180 \times 10^{-3} - 0.55553 \times 10^{-3}C \qquad (2)$$

$$\text{at 25 °C} \quad 1/\rho = 1.00271 \times 10^{-3} - 0.58632 \times 10^{-3}C \qquad (3)$$

Table IV. Density of Tetrahydrate Sodium Perborate Aqueous Solutions

at 20 °C		at 25 °C	
C, 100 kg of hydrate/ kg of free water	ρ, 10^{-3} kg/m^3	C, 100 kg of hydrate/ kg of free water	ρ, 10^{-3} kg/m^3
0	0.9982	0	0.9973
0.262	1.0002	0.249	0.9992
0.751	1.0028	0.772	1.0023
0.772	1.0027	1.075	1.0037
1.050	1.0045	1.488	1.0065
1.075	1.0045	2.030	1.0095
1.263	1.0056	2.500	1.0115
1.758	1.0083	2.749	1.0135
2.030	1.0098		
2.055	1.0098		
2.370	1.0112		
2.500	1.0118		
2.749	1.0132		

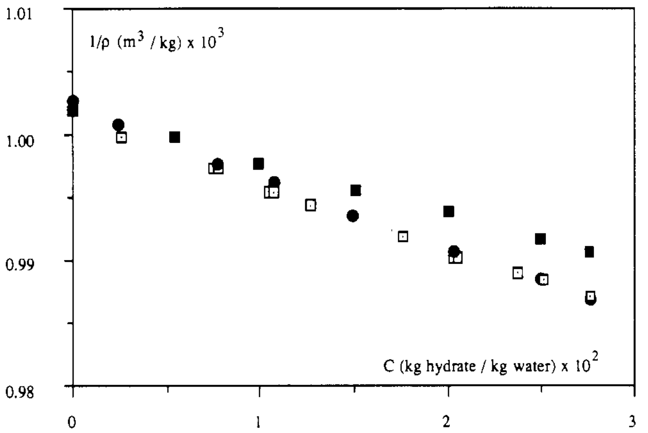

Figure 2. Density of tetrahydrate sodium perborate aqueous solutions: (□) our data, 20 °C; (●) our data, 25 °C; (■) data calculated from eq 4.

where ρ is the density of the solution in kg/m^3 and C the concentration expressed in kilograms of tetrahydrate sodium perborate/kilogram of free water. The maximum deviation between experimental data and calculated values is 0.06%.

If the dissolution of the salt in the solvent took place at constant molecular volumes, it would be possible to predict the density of the solution by

$$\rho = \frac{1 + C}{\dfrac{C}{\rho_c} + \dfrac{1}{\rho_w}} \tag{4}$$

where ρ_w is the density of water and ρ_c the density of tetrahydrate sodium perborate crystals.

ρ_w is given in the literature (*5*), and ρ_c has been measured with a pycnometer in the presence of a nonsolvent (chloroform). The density of quite spherical crystals obtained by this method for a temperature between 20 and 25 °C is 1.708 × 10^3 kg/m^3 (±1.0). This value does not differ much from the data given by Dugua (*2*) (1.731 × 10^3 kg/m^3). The variations of density as a function of concentration, given by the theoretical correlation, are also reported in Figure 2. The experimental values are higher than the calculated ones, and the deviation increases with increasing concentration. So, it can be concluded that the dissolution of sodium perborate in water occurs with an increase of the total volume.

Viscosity

The viscosities of the solutions have been determined at 20 °C from the terminal velocity of a falling sphere. The solutions were prepared in the same way as for density determination.

Table V. Viscosity of Tetrahydrate Sodium Perborate Aqueous Solutions at 20 °C

C, 100 kg of hydrate/ kg of free water	μ, 10^3 kg/(m·s)	C, 100 kg of hydrate/ kg of free water	μ, 10^3 kg/(m·s)
0	1.002	1.7536	1.0372
0.2618	1.0248	1.7584	1.0307
0.7511	1.0178	2.0188	1.0655
1.0352	1.0264	2.0549	1.0667
1.2451	1.0375	2.3704	1.0583

Table VI. Diffusivity of Tetrahydrate Sodium Perborate in Water at 20 °C

C_m, 100 kg of hydrate/ kg of free water	C_m, mol/L of free water	D, 10^{10} m^2/s
1.039	0.0675	7.133
1.251	0.081	6.554
1.908	0.124	6.547
2.108	0.137	4.698

The viscometer is constituted by a thermostated cylinder, filled with the solution in which the sphere drops. The results given in Table V are the average of at least five experimental values, for each concentration. The precision of such a procedure is estimated to 0.02 × 10^{-3} P. The data can be correlated by the equation

$$\mu = 1.0059 \times 10^{-3} + 0.00232C \tag{5}$$

The maximum difference between experimental and calculated values is about 1.5%. There is no comparable data on viscosity in the literature.

Diffusivity

The diffusivity of tetrahydrate sodium perborate in water has been determined at 20 °C by means of a porous fine membrane cell similar to that used by Lozar (*6*) and Laguerie (*7*). The membrane used is a Millipore filter type HA, 150 μm in thickness and of about 80% porosity. The pore diameter is 0.45 μm. The two cell compartments are filled with solutions at different concentrations. Both sides of the membrane are well stirred to prevent the development of a diffusional film. The integral diffusivity $\bar{D}$ is then obtained by the relation (*6*)

$$\bar{D} = \frac{1}{\beta t} \ln \frac{C_{1i} - C_{2i}}{C_{1f} - C_{2f}} \tag{6}$$

where β is a specific constant of the cell and the subscripts refer to initial (i) and final (f) concentrations of compartments 1 and 2.

$\bar{D}$ is not easily related to the more fundamental differential diffusion coefficient D. Nevertheless, a negligible error is introduced when using the relation, according to ref 8,

$$\bar{D} = \frac{1}{C' - C''}\int_{C'}^{C} D \, dC \tag{7}$$

with $C' = (C_{1i} + C_{1f})/2$ and $C'' = (C_{2i} + C_{2f})/2$.

If D varies linearly with concentration, the integral coefficient determined by eq 7 is equal to the differential coefficient at concentration C_m:

$$C_m = \frac{C_{1i} + C_{2i} + C_{1f} + C_{2f}}{4} \tag{8}$$

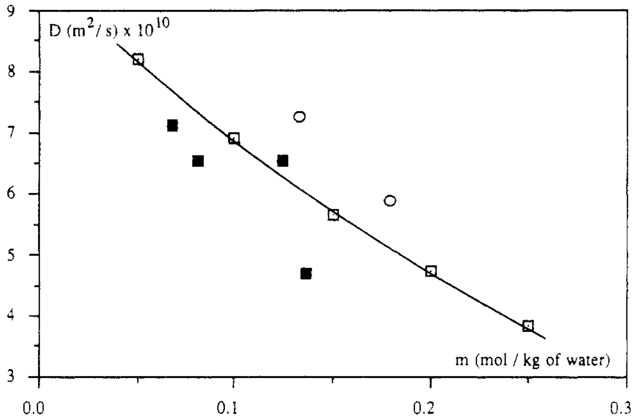

Figure 3. Diffusivity of sodium perborate in water: (■) our data; (O) Chianese's data; (⊡) data from Gordon's equation.

For these experiments, β is found equal to 3.3×10^{-4} m^{-2}.

Conditions of the experiments and the results are reported in Table VI and in Figure 3.

Results of this study fit reasonably with Gordon's empirical equation (*9*)

$$D = D_0\left(\frac{V}{nV_S}\right)\left(\frac{\mu}{\mu_w}\right)\left(1 + m\frac{\delta \ln \gamma_\pm}{\delta m}\right) \quad (9)$$

where the diffusion coefficient at infinite dilution D_0 is calculated by the Nernst-Haskell equation (*9*) and the values of $\ln \gamma_\pm$, as a function of the solute molality, are calculated on the basis of Pitzer's thermodynamic model. The parameters of Pitzer's equation have been determined by Chianese (*3*) from solubility measurements ($\beta_0 = -0.6250$, $\beta_1 = -1.2160$, $C_0 = 0.0440$). The data reported by Chianese (*10*) and determined by diffusion interferometry measurements at 23 °C are also shown in Figure 3. They are higher than those reported in this study, but the discrepancy is probably due to the difference of temperatures.

Glossary

C	concentration, kg of hydrate/kg of free water
C_m	mean concentration, kg of hydrate/kg of free water (or mol/L of water)
C_S	equilibrium solute concentration, kg of hydrate/kg of free water
C_0	third parameter of Pitzer's equation
C_{1i}	initial concentration in cell compartment 1
C_{2i}	initial concentration in cell compartment 2
C_{1f}	final concentration in cell compartment 1
C_{2f}	final concentration in cell compartment 2
D	differential diffusion coefficient, m^2/s
$\bar{D}$	integral diffusion coefficient, m^2/s
D_0	diffusion coefficient at infinite dilution, m^2/s
m	molality of solute, mol/kg of water
R	gas constant (8.314 J/(mol K))
T	temperature, °C (or Kelvin in eq 1)
t	time, s
V	volume of solution containing *n* moles of solvent, eq 9, m^3
V_S	partial molal volume of solvent, m^3/mol
β	cell constant, m^{-2}
β_0	first parameter of Pitzer's equation
β_1	second parameter of Pitzer's equation
$\gamma_\pm$	mean ionic activity coefficient of solute
μ	viscosity of the solution, P
μ_w	viscosity of water, P
ρ	density of the solution, kg/m^3
ρ_c	density of solid sodium perborate, kg/m^3
ρ_w	density of water, kg/m^3

Registry No. $NaBO_3 \cdot 4H_2O$, 10486-00-7; $NaBO_2$, 7775-19-1.

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Received for review September 18, 1989. Accepted May 1, 1990.