

SOLUBILITY OF $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ IN THE SYSTEM $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$

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Received February 2nd, 1981

The solubility of $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ in the multicomponent system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ has been investigated at temperatures of 12, 20, and 30°C. Comparison of the data with solubilities of the same compound in the simpler system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$ shows that the presence of potassium hydroxide increases the solubility at the same temperature and total content of hydroxide ions. The effect of potassium ions on the solubility of $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ is expressed by an empirical equation relating the apparent equilibrium constant of the dissolution reaction and the molalities of the perhydroxyl and potassium ions at a given temperature.

A previous work¹ has indicated that the preparation of alkaline solutions of hydrogen peroxide by cathodic reduction of oxygen can only be carried out in dilute solutions of sodium hydroxide, since little soluble sodium peroxide octahydrate separates, even at very small hydrogen peroxide content, from concentrated solutions ($c_{\text{NaOH}} > 2 \text{ mol dm}^{-3}$) at a temperature of electrolysis of about 20°C. The separation first occurs inside the pores of the carbonaceous cathodes where the hydrogen peroxide concentration is highest as a consequence of concentration gradient². The solid $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ causes the plugging of pores and mechanical disintegration of the porous cathodes, preventing long-term operation of the process. For these reasons, solutions of up to 1–1.5 mol dm⁻³ NaOH can only be used in the electrolysis at 20°C. A disadvantage of such dilute solutions, however, is their low electric conductivity leading to relatively high voltage of the electrolyzer. Also, there is a danger that the anolyte alkalinity may decrease below the value necessary to maintain the nickel anodes for oxygen evolution in the passive state.

When potassium hydroxide is used in the process, the solid phase will not separate however high the degree of conversion of OH^- into O_2H^- ions, and thus solutions of highest electrical conductivity (about 7M-KOH) may be used. However, the potassium hydroxide solutions have a major disadvantage of being much higher in cost than sodium hydroxide, which makes their use unattractive from the economic point of view. This is true especially where it is impracticable to make use of the alkali after utilization of hydrogen peroxide dissolved in the solution. An improvement of this situation may be achieved by using mixed solutions of sodium hydroxide and potassium hydroxide. The present work was undertaken to supply hitherto

lacking data on the solubility of $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in the system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$.

EXPERIMENTAL

Procedure. Stock solutions of molar ratios $\text{KOH} : \text{NaOH}$ of about 1 : 1 or 2 : 1 and a total hydroxide ion concentration of about 10 mol dm^{-3} were prepared from saturated, c. 50% solutions of NaOH and KOH containing only negligible amounts of carbonates (K_2CO_3 content lower than 1%). Appropriate amounts of c. 80% H_2O_2 (Chemické závody, Sokolov) were added to various volumes of the stock solutions and distilled water until desired amounts of $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ crystals had separated. The mixtures were then maintained for at least one hour at desired temperatures (30, 20, or 12°C) by passing thermostatted water through the jacket of the reaction vessel fitted with a Bunsen valve to prevent the entrance of carbon dioxide from the air. The reaction mixture was thoroughly stirred by a magnetic stirrer. When equilibrium was established, the stirring was stopped, and a sample of the clear, saturated solution was withdrawn for chemical analysis. The separated crystals were filtered off, and the remaining clear solution was transferred to a polyethylene bottle and allowed to stand until the hydrogen peroxide decomposed spontaneously. The density of the saturated solution was determined pycnometrically. The decomposed saturated solutions were analyzed for the content of sodium and potassium cations by the method of flame photometry.

The chemical analysis of the samples of saturated solutions consisted in the acidimetric determination of the total alkalinity and permanganometric determination of the total hydrogen peroxide, as in the previous work¹. The actual total concentrations of sodium hydroxide and potassium hydroxide in the saturated solutions were calculated from the total alkalinity at the time of sampling and the potassium-to-sodium molar ratio as determined by flame photometry. It should be noted that this molar ratio was always higher than that of the starting solution, since the separation of the $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ crystals resulted in an impoverishment of the solution with respect to sodium ions.

RESULTS AND DISCUSSION

A survey of the compositions of saturated $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ solutions with various contents of the basic components (in wt.%) at the temperatures 30, 20, and 12°C is given in Table I. These basic analytical data were used to calculate the molalities of the individual ions in the saturated solutions. Since the total molality of hydrogen peroxide, $m_{\text{H}_2\text{O}_2, \text{tot}}$, in the measured solution was in all the cases sufficiently lower than the total molality of hydroxide ion, $m_{\text{OH}^-, \text{tot}}$, it was justified, in view of a previous study³, to assume that nearly all of the hydrogen peroxide in the solution was present in the form of the O_2H^- anion, and that the amount of undissociated H_2O_2 molecules was negligible. As a result of the nearly complete ionization of hydrogen peroxide,



the true molality of the hydroxide ion is

$$m_{\text{OH}^-} = m_{\text{Na}^+} + m_{\text{K}^+} - m_{\text{O}_2\text{H}^-}. \quad (2)$$

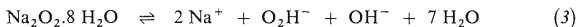
TABLE I

Experimentally determined compositions of saturated solutions of the system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$, calculated solubilities $m_{\text{O}_2\text{H}^-}$,_{calc}, and apparent equilibrium constants K' calculated from experimental data

Saturated solution								Density g cm^{-3}	p	K'
wt. %			mol/kg H_2O							
H_2O_2	KOH	NaOH	OH^-	K^+	Na^+	O_2H^- _{exp}	O_2H^- _{calc}			
30°C										
0.65	21.11	11.69	9.76	5.65	4.39	0.29	0.16	1.3336	1.29	54.10
1.28	21.21	9.13	8.32	5.53	3.34	0.55	0.34	1.3006	1.66	51.25
2.38	18.53	7.83	6.40	4.63	2.75	0.98	0.82	1.2714	1.69	47.46
6.57	15.27	7.28	4.08	4.25	2.84	3.01	3.84	1.2457	1.50	99.13
11.08	17.13	7.34	2.53	4.74	2.85	5.06	4.45	1.2419	1.66	103.58
3.76	22.04	6.41	6.53	5.79	2.36	1.63	0.99	1.2835	2.45	59.47
3.98	21.85	6.29	6.33	5.74	2.32	1.72	1.12	1.2695	2.48	58.43
8.30	19.96	6.13	4.04	5.50	2.26	3.72	2.90	1.2716	2.43	76.90
10.35	22.14	5.94	3.88	6.41	2.41	4.94	4.93	1.2957	2.66	111.29
11.38	20.87	6.28	3.16	5.05	2.55	5.44	5.03	1.2770	2.37	112.03
20°C										
0.27	20.68	12.09	9.90	5.51	4.51	0.12	0.07	1.3344	1.22	23.69
0.61	21.49	8.56	8.35	5.52	3.09	0.26	0.19	1.2975	1.79	20.53
1.54	19.85	6.15	6.38	4.88	2.12	0.62	0.64	1.2817	2.30	17.90
3.72	16.31	5.64	4.34	3.91	1.90	1.47	(0.97)	1.2274	2.06	22.96
5.35	18.33	5.41	4.29	4.61	1.91	2.22	2.98	1.2395	2.42	34.62
9.32	16.67	5.79	2.46	4.35	2.12	4.01	3.65	1.2405	2.05	44.59
10.37	17.79	5.17	2.12	4.76	1.94	4.57	3.38	1.2318	2.45	36.47
13.89	15.72	6.98	0.73	4.42	2.75	6.44	5.47	1.2390	1.61	39.49
2.97	23.22	4.74	6.45	5.99	1.72	1.26	0.94	1.2835	3.49	23.92
3.09	22.94	4.77	6.32	5.91	1.72	1.31	0.95	1.2745	3.43	24.61
9.03	21.08	4.72	3.50	5.77	1.81	4.08	4.08	1.2694	3.19	46.74
9.42	23.71	4.06	3.94	6.73	1.62	4.41	4.27	1.2910	4.16	45.35
7.26	22.95	4.07	4.52	6.22	1.55	3.25	3.03	1.2765	4.02	35.21
12°C										
0.11	19.31	13.85	10.30	5.16	5.19	0.05	0.03	1.3468	0.99	12.89
0.24	20.86	9.74	8.80	5.38	3.52	0.10	0.07	1.3062	1.53	11.04
1.04	19.95	5.57	6.32	4.84	1.90	0.42	0.41	1.2978	2.56	9.46
2.64	16.55	4.88	4.47	3.89	1.61	1.02	1.08	1.2194	2.42	11.82
3.68	20.11	3.68	4.72	4.94	1.27	1.49	—	1.2363	3.90	11.35
6.21	17.66	4.28	3.33	4.38	1.49	2.54	2.58	1.2307	2.94	18.80
7.39	18.77	3.92	3.08	4.78	1.40	3.11	2.57	1.2315	3.41	18.82
8.56	17.17	4.13	2.25	4.36	1.47	3.59	2.39	1.2307	2.96	17.50
2.52	23.77	3.94	4.30	6.07	1.41	1.06	0.69	1.2755	4.30	13.56
2.45	23.36	3.88	4.29	5.90	1.38	0.94	0.80	1.2757	4.29	11.22
10.13	20.76	4.33	2.79	5.71	1.67	4.60	5.12	1.2665	3.42	35.80
8.75	24.20	3.24	4.00	6.77	1.27	4.04	4.48	1.2902	5.32	26.13
6.28	23.59	3.27	4.75	6.29	1.22	2.76	3.49	1.2736	5.14	19.62

The molalities of the individual ions calculated in this way are also included in Table I.

At this point, it should be pointed out that in the treatment of the solubility data¹ for the system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$, due allowance was not made for enrichment of the system with water generated from hydrogen peroxide in accordance with Eq. (1), and the molalities m_{Na^+} and $m_{\text{O}_2\text{H}^-}$ were identified with the total molalities $m_{\text{NaOH}, \text{tot}}$ and $m_{\text{H}_2\text{O}_2, \text{tot}}$, respectively. Consequently, the originally calculated¹ values of the apparent equilibrium constant, K' , for the dissolution of sodium peroxide octahydrate



$$K' = m_{\text{Na}^+}^2 \cdot m_{\text{O}_2\text{H}^-} \cdot m_{\text{OH}^-} \quad (4)$$

are subject to some error whose magnitude depends on the total alkalinity, and primarily on the total hydrogen peroxide content of the solution. For very low hydrogen peroxide content, however, the differences between $m_{\text{O}_2\text{H}^-}$ and $m_{\text{H}_2\text{O}_2, \text{tot}}$, or between m_{Na^+} and $m_{\text{NaOH}, \text{tot}}$ are very small.

On recalculation of the analytical data as presented in the previous paper¹ to the true molalities of the individual ions, the dependence of the apparent equilibrium constant K' on the molality of O_2H^- ions in the system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$ in the temperature range 0–40°C may be expressed with sufficient accuracy by the relation

$$K' = K'_0(1 + 0.3385m_{\text{O}_2\text{H}^-} + 0.05937m_{\text{O}_2\text{H}^-}^2). \quad (5)$$

The dependence of the apparent equilibrium constant K'_0 , obtained by extrapolation to infinitely low concentration of O_2H^- ions in saturated solution, on temperature in the above specified range is expressed by the relation

$$\log K'_0 = 10.7706 - 2.2765/T. \quad (6)$$

The temperature dependence of the solubility of pure sodium peroxide octahydrate in water, where in consequence of the dissolution reaction (3) it holds

$$m_{\text{Na}^+} = 2m_{\text{O}_2\text{H}^-} = 2m_{\text{OH}^-} = 2m_{\text{sat}}, \quad (7)$$

is expressed by the relation

$$4m_{\text{sat}}^2/K'_0 - 0.05937m_{\text{sat}}^2 - 0.3385m_{\text{sat}} - 1 = 0 \quad (8)$$

which has been obtained by combining Eqs (4), (5), and (7). Substituting into Eq. (8) K'_0 values as calculated from Eq. (6) for the individual temperatures, we obtained solubilities of $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in mol kg^{-1} , which are listed in Table II. Also included

in the table are the values of the solubility product, K_s , defined¹, on the basis of Eqs (3) and (4), as $K_s = 4m_{\text{sat}}^4$. The temperature dependence of this quantity is expressed as

$$\log K_s = 12.46966 - 3.19974/T. \quad (9)$$

The data presented here are to replace those published in the previous paper¹, as the former result from a more accurate treatment of the previously determined data on the solubility in the system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$. The basic analytical data on the compositions of saturated solutions in terms of wt. % NaOH_{10t} and $\text{H}_2\text{O}_{2,10t}$, as reported in ref.¹, remain unchanged.

The evaluation of the solubility data for the multicomponent system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ is based on the same assumption that the solubility equilibrium is determined by the equilibrium constant of reaction (3). With respect to the above given condition, *i.e.*, $m_{\text{H}_2\text{O}_2,10t} < m_{\text{OH}^-,10t}$, however, the concentration of the OH^- ions is given by Eq. (2). Substituting this equation into Eq. (4) for the apparent equilibrium constant yielded K' values for the individual saturated solutions at a given temperature, which are also listed in Table I. The dependence of K' on the true molality of O_2H^- ions is shown in Fig. 1 from which it is seen that the experimental points follow essentially the same trend as found for the basic ternary system¹ (denoted by full lines) but there is not a quantitative agreement. Though there is a greater scatter in the experimental data for the quaternary system as compared to the ternary system, which is due to the different molar ratio of potassium to sodium ions as a result of the above mentioned impoverishment of the solution with respect to sodium ions, and to the lower accuracy of the analytical determina-

TABLE II

Values of characteristic solubility quantities for $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in the temperature range 0 to 40°C

$t, ^\circ\text{C}$	K'_0	m_{sat}		K_s	
		a	b	a	b
0	4.035	1.098	1.092	5.824	5.694
10	9.222	1.382	1.386	14.581	14.763
12	10.805	1.445	1.451	17.425	17.718
20	19.922	1.720	1.730	35.022	35.863
30	40.904	2.122	2.129	81.242	82.167
40	80.212	2.601	2.585	183.046	178.549

^a Calculated from Eq. (8), ^b calculated from Eq. (9).

tion of the ratio of the alkali metal ions by flame photometry, it is obvious that the deviations from the curves for the ternary system arise from the presence of potassium ions in the saturated solutions. Therefore, it seems justified to assume that the deviations reflecting the effect of potassium ions on the value of the apparent equilibrium constant K' may be described by an empirical equation, which has been found to be of the form

$$K' / (K'_0(1 + 0.3385m_{\text{O}_2\text{H}^-} + 0.05937m_{\text{O}_2\text{H}^-}^2)) = 1 - 0.053m_{\text{K}^+} \quad (10)$$

Here, the denominator on the left-hand side represents the value of the apparent equilibrium constant for the basic ternary system at an actual molality of O_2H^- ion and temperature considered (Eqs (5) and (6)). Owing to the relatively low accuracy in determining the potassium-to-sodium concentration ratio in saturated solutions by flame photometry the coefficient on the right-hand side of Eq. (10) exhibits a rather large standard deviation (0.053 ± 0.030).

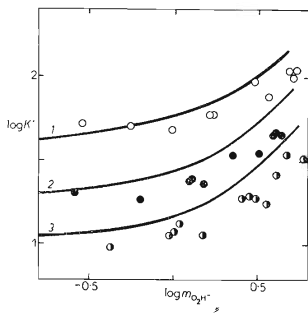


FIG. 1

The apparent equilibrium constant K' as a function of the molality $m_{\text{O}_2\text{H}^-}$. Full curves calculated on the basis of Eq. (10) (—) for the system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$ for 30 (1), 20 (2), and 12°C (3); experimentally obtained values for the system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ at 30 (○), 20 (●), and 12°C (●)

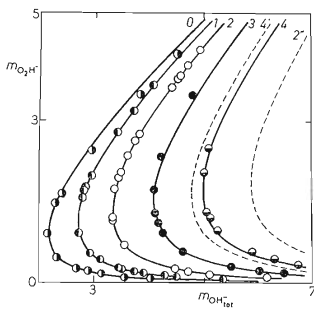


FIG. 2

Experimental and calculated (—) solubility curves for $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in the system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$ at 0 (0), 10 (1), 20 (2), 30 (3), and 40°C (4), and calculated solubility curves for the same compound in the system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ at 20°C (----) for molar ratios $p = 1$ (2') and 2 (2')

Combining Eqs (10) and (4) allows one to derive an expression for calculating the solubility curve for $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in terms of the molality $m_{\text{O}_2\text{H}^-}$, applicable at any molar ratio of sodium hydroxide to potassium hydroxide in the mixed system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$. Denoting this ratio as $p = m_{\text{K}^+}/m_{\text{Na}^+}$, and introducing, for the case where $m_{\text{O}_2\text{H}^-} < m_{\text{OH}^-, \text{tot}}$, the relation

$$m_{\text{OH}^-} = (p + 1) m_{\text{Na}^+} - m_{\text{O}_2\text{H}^-}, \quad (11)$$

we obtain a quadratic equation whose roots

$$m_{\text{O}_2\text{H}^-, 1,2} = ((p + 1) m_{\text{Na}^+}^3 - AK'_0(1 + pCm_{\text{Na}^+}) \pm (((p + 1) m_{\text{Na}^+}^3 - AK'_0(1 + pCm_{\text{Na}^+}))^2 - 4K'_0(m_{\text{Na}^+}^2 + BK'_0(1 + pCm_{\text{Na}^+}))(1 + pCm_{\text{Na}^+}))^{0.5}) / (2(m_{\text{Na}^+}^2 + BK'_0(1 + pCm_{\text{Na}^+}))) \quad (12)$$

represent the desired solubility values. The symbols A , B , and C stand for the coefficients of Eq. (10), i.e., $A = 0.3385$, $B = 0.05937$, and $C = -0.053$. Substituting into Eq. (12) K'_0 values obtained from Eq. (6) for the relevant temperatures, we first calculated the solubility curves for $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in the basic system $\text{H}_2\text{O}_2\text{-NaOH-H}_2\text{O}$ (i.e., for $p = 0$) for temperatures of 0, 10, 20, 30, and 40°C. The results are shown in Fig. 2 which provides comparison between the calculated solubility curves for the above temperatures and the experimental data. As can be seen from the figure, Eq. (12) gives a very good fit to the experimental data¹.

The extent of agreement between the solubility data calculated from Eq. (12) and the experimentally obtained values for the quaternary system is demonstrated in Table I which includes values of the quantities $m_{\text{O}_2\text{H}^-, \text{calc}}$ and $m_{\text{O}_2\text{H}^-, \text{exp}}$. Comparison of the corresponding pairs reveals that the agreement is less satisfactory than in the case of the basic ternary system, as has been discussed earlier. This is also reflected in the large standard deviation for the coefficient C .

Fig. 2 also shows the calculated solubility curves for $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ in the quaternary system $\text{H}_2\text{O}_2\text{-NaOH-KOH-H}_2\text{O}$ at 20°C for molar ratio values p equal to 1 and 2 (dashed lines). It is seen from the figure that as the potassium-to-sodium molar ratio is increased, the crystallization region of $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ diminishes, or in other words, at the same total alkalinity of the solution, given for the mixed system by the expression

$$m_{\text{OH}^-, \text{tot}} = m_{\text{Na}^+} + m_{\text{K}^+} = (1 + p) m_{\text{Na}^+}, \quad (13)$$

the solubility of $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ quite markedly increases. For example, for $p = 1$, i.e. for mixed solutions of sodium hydroxide and potassium hydroxide of a molar ratio of 1 : 1, the increase in the solubility at 20°C is nearly equivalent to that induced

in the basic ternary system by a temperature increase to about 38°C . This means that the use of mixed $\text{NaOH} + \text{KOH}$ solutions of a total alkalinity $c_{\text{OH}^-} = 2 \text{ mol} \cdot \text{dm}^{-3}$ and molar ratio p as 1 should permit smooth operation of the electrolytic preparation of hydrogen peroxide by cathodic reduction of oxygen, and that it should do so at degrees of conversion of OH^- to O_2H^- as high as 0.7 to 0.8. This conclusion has been fully confirmed by experimental studies on the preparation of hydrogen peroxide in a laboratory-scale continuously working electrolyzer⁴. By contrast, the use of solutions of sodium hydroxide alone of the same concentration resulted, under otherwise the same conditions, in disintegration of the carbonaceous cathodes after several tens to hundreds of hours of operation.

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Translated by M. Škubalová.