Phase Equilibria in the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ System

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Equilibrium data for the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ quaternary system from (313 to 393) K were measured, and the phase diagram at 393 K was constructed, with the crystallization areas in the phase diagram discussed in detail. In addition, the solubility isotherms of Na_2CrO_4 and $NaNO_3$ in NaOH solutions were plotted. The solubility of Na_2CrO_4 in NaOH solutions was compared with that in NaOH solutions saturated with $NaNO_3$. On the basis of the phase diagram, a strategy for effective separation of Na_2CrO_4 and $NaNO_3$ from the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ quaternary system has been proposed.

Introduction

Sodium chromate is an important alkali metal chromate for the production of other chromium chemicals, such as sodium dichromate, CrO_3, and Cr_2O_3. In industry, sodium chromate is mainly produced from chromite ore. Traditionally, chromite ore is processed by roasting with sodium carbonate at 1473 K in a rotary kiln with the addition of limestone and dolomite, yielding only 75 % of the Cr in the ore to sodium chromate. Furthermore, the residue discharged [(2.5 to 3.0) ton per ton of chromate product] contains hexavalent chromium causing significant environmental pollution.[1−3]

Recently, a novel cleaner process[1−4] of oxidizing chromite ore using a high-concentration potassium hydroxide solution by air was proposed by the Institute of Process Engineering, Chinese Academy of Sciences. In this process, the Cr yield could be raised to 99 % at a temperature of 573 K with an alkali-to-ore ratio of 4:1. To separate K_2CrO_4 from the leaching liquor, the phase equilibria of $KOH-K_2CO_3-K_2CrO_4-H_2O$[5] and $K_2CO_3-K_2CrO_4-H_2O$[6] have been studied, though the process can only produce potassium-containing chromate products (such as K_2CrO_4 and $K_2Cr_2O_7$) instead of sodium chromate and dichromate as products, which have a larger utilization than potassium-containing products in industry.

An optimized process production of sodium chromate by oxygen has been proposed. The tests were executed by introducing $NaNO_3$ to the decomposition process of chromite ore in molten NaOH to decrease the decomposition temperature. After the residue was leached and filtered, separation of Na_2CrO_4 crystals from the leaching liquor would be carried out. The leaching liquor mainly consists of NaOH, $NaNO_3$, Na_2CrO_4, and H_2O. In this regard, it is necessary to study the phase diagram of the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ quaternary system to get a separation method of Na_2CrO_4, $NaNO_3$, and NaOH.

So far, the phase equilibria of the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ quaternary system have not been reported. However, some research has been done regarding the phase diagrams of the ternary subsystems of the $NaOH-NaNO_3-Na_2CrO_4-H_2O$ quaternary system. The phase equilibria of the $NaOH-Na_2CrO_4-H_2O$ ternary system at (288, 298, 308, and 318) K have been reported by Kashiwase,[7] and at (313 and 353) K by Zou.[8] The $NaOH-NaNO_3-H_2O$ ternary system from (273 to 398) K[9,10] and the $NaNO_3-Na_2CrO_4-H_2O$ ternary system from (254.5 to 371.5) K[10] have also been studied.

Experimental Section

Apparatus and Reagents. A HZQ-type thermostatic vibrator with a temperature control (precision of 0.1 K) was used to prepare the samples to equilibrium states. The concentration of sodium chromate in all samples was determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, PE Optima 5300DV, Perkin-Elmer). The concentration of sodium nitrate was analyzed using ion chromatography (Dionex DX-500). The solid-phase analysis was done by X-ray diffraction (XRD, Phillips PW223/30).

The chemicals used in the experiments are all of analytical grade, and deionized water is used in all the experiments.

Experimental Method. The solubility was determined employing the isothermal solution saturation method.[11] A predetermined amount of sodium hydroxide, tetrahydrate sodium chromate, and sodium nitrate was mixed homogenously in a given amount of water before being put into sealed polyethylene bottles, and then the bottles were placed in the thermostatic vibrator. The experiments were performed at ambient pressure, and the temperature was fixed at five specific values: (313, 333, 353, 373, and 393) K. The liquid phase of each sample was examined every two days, and an equilibrium state was believed to be achieved when the liquid phase components became stable. After equilibrium was attained, the shaking was discontinued, and then the samples were allowed to settle for one day before further treatment and analysis.

The content of sodium chromate in the liquid phase was determined using ICP-OES by measuring the content of chromium. The content of sodium nitrate was determined using ion chromatography by analyzing NO_3^-. For each sample, about 1 mL of aqueous phase was filtered, weighed, and diluted into a 100 mL volumetric flask. For the determination of chromium contents, 2 mL of the previously diluted solution was further diluted 50 times after addition of 2 mL of concentrated

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Table 1. Solubility Data of the NaOH−$NaNO_3$−Na_2CrO_4−H_2O System

composition of the liquid phase, g/100 g of dry salt				
NaOH	$NaNO_3$	Na_2CrO_4	H_2O	equilibrium solid phase
			t = 393 K	
0.00	51.84	48.16	47.11	$NaNO_3 + Na_2CrO_4$
6.09	48.81	45.10	44.61	$NaNO_3 + Na_2CrO_4$
15.99	48.36	35.65	52.06	$NaNO_3 + Na_2CrO_4$
25.72	48.09	26.19	57.51	$NaNO_3 + Na_2CrO_4$
31.48	47.57	20.95	56.6	$NaNO_3 + Na_2CrO_4$
36.9	46.64	16.46	58.29	$NaNO_3 + Na_2CrO_4$
40.65	45.71	13.64	51.52	$NaNO_3 + Na_2CrO_4$
47.39	41.53	11.08	48.46	$NaNO_3 + Na_2CrO_4$
55.98	34.38	9.64	33.25	$NaNO_3 + Na_2CrO_4$
84.67	13.58	1.75	26.70	$NaOH·H_2O + Na_2CrO_4 + NaNO_3$
89.64	10.36	0.00	21.64	$NaOH·H_2O + NaNO_3$
96.02	0.00	3.98	55.35	$NaOH·H_2O + Na_2CrO_4$
			t = 373 K	
0.00	42.6	57.4	55.8	$NaNO_3 + Na_2CrO_4$
6.84	38.34	54.82	70.9	$NaNO_3 + Na_2CrO_4$
18.04	39.11	42.85	69.88	$NaNO_3 + Na_2CrO_4$
21.5	39.2	39.3	67.48	$NaNO_3 + Na_2CrO_4$
29.88	38.78	31.34	67.96	$NaNO_3 + Na_2CrO_4$
36.49	39.12	24.39	67.78	$NaNO_3 + Na_2CrO_4$
44.38	37.55	18.07	65.6	$NaNO_3 + Na_2CrO_4$
51.43	35.15	13.42	62.54	$NaNO_3 + Na_2CrO_4$
59.28	31.92	8.8	41.93	$NaNO_3 + Na_2CrO_4$
87.57	11.26	1.17	27.14	$NaOH·H_2O + Na_2CrO_4 + NaNO_3$
90.45	9.55	0	24.59	$NaOH·H_2O + NaNO_3$
98.27	0.00	1.73	49.68	$NaOH·H_2O + Na_2CrO_4$
			t = 353 K	
0.00	32.49	67.51	59.85	$NaNO_3 + Na_2CrO_4$
7.01	31.53	61.46	68.37	$NaNO_3 + Na_2CrO_4$
20.16	31.24	48.6	71.46	$NaNO_3 + Na_2CrO_4$
32.67	32.06	35.27	76.19	$NaNO_3 + Na_2CrO_4$
40.84	32.26	26.9	75.56	$NaNO_3 + Na_2CrO_4$
55.06	30.19	14.75	67.56	$NaNO_3 + Na_2CrO_4$
64.64	27.09	8.27	45.09	$NaNO_3 + Na_2CrO_4$
89.12	10.14	0.74	29.08	$NaOH·H_2O + Na_2CrO_4 + NaNO_3$
90.99	9.01	0.00	21.53	$NaOH·H_2O + NaNO_3$
98.76	0.00	1.24	47.92	$NaOH·H_2O + Na_2CrO_4$
			t = 333 K	
0.00	27.96	72.04	76.20	$NaNO_3 + Na_2CrO_4·4H_2O$
11.53	24.47	63.99	83.25	$NaNO_3 + Na_2CrO_4·4H_2O$
20.14	21.85	58.01	83.91	$NaNO_3 + Na_2CrO_4·4H_2O$
25.13	22.21	52.66	87.73	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
34.94	22.76	42.30	88.46	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
45.48	22.76	31.76	89.61	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
56.05	22.55	21.40	86.51	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
62.52	21.84	15.64	83.18	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
70.35	19.95	9.71	71.28	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
74.43	18.82	6.75	59.50	$NaNO_3 + Na_2CrO_4·4H_2O + Na_2CrO_4$
92.14	6.25	1.61	48.78	$NaOH·H_2O + Na_2CrO_4 + NaNO_3$
92.21	7.79	0.00	56.26	$NaOH·H_2O + NaNO_3$
97.56	0.00	2.44	58.07	$NaOH·H_2O + Na_2CrO_4$
			t = 313 K	
0.00	28.29	71.71	81.47	$NaNO_3 + Na_2CrO_4·4H_2O$
30.76	15.82	53.43	98.66	$NaNO_3 + Na_2CrO_4·4H_2O$
37.86	14.71	47.43	96.16	$NaNO_3 + Na_2CrO_4·4H_2O$
49.71	15.52	34.77	97.28	$NaNO_3 + Na_2CrO_4·4H_2O$
61.18	15.30	23.52	95.26	$NaNO_3 + Na_2CrO_4·4H_2O$
71.35	14.85	13.79	89.76	$NaNO_3 + Na_2CrO_4·4H_2O$
81.06	13.42	5.52	67.62	$NaNO_3 + Na_2CrO_4·4H_2O$
85.31	9.16	5.53	62.90	$NaOH·H_2O + Na_2CrO_4 + NaNO_3$
91.30	8.70	0.00	61.43	$NaOH·H_2O + NaNO_3$
93.62	0.00	6.38	71.10	$NaOH·H_2O + Na_2CrO_4$

hydrochloric acid. The same dilution methods were used for the determination of sodium nitrate except for the addition of concentrated hydrochloric acid. Sodium hydroxide was determined by titration using hydrochloric acid solution with phenolphthalein solution as the indicator. The equilibrium solid phase was dried in desiccators at room temperature and then grinded to powder in a mortar. The powder was analyzed by an X-ray diffraction analyzer to determine the composition of the equilibrium solid phase.

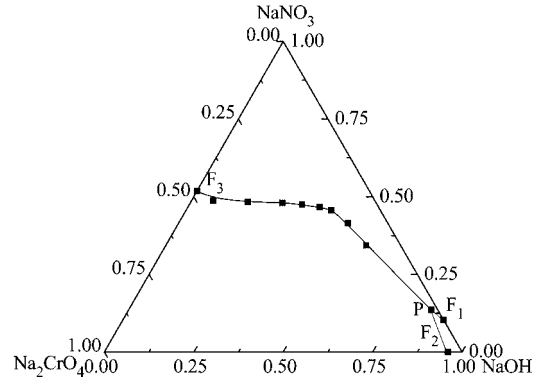

Figure 1. Phase diagram of the NaOH−$NaNO_3$−Na_2CrO_4−H_2O system at 393 K. Point P is the invariant point, and points F_1, F_2, and F_3 represent the equilibrium composition of the solid phases at the two extremes of the corresponding side, respectively.

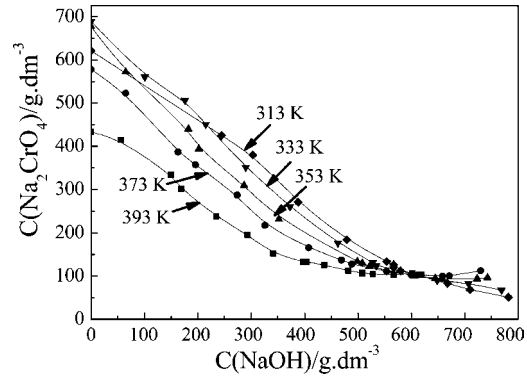

Figure 2. Solubility isotherms of Na_2CrO_4 in $NaNO_3$-saturated NaOH solution.

All the solubility data were the average values of three measurements, with the relative standard deviation (RSD) values of less than 2 %.

Results and Discussion

NaOH−$NaNO_3$−Na_2CrO_4−H_2O Quaternary System. The solubility data for the NaOH−$NaNO_3$−Na_2CrO_4−H_2O quaternary system at (313, 333, 353, 373, and 393) K were measured and are presented in Table 1. The phase diagram at 393 K is plotted in Figure 1. The phase diagrams at the other temperatures are similar to that at 393 K and are therefore not shown in this paper.

Figure 1 shows that the NaOH−$NaNO_3$−Na_2CrO_4−H_2O quaternary system has three crystallization zones, which are the Na_2CrO_4 crystallization zone, the $NaNO_3$ crystallization zone, and the $NaOH·H_2O$ crystallization zone. It suggests that Na_2CrO_4 and $NaNO_3$ can be easily separated from NaOH aqueous solution. The phase diagram provides a theoretical basis for the separation of Na_2CrO_4 from the system.

Solubility Isotherms of Na_2CrO_4 from (313 to 393) K. As shown in Figure 2, the solubility isotherms of Na_2CrO_4 decline sharply with an increase of the concentration of NaOH when $NaNO_3$ is saturated. That is, the salting-out effect of NaOH on Na_2CrO_4 is strong. It can also be seen from Figure 2 that the solubility of Na_2CrO_4 decreases significantly with an increase of temperature when the concentration of NaOH is below 600 $g·dm^{-3}$. On the contrary, the solubility of Na_2CrO_4 increases when the concentration of NaOH is higher than 600 $g·dm^{-3}$. Generally, the solubility of Na_2CrO_4 increases with the increase of temperature.[7,8] The unusual phenomena of the solubility of Na_2CrO_4 in NaOH solutions saturated with $NaNO_3$ may be due to the strong decrease of the $NaNO_3$ solubility with the decrease of temperature, which will be revealed in the next section.

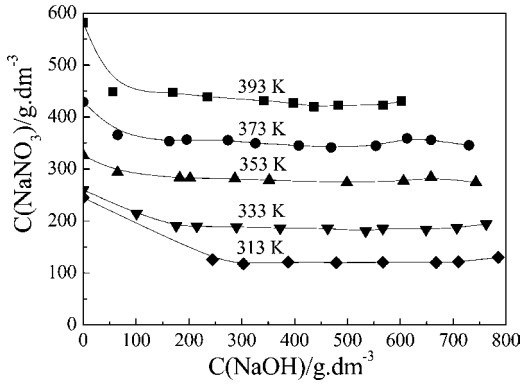

Figure 3. Solubility isotherms of $NaNO_3$ in Na_2CrO_4-saturated NaOH solution.

Table 2. Comparison of Solubility of Na_2CrO_4 in NaOH Solution with that in $NaNO_3$-Saturated NaOH Solution at 353 K

solubility in NaOH aqueous without $NaNO_3$ coexistence		solubility in NaOH aqueous saturated with $NaNO_3$	
c/g·dm^{-3}		c/g·dm^{-3}	
NaOH	Na_2CrO_4	NaOH	Na_2CrO_4
0.00	887.33	0.00	676.97
83.00	775.73	65.16	571.67
98.00	760.15	182.45	439.89
166.00	641.77	202.00	393.78
229.00	538.97	286.70	309.42
276.00	479.77	351.86	231.72
290.00	457.97	499.13	133.77
330.00	408.12	508.25	130.44
417.00	314.66	521.28	121.69
464.00	264.81	605.99	99.97
502.00	234.59	645.08	94.83
570.00	196.27	658.12	92.75
604.00	176.02	723.28	93.77
629.00	164.18	729.79	93.43
642.00	162.62	742.82	96.39
678.00	153.28		

From the above analysis, Na_2CrO_4 can be separated efficiently by evaporation crystallization from the NaOH−$NaNO_3$−Na_2CrO_4−H_2O system.

Solubility Isotherms of $NaNO_3$ from (313 to 393) K. Figure 3 shows the solubility isotherms of $NaNO_3$ in Na_2CrO_4-saturated NaOH solution from (313 to 393) K. As shown in Figure 3, the solubility of $NaNO_3$ decreases strongly with a decrease of temperature. Compared with the sharp decline of solubility isotherms of Na_2CrO_4, the concentration of NaOH has a slight influence on the solubility isotherms of $NaNO_3$.

The results indicate that $NaNO_3$ can be separated from the NaOH−$NaNO_3$−Na_2CrO_4−H_2O system by cooling crystallization due to the sensitivity of solubility to temperature. Na_2CrO_4 will not crystallize together with $NaNO_3$ when the system is cooled due to the increase of the solubility of Na_2CrO_4. It supplies the basis for the efficient separation of $NaNO_3$.

Comparison of the Solubility of Na_2CrO_4 in NaOH Solution with that in $NaNO_3$-Saturated NaOH Solution. The solubility data of Na_2CrO_4 in NaOH solution and in $NaNO_3$-saturated NaOH solution at 353 K are presented in Table 2, and the isotherms are plotted in Figure 4. As shown in Table 2 and Figure 4, compared with NaOH solutions without $NaNO_3$, the solubility of Na_2CrO_4 in $NaNO_3$-saturated NaOH solutions decreases significantly at 353 K. There are similar results at other temperatures.

That is, a higher crystallization ratio of Na_2CrO_4 in the NaOH−$NaNO_3$−Na_2CrO_4−H_2O system will be attained compared with the NaOH−Na_2CrO_4−H_2O system.

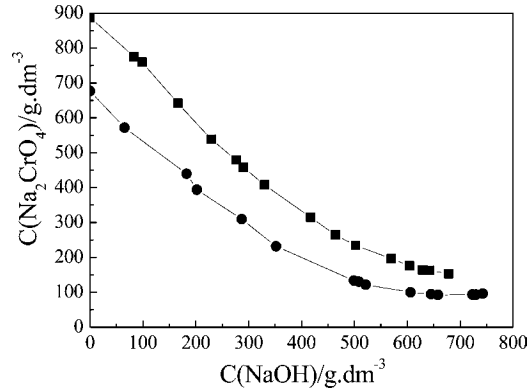

Figure 4. Solubility isotherms of Na_2CrO_4 at 353 K: ■, in NaOH solution; ●, in $NaNO_3$-saturated NaOH solution.

Conclusion

Phase equilibria for the NaOH−$NaNO_3$−Na_2CrO_4−H_2O quaternary system from (313 to 393) K were studied. The phase diagrams of the system and the solubility isotherms of Na_2CrO_4 and $NaNO_3$ were plotted. This study provides a theoretical basis for the separation of Na_2CrO_4 and $NaNO_3$ from NaOH solutions. The results show that the solubility isotherms of Na_2CrO_4 decline sharply with an increase of the concentration of NaOH when $NaNO_3$ is saturated, and evaporation crystallization is a highly efficient way to separate most of the Na_2CrO_4 from the liquor. The solubility of $NaNO_3$ decreases strongly with a decrease of temperature, and a large mass of $NaNO_3$ can be separated by cooling crystallization.

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