Solid−Liquid Equilibria of $K_2CO_3 + K_2CrO_4 + H_2O$ System

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Solubility data for the $K_2CO_3 + K_2CrO_4 + H_2O$ system at 40 °C, 60 °C, 80 °C, and 100 °C were determined, and the phase diagram at 100 °C was constructed. Furthermore, the crystallization areas in the phase diagram were elaborately analyzed and discussed. On the basis of the solubility data, a separation method of potassium chromate from the $K_2CO_3 + K_2CrO_4 + H_2O$ system for the cleaner production of potassium dichromate by carbonating process using carbon dioxide was evaluated.

Introduction

Hexavalent chromium compounds, such as alkali metal chromates and bichromates, find wide applications in many industries, including metal plating, leather tanning, and pigment manufacturing. They are typically produced from chromite ($FeO \cdot Cr_2O_3$). In the traditional production process based on the oxidative roasting of chromium ore with alkali metal carbonate, limestone, and dolomite additives, large amounts of residues with high Cr^{6+} content are discharged. The environmental problems resulted from the traditional process have spawned wide public concerns. Recently, a new cleaner manufacturing process for chromium compounds has been developed.[1,2]

In the green process, the crystalline product $K_2Cr_2O_7$ is produced from K_2CrO_4 by carbonating. To reutilize the caustic potash and unreacted K_2CrO_4, the mother liquid is heated and thus becomes the mixed aqueous solution of K_2CrO_4 and K_2CO_3 by pyrogenation. The phase equilibrium information for the $K_2CO_3 + K_2CrO_4 + H_2O$ system is highly desirable in investigating the separation approaches of K_2CrO_4 from K_2CO_3 aqueous solution.

Some studies have been done on the normal melting points,[3] densities,[3] and solubilities[4] for K_2CrO_4 and K_2CO_3. In Cui and Zhang's paper,[5] the phase equilibrium data for the quaternary system $KOH + K_2CO_3 + K_2CrO_4 + H_2O$ from 20 °C to 80 °C were measured, but the study of the phase equilibria for the boundary ternary system $K_2CO_3 + K_2CrO_4 + H_2O$ has not been reported so far. In this paper, extensive work was carried out on the phase equilibrium for the above system at 40 °C, 60 °C, 80 °C, and 100 °C, and the phase diagram at 100 °C was constructed. The studied system is similar to the $Na_2CO_3 + Na_2CrO_4 + H_2O$ system in compound structure, and the formation of the limited solid solutions at 35 °C for the latter system[6] greatly increases the difficulty in the solid−liquid separation process. Therefore, this work was aimed to find whether solid solutions are formed in the studied system and to further give an evaluation of the separation method based on these results.

Experimental Section

Apparatus and Reagents. An HZS-H type thermostated shaking water bath with a precision of 0.1 °C was used for measurements at 40 °C and 60 °C. A specially designed HZ-9613Y thermostated shaking oil bath with a precision of 0.2 °C was used for measurements at 80 °C and 100 °C. A Rigaku D/max-2400 X-ray diffraction analyzer was used for solid-phase X-ray analysis.

The chemicals used were of analytical grade and produced by the Beijing Chemical Plant. The mass fraction purities of potassium chromate and potassium carbonate are no less than 99.5 %.

Experimental Method. The solubility was determined by employing the method of isothermal solution saturation,[7] and the solid phase was determined by Screinemaker's method[7] and rechecked by an X-ray diffraction method. The experiments were performed according to the following procedures: (a) The experimental system prepared according to a specified component ratio was placed in the corresponding shaking bath. The experiments were performed at ambient pressure, and the temperature was fixed at four specific values: 40 °C, 60 °C, 80 °C, and 100 °C. (b) Sampling was performed at 2-h intervals until equilibrium was attained. If two analyses gave identical results, it was assumed that the equilibrium had been reached. The samples were always shaken for at least 24 h and then allowed to stand for at least 12 h, which enables the suspended crystals to be fully sedimented. (c) After equilibrium, the liquid phase and solid phases with a little of saturated liquid were taken out and then quantitative analyzed. (d) The equilibrium solid phases were dried in a desiccator at room temperature, pestled into powder, and then analyzed by X-ray diffraction analyzer. The chromate ion CrO_4^{2-} was titrated using *N*-phenylanthranilic acid solution as indicator (with a mass fraction uncertainty of 0.1 mass %), the carbonate ion CO_3^{2-} was determined by hydrochloric acid solution using phenolphthalein solution as the indicator (with a mass fraction uncertainty of 1.5 %), and the potassium ion K^+ was analyzed by a gravimetric method (with a mass fraction uncertainty of 0.6 %). All titrations were performed three times, and the amount of sample was chosen for a required titrant volume more than 5 mL. Points in Table 1 give the mean values of the triplicate titration results.

Results and Discussion

The equilibrium data of the $K_2CO_3 + K_2CrO_4 + H_2O$ system at 40 °C, 60 °C, 80 °C, and 100 °C were determined and are presented in Table 1. The phase diagram at 100 °C was plotted in Figure 1, and those at 40 °C, 60 °C, and 80 °C are similar to

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Table 1. Equilibrium Data for K_2CO_3 (1) + K_2CrO_4 (2) + H_2O (3) System from 40 °C to 100 °C

composition of liquid phase (mass %)			
$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_3$	equilibrium solid phases
	t = 40 °C		
0.00	40.47	59.53	K_2CrO_4
2.07	38.08	59.85	K_2CrO_4
5.30	33.90	60.80	K_2CrO_4
13.30	25.15	61.55	K_2CrO_4
19.26	18.53	62.21	K_2CrO_4
24.40	13.54	62.06	K_2CrO_4
32.88	6.40	60.72	K_2CrO_4
41.62	1.81	56.57	K_2CrO_4
48.88	0.49	50.63	K_2CrO_4
51.10	0.33	48.57	$K_2CrO_4 + K_2CO_3 \cdot 1.5H_2O$
53.12	0.17	46.71	$K_2CO_3 \cdot 1.5H_2O$
53.90[4]	0.00	46.1	$K_2CO_3 \cdot 1.5H_2O$
	t = 60 °C		
0.00	41.93	58.07	K_2CrO_4
2.80	38.69	58.51	K_2CrO_4
5.36	35.84	58.80	K_2CrO_4
7.92	32.94	59.14	K_2CrO_4
13.50	27.20	59.30	K_2CrO_4
20.00	20.56	59.44	K_2CrO_4
25.70	14.40	59.90	K_2CrO_4
32.44	9.11	58.45	K_2CrO_4
37.55	5.19	57.26	K_2CrO_4
43.35	2.46	54.19	K_2CrO_4
46.17	1.40	52.43	K_2CrO_4
50.21	0.78	49.01	K_2CrO_4
55.48	0.36	44.16	$K_2CrO_4 + K_2CO_3 \cdot 1.5H_2O$
55.90[4]	0.00	44.10	$K_2CO_3 \cdot 1.5H_2O$
	t = 80 °C		
0.00	43.27	56.73	K_2CrO_4
2.30	41.30	56.40	K_2CrO_4
5.79	37.53	56.68	K_2CrO_4
8.58	34.80	56.62	K_2CrO_4
11.27	32.12	56.61	K_2CrO_4
18.11	25.02	56.87	K_2CrO_4
25.48	17.60	56.92	K_2CrO_4
35.73	8.04	56.23	K_2CrO_4
44.46	2.68	52.86	K_2CrO_4
47.70	1.60	50.70	K_2CrO_4
50.55	0.97	48.48	K_2CrO_4
56.54	0.57	42.89	K_2CrO_4
58.47	0.50	41.03	$K_2CrO_4 + K_2CO_3 \cdot 1.5H_2O$
60.90[4]	0.00	39.10	$K_2CO_3 \cdot 1.5H_2O$
	t = 100 °C		
0.00	44.60	55.40	K_2CrO_4 (A)
7.55	37.86	54.59	K_2CrO_4 (A)
10.50	34.80	54.70	K_2CrO_4 (A)
16.05	29.31	54.64	K_2CrO_4 (A)
20.83	24.30	54.87	K_2CrO_4 (A)
24.68	20.76	54.56	K_2CrO_4 (A)
30.04	15.54	54.42	K_2CrO_4 (A)
31.93	13.36	54.71	K_2CrO_4 (A)
35.83	10.16	54.01	K_2CrO_4 (A)
37.73	8.51	53.76	K_2CrO_4 (A)
39.90	6.90	53.20	K_2CrO_4 (A)
42.73	4.51	52.76	K_2CrO_4 (A)
44.46	3.74	51.80	K_2CrO_4 (A)
49.52	1.85	48.63	K_2CrO_4 (A)
51.33	1.60	47.07	K_2CrO_4 (A)
51.78	1.48	46.74	K_2CrO_4 (A)
55.31	0.96	43.73	K_2CrO_4 (A)
58.51	0.67	40.82	K_2CrO_4 (A) + $K_2CO_3 \cdot 1.5H_2O$ (C)
60.90[4]	0.00	39.10	$K_2CO_3 \cdot 1.5H_2O$ (C)

that in Figure 1. The solubility data saturated with solid K_2CrO_4 were also plotted in Figure 2.

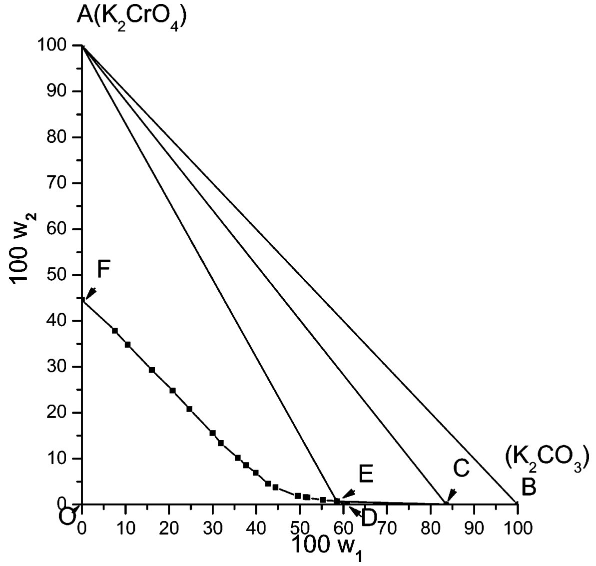

Figure 1. Phase diagram of the K_2CO_3 (1) + K_2CrO_4 (2) + H_2O(3) system at 100 °C.

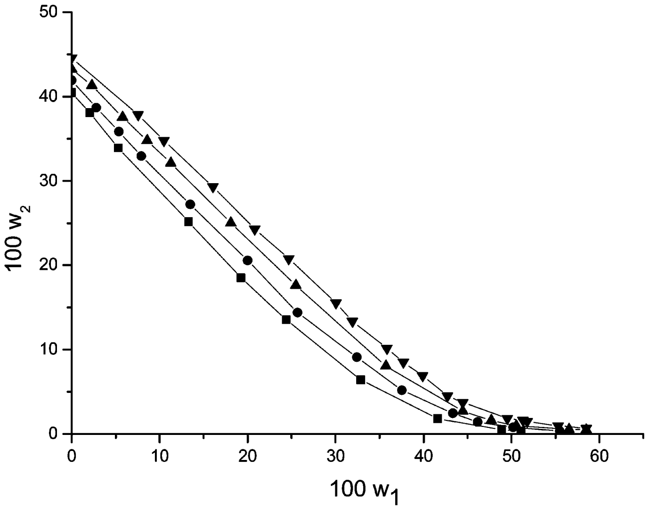

Figure 2. Solubility isotherms of K_2CrO_4 (2) in K_2CO_3 (1) aqueous solution respectively, ■, at 40 °C; ●, at 60 °C; ▲, at 80 °C; ▼, and at 100 °C.

Phase Diagram for the K_2CO_3 + K_2CrO_4 + H_2O System at 100 °C. In Figure 1, points A, B, and C represent the solids K_2CrO_4, K_2CO_3, and $K_2CO_3 \cdot 1.5H_2O$, respectively. Points D, E, and F are all located on the saturated liquid line. Points F and D show the solubilities of K_2CrO_4 and K_2CO_3, respectively.

Curves FE and ED indicate the compositions of saturated ternary solutions that are in equilibrium with the solids K_2CrO_4 (A) and $K_2CO_3 \cdot 1.5H_2O$ (C), respectively. There is no solubility line saturated with anhydrous potassium carbonate (K_2CO_3) (B). Point E is an invariant point saturated with the coexisting solids K_2CrO_4 (A) and $K_2CO_3 \cdot 1.5H_2O$ (C) whose composition is shown in Table 1. As seen in Figure 1, it is clear that the ternary system does not form a solid solution.

Figure 1 shows that the crystallization zone of K_2CrO_4 is far larger than that of $K_2CO_3 \cdot 1.5H_2O$. Therefore, K_2CrO_4 is very easily separated out from the system. The area AECBA is the all solids phase region, and the area FEDOF is the unsaturated solution region.

Solubility Isotherms of K_2CrO_4 from 40 °C to 100 °C. As can be seen in Figure 2, the solubility isotherms of K_2CrO_4 decline sharply with the increase of the concentration of K_2CO_3. That is, the salting-out effect of K_2CO_3 on K_2CrO_4 is very strong. It can be also concluded from these isotherms that the solubility of K_2CrO_4 decreases slightly with the decrease of the temperature, especially for the aqueous solution with high concentrations of K_2CO_3. Obviously, evaporating crystallization is a preferential way to separate out most of the K_2CrO_4.

Conclusions

Phase equilibria for the ternary $K_2CO_3 + K_2CrO_4 + H_2O$ system between 40 °C and 100 °C were studied, and the phase diagram and solubility isotherms were plotted. The experimental results show that the system does not form solid solutions, the salting-out effect of K_2CO_3 on K_2CrO_4 is very strong, and evaporating crystallization is a preferential and highly efficient way to separate most of K_2CrO_4 from the system.

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