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Solubility Data in the System $KCl + K_2CrO_4 + H_2O$

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Solubility data for the $KCl + K_2CrO_4 + H_2O$ system at 30 °C, 60 °C, and 90 °C were determined, and the phase diagrams were constructed. In addition, the crystalline areas in the phase diagrams were analyzed and discussed. On the basis of the solubility data, a method of separating potassium chromate from the $KCl + K_2CrO_4 + H_2O$ system in a new, cleaner process of producing potassium chromate was evaluated.

Introduction

Hexavalent chromium compounds are important raw materials in many chemical industries. The traditional manufacturing process is mainly based on the oxidation roasting of chromium ore with sodium carbonate, limestone, and dolomite additives, which brings about a great amount of residues with high chromium content. In order to solve this potentially serious environmental problem, another cleaner manufacturing process for chromium compounds has been developed by the Institute of Process Engineering, Chinese Academy of Sciences. Moreover, because of the whole closed process design, resource utilization efficiency and zero emission of chromium-containing waste residues are achieved in the green process.[1−3]

Recently, the new production technology of chromate from chromite with molten KOH as the reaction medium has been put forward in the clean production of toxic chromium to replace the original NaOH as the reaction medium. After the liquid phase oxidation process of chromite and the separation process of chromate and alkali, excessive potassium hydroxide solution will go back to the process of the liquid phase oxidation. With the recycle of potassium hydroxide, the potassium chloride which is carried in industrial potassium hydroxide will accumulate consistently, so it is of great necessity to control the chlorine ion content in the potassium chromate product in order to improve the product quality. It is important therefore to find crystallization approaches for K_2CrO_4 from mother liquors containing KCl. The phase diagram of the ternary system $KCl + K_2CrO_4 + H_2O$ is required to provide the theoretical basis for any developed crystallization process.

Melting points,[4] densities,[4] and solubility[5] data for K_2CrO_4 and KCl can be found in previous studies. Christov et al. has investigated the solubilities using the Pitzer model of the ternary systems $NaCl + Na_2CrO_4 + H_2O$ and $KCl + K_2CrO_4 + H_2O$ at $T = 298.15$ K.[6] However, the data provided is far from enough to solve the practical separation above, so an extensive study needs to be done. This paper provides the solubility data for the ternary system $KCl + K_2CrO_4 + H_2O$ at 30 °C, 60 °C, and 90 °C.

Experimental Section

Apparatus and Reagents. A HZQ-C type thermostated water bath (CH-2501) with a precision of 0.1 °C and a special designed rotating stainless steel disk were used for the equilibrium measurement. A 1 mL sampler and a precision balance with an uncertainty of 0.001 g were used for density measurements. A water-circulation multifunction vacuum pump was used to separate the solid phases. A Siemens D500 X-ray diffraction analyzer was used for solid-phase X-ray diffraction analysis.

The main chemicals potassium chromate (≥ 99.5 % by mass) and potassium chloride (≥ 99.8 % by mass) used were all of analytical grade and were purchased from the Beijing Chemical Plant.

Experimental Method. The solubility was determined by employing the method of isothermal solution saturation. The experiments were performed according to the following procedure: The experimental components were added into a series of sealed tubes gradually according to a fixed ratio and making sure that one of the components was in excess. Then the disk with the sealed tubes was put into the superthermostatic water bath and rotated continuously at the three specific temperatures: 30 °C, 60 °C, and 90 °C. A pre-experiment showed that equilibrium can be reached in about 3 days to 4 days. In order to guarantee the system reaching the total equilibrium, the stirring lasted for 5 days. After equilibrium, the agitating was stopped and the solution was then allowed to stand for at least 24 h to ensure that all the suspended crystals settled. Then 5 mL of the liquid phase was taken from every tube and analyzed. The denisities of the equilibrium solutions were calculated by weighing 1 mL samples on an electric balance. A small amount of the wet solid phases was weighed and placed in a 100 mL measuring flask, diluted with water to volume, and analyzed by chemical methods. The solid phases were separated quickly by suction filtration with a water-circulation multifunction vacuum pump and dried at room temperature, pestled into powder, and analyzed by X-ray diffraction.

Analytical Method. The chromate ion CrO_4^{2-} was titrated using *N*-phenylanthranilic acid solution as indicator (with a mass uncertainty of 0.5 %),[7] the amount of chloride was found

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Table 1. Solubility Data for the Ternary System KCl (1) + K_2CrO_4 (2) + H_2O (3) from 25 °C to 90 °C

composition of liquid phase (mass %)			ρ	equilibrium solid phases
$100w_1$	$100w_2$	$100w_3$	$kg \cdot dm^{-3}$	
t = 25 °C[6]				
26.2	0	73.8		KCl
19.1	10	70.9		KCl
12.7	19.9	67.4		K_2CrO_4
7.98	26.9	65.12		K_2CrO_4
5.02	31	63.98		K_2CrO_4
3.04	34.9	62.06		K_2CrO_4
0	39.5	60.5		K_2CrO_4
t = 30 °C				
27.11	0.00	72.89		KCl
25.35	3.14	71.51	1.197	KCl
24.55	5.89	69.56	1.173	KCl
23.64	7.81	68.56	1.182	KCl
20.91	12.22	66.87	1.270	KCl
18.63	17.18	64.19	1.281	KCl
15.82	22.65	61.53	1.325	KCl + K_2CrO_4
14.99	23.24	61.77	1.324	K_2CrO_4
10.46	27.98	61.56	1.335	K_2CrO_4
7.37	31.54	61.09	1.346	K_2CrO_4
5.35	34.01	60.64	1.355	K_2CrO_4
3.18	36.74	60.08	1.354	K_2CrO_4
0.28	39.84	59.88	1.382	K_2CrO_4
0.00	40.01	59.99		K_2CrO_4
t = 60 °C				
31.41	0.00	68.59		KCl
29.73	3.25	67.02	1.205	KCl
27.74	5.70	66.55	1.223	KCl
26.68	7.91	65.41	1.244	KCl
25.27	10.65	64.08	1.256	KCl
23.31	14.04	62.64	1.278	KCl
21.70	16.88	61.42	1.312	KCl
20.04	20.32	59.64	1.329	KCl
19.67	21.19	59.14	1.325	KCl + K_2CrO_4
19.61	21.19	59.20	1.326	K_2CrO_4
15.06	26.15	58.79	1.335	K_2CrO_4
10.17	30.97	58.86	1.350	K_2CrO_4
7.67	33.65	58.68	1.348	K_2CrO_4
5.31	35.88	58.80	1.368	K_2CrO_4
2.72	38.72	58.56	1.374	K_2CrO_4
0.00	41.21	58.79		K_2CrO_4
t = 90 °C				
35.06	0.00	64.94		KCl
32.19	3.57	64.23	1.230	KCl
30.85	6.64	62.50	1.246	KCl
29.30	9.46	61.24	1.262	KCl
26.35	14.86	58.79	1.300	KCl
24.14	16.98	58.89	1.327	KCl
23.36	18.89	57.76	1.334	KCl
23.12	19.00	57.88	1.342	KCl
22.96	19.32	57.72	1.332	KCl
22.89	19.63	57.48	1.345	KCl + K_2CrO_4
22.80	19.91	57.29	1.332	K_2CrO_4
19.05	23.84	57.11	1.347	K_2CrO_4
15.00	28.00	57.00	1.370	K_2CrO_4
9.67	33.40	56.92	1.374	K_2CrO_4
7.69	35.35	56.96	1.374	K_2CrO_4
5.07	37.87	57.06	1.384	K_2CrO_4
2.54	40.94	56.52	1.394	K_2CrO_4
0.00	42.69	57.31		K_2CrO_4

argentometrically by the Mohr method (with a mass uncertainty of 0.3 %),[8−11] and the potassium ion was analyzed by titration with sodium tetraphenylboron (with a mass uncertainty of 0.5 %).[12,13] Each experimental result was achieved from the mean value of three parallel determinations.

Results and Discussions

The solubilities of the KCl + K_2CrO_4 + H_2O system at 30 °C, 60 °C, and 90 °C were determined and are presented in Table 1 and the related data that Christov et al. measured at 25 °C are also put in Table 1 as a reference. The phase diagram at 90 °C is plotted in Figure 1, and the diagrams for other temperatures are similar to that in Figure 1. The comparison of the studied system at 25 °C and 30 °C has been done in Figure 3 and X-ray diffraction patterns of the solid phases can be seen in Figure 4.

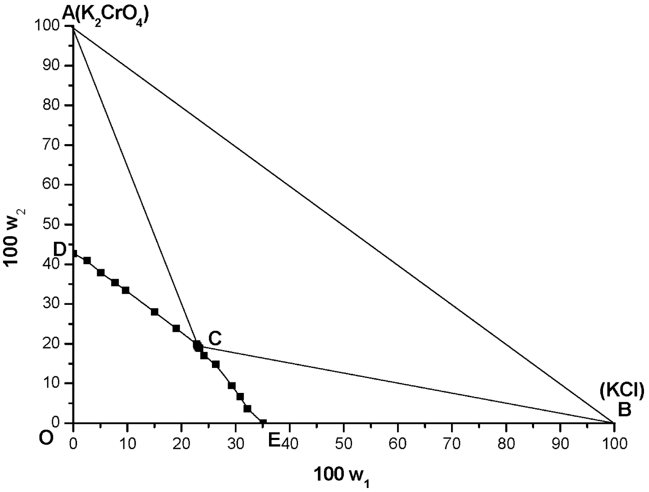

Figure 1. Phase diagram of the KCl (1) + K_2CrO_4 (2) + H_2O (3) system at 90 °C. Crystallization zones: CDA, the K_2CrO_4 crystallization zone; CEB, the KCl crystallization zone; ACB, the coexisting crystallization zone of two solids; ADCEB, the all-solids phase region.

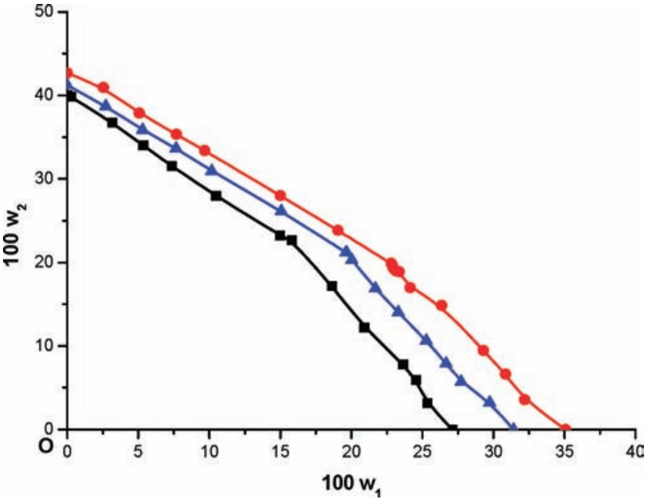

Figure 2. Solubility isotherms of K_2CrO_4 (2) in KCl (1) aqueous solution, respectively: ■, at 30 °C; ▲, at 60 °C; ●, and at 90 °C.

Phase Diagram for the KCl + K_2CrO_4 + H_2O System at 90 °C. As can be seen in Figure 1, points A and B represent the solids K_2CrO_4 and KCl, respectively. Point C is an invariant point, which represents the equilibrium of the two solid phases. Points D and E show the solubilities of K_2CrO_4 and KCl, respectively.

The saturated liquid line DCE includes two parts, that is, curves DC and CE, which represent the compositions of saturated solutions in equilibrium with the solids K_2CrO_4 (A) and KCl (B).

Figure 1 shows that the system has two crystallization zones, the K_2CrO_4 crystallization zone (CDA) and the KCl crystallization zone (CEB). The zone ACB denotes the coexisting crystallization zone of two solids. The area ADCEB represents the all-solids phase region, while the rest represents the unsaturated solution region. Indicated in Figure 1, the crystallization zone of K_2CrO_4 is almost the same size as that of KCl.

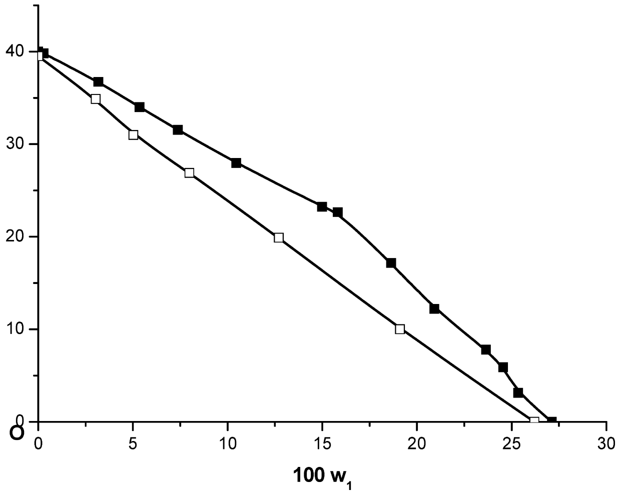

Figure 3. The comparison of solubility isotherms of K_2CrO_4 (2) in KCl (1) aqueous solution: □, at 25 °C; ■, at 30 °C.

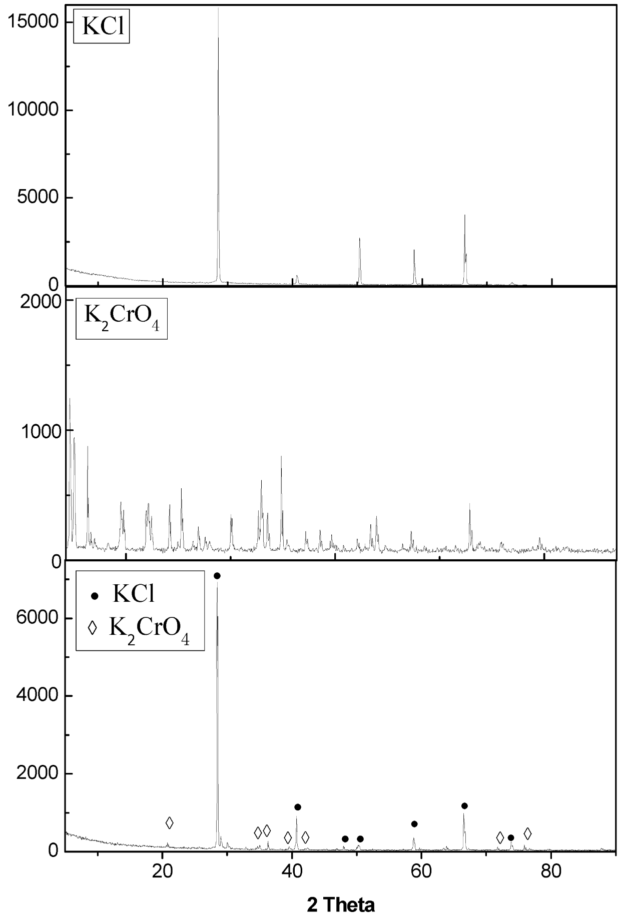

Figure 4. X-ray diffraction patterns of the solid phases.

Solubility Isotherms of K_2CrO_4 from 30 °C to 90 °C. Figure 2 indicates that the solubility isotherms of K_2CrO_4 decline sharply with an increase of the concentration of KCl. That is, the salting-out effect of KCl on K_2CrO_4 is very strong. It also can be seen that the solubility of K_2CrO_4 decreases slightly with a decrease of the temperature.

In Figure 1, most of the K_2CrO_4 crystals can be precipitated singly during the evaporating crystallization at 90 °C, for the content of KCl in the chromate production is very low. The composition of the remaining solution will be located in the invariant point C.

Comparison of the Studied System at 25 °C and at 30 °C. The consistency of the effect of temperature on the solubility can be seen in Figure 3. However, the data measured in the paper seems to disagree with that presented by Christov et al., and maybe it was caused by different apparatuses and shaking time.

Conclusions

Phase equilibrium data for the system KCl + K_2CrO_4 + H_2O between 30 °C and 90 °C were studied. According to the solubility data measured, the phase diagram and solubility isotherms were plotted. Analyses and discussions were made based on the phase diagram. The studies in the paper show that the salting-out effect of KCl is very strong. It is also concluded that evaporating crystallization is still a highly efficient way to separate most of the K_2CrO_4 from the system. This conclusion will play an important part in the cleaner production of potassium chromate.

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