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Solubility in the $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ System

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The solubility data of the $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ system at 25 °C and 40 °C were determined, and the phase diagram was constructed. Furthermore, analyses and discussions are made on the crystalline areas in the phase diagram. On the basis of these solubility data, the utilization of Na^+ and NH_3 in the carbonating process for cleaner production of sodium dichromate was evaluated.

Introduction

Chromium salts are essential materials to develop the national economy. In the traditional production process for chromium salts, pollution of byproducts with high Cr^{6+} content is serious. Recently, an original conversion process for chromium salts green technology, which eliminated the pollution from the very source, was proposed by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. Its general reaction equation is

$$FeCr_2O_4 + O_2 \xrightarrow[\text{media inner recycle}]{Na^+,\ NH_4^+,\text{ and }CO_2\text{ reaction}} Fe_2O_3 + \text{series of Cr products} \quad (1)$$

Carbonating is one of the main processes in the cleaner production of chromium salts. The phase diagram for the reciprocal system $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ is the theoretical basis of the carbonating process above.

Some studies have been done on solubility for the subsystems of the reciprocal system (Cui and Zhang, 1999; Cui et al., 1999; Karnaukhov and Guseva, 1967; Molchanov, 1965; Stephen and Stephen, 1963; Trypuć and Kielkowska, 1998). With regard to the carbonating process, Wolf (Wolf and Popov, 1929) reported its industrial transformation, but a study of the phase equilibrium for the reciprocal system $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ has not been reported so far. This paper just studied the solubility data of the $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ system at 25 °C and 40 °C and constructed the phase diagram. From the solubility data at 25 °C and 40 °C, the utilization of Na^+ and NH_3 was calculated.

Experimental Section

Apparatus and Reagents. A HZQ-C type thermostated vibrator with a precision of 0.1 °C was used for experimental equilibrium. SIEMENS D500 X-ray diffraction analyzer was used for solid-phase X-ray diffraction analysis.

The chemicals used were of analytical grade and purchased from Beijing Chemical Plant: sodium chromate ($Na_2CrO_4{\cdot}4H_2O$, ≥99 mass %), ammonium chromate (≥99.5 mass %), sodium bicarbonate (≥99.5 mass %), and ammonium bicarbonate (≥95 mass %).

Experimental Method. The system points were compounded by the drawing point method. For the reciprocal system, the system points were prepared by taking out some water and adding the third and/or fourth component gradually on the basis of the two salt cosaturation points. And then the mixtures were put into a sealed tube in the thermostated vibrator, whose temperature was controlled at 25 (±0.1) °C or 40 (±0.1) °C. The equilibrium is achieved by agitation for 24 h. After equilibrium, liquid phases were taken out and given a quantitative analysis. Solid phases were separated by vacuum filtration at the corresponding constant temperature. One part of the solid phases was dissolved into water and analyzed by chemical methods. The other part was dried at room temperature, pestled into powder, and then analyzed by X-ray diffraction.

Analytical Method. CrO_4^{2-} was titrated by using *N*-phenylanthranilic acid as indicator (precision: ±0.08 mass %). HCO_3^- was determined by acid−alkali titration and potentiometric titration (precision: ±0.18 mass %). NH_4^+ was analyzed by the formaldehyde method and the sodium tetraphenylboron mass method (precision: ±0.11 mass %). Na^+ was determined by atomic absorption spectrometry (precision: ±0.16 mass %) (Institute, 1988).

Results and Discussion

Main Reaction in Carbonating Process. The main reaction in the carbonating process is that an aqueous solution of ammonia and sodium chromate is carbonated to form sodium bicarbonate sediment:

$$Na_2CrO_4 + 2NH_4HCO_3 \rightarrow 2NaHCO_3\downarrow + (NH_4)_2CrO_4 \quad (2)$$

Phase Diagram. The solubility data of the $Na_2CrO_4 + (NH_4)_2CrO_4 + NaHCO_3 + NH_4HCO_3 + H_2O$ system at 25 °C and 40 °C were determined and presented respectively in Tables 1 and 2. The phase diagram at 25 °C was plotted in Figure 1, and that at 40 °C is similar to Figure 1.

Figure 1 shows that there are five species in total, $NaHCO_3$, NH_4HCO_3, Na_2CrO_4, $(NH_4)_2CrO_4$, and the double salt $NaNH_4CrO_4{\cdot}2H_2O$, in the system. Among them the

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Table 1. Solubility Data of the Na_2CrO_4 + $(NH_4)_2CrO_4$ + $NaHCO_3$ + NH_4HCO_3 + H_2O System at 25 °C

	composition of liquid phase/(mol/100 mol of dry salt)					
no.	$[CrO_4^{2-}]$	$[(NH_4)_2^{2+}]$	$[H_2O]$	U_{Na}/mass %	U_{NH_3}/mass %	equilibrium solid phase
A	0	0	4028			$NaHCO_3$
B	100	0	153			Na_2CrO_4
C	100	100	971			$(NH_4)_2CrO_4$
D	0	100	1329			NH_4HCO_3
E_1	97.53	0	1053			Na_2CrO_4 + $NaHCO_3$
E_2	100	4.18	1050			Na_2CrO_4 + double salt
E_3	57.09	100	1557			$(NH_4)_2CrO_4$ + NH_4HCO_3
E_4	0	78.63	2756			$NaHCO_3$ + NH_4HCO_3
K	100	50.85	1442			$(NH_4)_2CrO_4$ + double salt
1	98.50	5.56	971	4.12	73.02	$NaHCO_3$ + Na_2CrO_4
2	98.47	5.63	1066	4.16	72.82	$NaHCO_3$ + Na_2CrO_4
3	98.35	8.14	1112	6.60	79.73	$NaHCO_3$ + Na_2CrO_4
4	98.28	9.18	1129	7.59	81.26	$NaHCO_3$ + Na_2CrO_4
5	98.22	11.03	1180	9.42	83.86	$NaHCO_3$ + Na_2CrO_4
6	97.37	12.10	1196	9.73	78.26	$NaHCO_3$ + Na_2CrO_4
7	97.02	14.85		12.23	79.93	$NaHCO_3$ + Na_2CrO_4
8	96.02	21.46	1255	18.20	81.45	$NaHCO_3$ + Na_2CrO_4
P_1	95.79	25.03	1703	21.74	83.18	$NaHCO_3$ + Na_2CrO_4 + double salt
9	95.68	28.90	1452	25.69	85.05	$NaHCO_3$ + double salt
10	95.25	29.27		25.74	83.77	$NaHCO_3$ + double salt
11	94.85	34.79	1220	31.25	85.20	$NaHCO_3$ + double salt
12	94.07	47.17	1543	43.84	88.57	$NaHCO_3$ + double salt
13	93.75	62.75		60.27	90.04	$NaHCO_3$ + double salt
P_2	93.62	65.28	1618	62.91	90.23	$NaHCO_3$ + double salt +$(NH_4)_2CrO_4$
14	88.28	67.89		63.63	82.74	$NaHCO_3$ + $(NH_4)_2CrO_4$
15	81.08	72.57	1611	66.17	73.93	$NaHCO_3$ + $(NH_4)_2CrO_4$
16	81.19	74.65	1560	68.78	74.80	$NaHCO_3$ + $(NH_4)_2CrO_4$
17	70.75	81.85	1500	74.35	64.26	$NaHCO_3$ + $(NH_4)_2CrO_4$
18	65.98	84.64	1370	76.72	59.81	$NaHCO_3$ + $(NH_4)_2CrO_4$
P_3	64.45	84.95	1240	76.65	58.15	$NaHCO_3$ + $(NH_4)_2CrO_4$ +NH_4HCO_3
19	59.01	83.88	1187	72.68	51.13	$NaHCO_3$ + NH_4HCO_3
20	54.03	83.31	1134	69.11	44.82	$NaHCO_3$ + NH_4HCO_3
21	43.65	83.68	1322	62.61	32.66	$NaHCO_3$ + NH_4HCO_3
22	42.04	83.78	1325	61.42	30.82	$NaHCO_3$ + NH_4HCO_3
23	38.64	82.91	1488	55.77	25.99	$NaHCO_3$ + NH_4HCO_3

Table 2. Solubility Data of the Na_2CrO_4 + $(NH_4)_2CrO_4$ + $NaHCO_3$ + NH_4HCO_3 + H_2O System at 40 °C

	composition of liquid phase /(mol/100 mol of dry salt)					
no.	$[CrO_4^{2-}]$	$[(NH_4)_2^{2+}]$	$[H_2O]$	U_{Na}/mass %	U_{NH_3}/mass %	equilibrium solid phase
A	0	0	3198			$NaHCO_3$
B	100	0	38			Na_2CrO_4
C	100	100	996			$(NH_4)_2CrO_4$
D	0	100	760			NH_4HCO_3
E_1	93.86	0	1002			$NaHCO_3$ + Na_2CrO_4
E_2	100	5.14	945			Na_2CrO_4 + double salt
E_3	44.87	100	1184			$(NH_4)_2CrO_4$ + NH_4HCO_3
E_4	0	82.37	1842			$NaHCO_3$ + NH_4HCO_3
K	100	52.22	1218			$(NH_4)_2CrO_4$ + double salt
1	95.96	9.02	996	5.19	55.21	$NaHCO_3$ + Na_2CrO_4
2	95.82	18.01	1018	14.43	76.79	$NaHCO_3$ + Na_2CrO_4
P_1	96.14	20.80	1331	17.62	81.44	$NaHCO_3$ + Na_2CrO_4 + double salt
3	95.00	28.75	1212	25.01	82.61	$NaHCO_3$ + double salt
4	93.27	42.59	1158	38.45	84.20	$NaHCO_3$ + double salt
5	93.68	45.85	1142	42.20	86.22	$NaHCO_3$ + double salt
6	93.34	52.07	1135	48.65	87.21	$NaHCO_3$ + double salt
P_2	91.06	58.96	1415	54.93	88.84	$NaHCO_3$ + double salt +$(NH_4)_2CrO_4$
7	88.18	60.98	1305	55.75	80.62	$NaHCO_3$ + $(NH_4)_2CrO_4$
8	72.29	72.00	1128	61.27	61.51	$NaHCO_3$ + $(NH_4)_2CrO_4$
P_3	50.73	83.92	927	68.30	41.29	$NaHCO_3$+ $(NH_4)_2CrO_4$ + NH_4HCO_3
9	45.36	85.75	651	68.58	36.28	$NaHCO_3$ + NH_4HCO_3
10	36.53	85.84	784	61.24	26.06	$NaHCO_3$ + NH_4HCO_3
11	25.21	84.77	824	39.59	11.77	$NaHCO_3$ + NH_4HCO_3

crystallization zones of NH_4HCO_3 and Na_2CrO_4 at the diagonal vertexes are not connected to each other. The pair of these two salts is called an unstable salt-pair, which means solid phases consisting of these two cannot exist simultaneously in the solution, for the other salt-pair of $NaHCO_3$ and $(NH_4)_2CrO_4$ will be formed. In the phase diagram, the crystallization zones of $NaHCO_3$ and $(NH_4)_2CrO_4$ are connected. They are called a stable salt-pair and can exist in the solution in the form of solid phases at the same time. Points P_1, P_2, and P_3 are isothermal invariant points. Points E_1, E_2, E_3, E_4, and K represent respectively the equilibrium of two phases at the two extremes of the corresponding side.

According to the composition of the mother solution, the utilization of Na^+ and NH_3 in the carbonating process for sodium dichromate production can be calculated, as listed in Tables1 and 2.

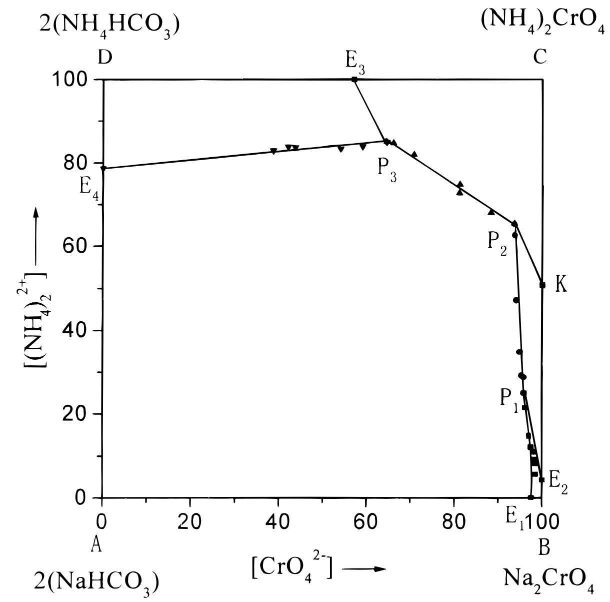

Figure 1. Phase diagram of the Na_2CrO_4 + $(NH_4)_2CrO_4$ + $NaHCO_3$ + NH_4HCO_3 + H_2O system at 25 °C.

Tables 1 and 2 show that the utilization of Na^+ reaches the maximum value around point P_3. On the other hand, the utilization of NH_3 reaches the maximum near point P_2.

Conclusion

The solubility data of the Na_2CrO_4 + $(NH_4)_2CrO_4$ + $NaHCO_3$ + NH_4HCO_3 + H_2O system at 25 °C and 40 °C were determined in this paper. According to the solubility data measured, the phase diagram was constructed, and the analyses and discussions are made on the construction of the phase diagram.

On the basis of the solubility data, the utilization of Na^+ and NH_3 in the carbonating process for cleaner production of sodium dichromate was calculated.

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