Phase Diagram for the System $K_2Cr_2O_7 + KNO_3 + H_2O$ in the Temperature Range 10 °C to 40 °C

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The phase diagram for the ternary system $K_2Cr_2O_7 + KNO_3 + H_2O$ was determined at four temperatures, (10, 20, 30, and 40) °C. In addition, the densities of the saturated aqueous solutions were measured. The experimental results show that, in the temperature range (10 to 40) °C, only potassium nitrate and potassium dichromate were present as solid phases and that the solubility of KNO_3 was almost independent of the $K_2Cr_2O_7$ concentration, whereas the solubility of $K_2Cr_2O_7$ decreased sharply with increases in the concentration of KNO_3.

Introduction

Chromate and dichromate salts are used in many industrial processes, such as the manufacture of paints, wood preservation, and leather curing. The conventional industrial production process for these materials is based on the oxidation of chromate compounds at high temperatures, (1100 to 1150) °C (Kirk-Othmer, 1993).

An oxidation process that takes place at lower temperatures has been under study by us as an alternative to the high-temperature process. The method is based on KNO_3 as the oxidizing agent, which enables the chemical reaction to be performed at relatively low temperatures, (400 to 600) °C. A multicomponent mixture is produced in this chemical reaction; the mixture contains KNO_3 and $K_2Cr_2O_7$, which are both highly soluble in water. It is thought that simple separation of these salts is possible by dissolution in water and recrystallization. However, a phase diagram of the ternary system is required as basic data for the design of this separation process.

Solubility data for the two binary systems are available in the literature, $K_2Cr_2O_7 + H_2O$ and $KNO_3 + H_2O$ in the temperature range (10 to 40) °C (Sohnel and Novotny, 1985; Seidell, 1965; Mullin, 1993). For the ternary system $K_2Cr_2O_7 + KNO_3 + H_2O$, only the compositions at the isobaric isothermal invariant equilibrium (eutonic) point at (10, 20, and 40) °C have been reported (Seidell, 1965). The aim of this work was thus to determine experimentally the phase diagram of the ternary system $K_2Cr_2O_7 + KNO_3 + H_2O$ at four temperatures, (10, 20, 30, and 40) °C, and to measure the density of the saturated aqueous solution.

Experimental Section

Materials. Extra-pure potassium nitrate (DABG E251, 99.0%), potassium dichromate (99.5%), and Mohr's salt [extra-pure $(NH_4)_2(FeSO_4)_2 \cdot 6H_2O$, >99%] were supplied by Merck. Deionized water was obtained by means of a Modulab Mode Pure Plus system (Continental Water System Corp.).

Apparatus. The experiments were performed with the instrumentation (solubility measurement apparatus) procedure described in our previous paper (Korin and Soifer, 1996). Therefore, we give here only information relevant to the measurement method. The temperatures in the flask and in the water bath were measured by copper−constantan thermocouples (±0.2 deg), which were calibrated by thermometer model Lauda R 42 (±0.01 deg). The compositions of the solid phases were determined by Schreinemakers' method [Schreinemakers, 1907 (quoted in Mullin, 1993)]. In addition, for the isobaric isothermal invariant equilibrium points and for at least one point on

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Table 1. Comparison of Solubility Data Measured in This Work with the Literature Data for the Binary System $KNO_3 + H_2O$

ref	b/(kg/100 kg of H_2O) 10 °C	20 °C	30 °C	40 °C
this work	19.91	31.15	44.60	67.70
Berkeley (1904)	21.2	31.6	45.3	61.3
Bergman and Bochkarev (1938)	20.9	31.6	45.9	*a*
Mullin (1993)	*a*	*a*	45.60	64.50
Sohnel and Novotny (1985)	21.37	41.22	45.77	62.97
Palkin and Bogoyavlenskii (1941)	21.5	31.8	*a*	64.2
Seidell (1965)[b]	63.9	31.6	31.6	45.6

[a] Not determined. [b] Average of the results of several authors.

Table 2. Comparison of Solubility Data Measured in This Work with the Literature Data for the Binary System $K_2Cr_2O_7 + H_2O$

ref	b/(kg/100 kg of H_2O) 10 °C	20 °C	30 °C	40 °C
this work	7.53	10.45	19.93	25.00
Mullin (1993)	7.00	11.98	20.05	25.94
Sohnel and Novotny (1985)	7.67	12.22	18.37	26.18
Tilden and Sheuston (1884)	6.95	11.98	20.05	26.90
Rakovskii and Babaeva (1931)	*a*	12.32	*a*	26.31
Bogoyavlenskii (1949)	8.11	12.48	18.20	25.94
Seidell (1965)[b]	6.60	12.20	18.00	26.00

[a] Not determined. [b] Average of the results of several authors.

Table 3. Comparison of Solubility Data Measured in This Work with the Literature Data for the Ternary System $K_2Cr_2O_7 + KNO_3 + H_2O$

	b/(kg/100 kg of H_2O)			
	this work		Palkin and Bogoyavlenskii (1941)	
t/°C	KNO_3	$K_2Cr_2O_7$	KNO_3	$K_2Cr_2O_7$
10	3.90	20.60	3.46	20.57
20	6.90	30.83	6.43	30.94
30	10.82	45.97	*a*	*a*
40	15.78	67.00	16.27	71.78

[a] Not determined.

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Table 4. Solubility Data for the Ternary System $K_2Cr_2O_7$ + KNO_3 + H_2O at 10 °C

b/(kg/100 kg of H_2O)			
KNO_3	$K_2Cr_2O_7$	solid phase	ρ/kg·dm^{-3}
19.91	0.00	KNO_3	1.131
19.79	2.90	KNO_3	1.139
20.17	3.35	KNO_3	1.143
20.60	3.90	$KNO_3 + K_2Cr_2O_7$	1.153
20.17	3.96	$K_2Cr_2O_7$	1.141
17.60	4.17	$K_2Cr_2O_7$	1.134
10.08	4.47	$K_2Cr_2O_7$	1.100
5.22	5.34	$K_2Cr_2O_7$	1.080
0.00	7.53	$K_2Cr_2O_7$	1.058

Table 5. Solubility Data for the Ternary System $K_2Cr_2O_7$ + KNO_3 + H_2O at 20 °C

b/(kg/100 kg of H_2O)			
KNO_3	$K_2Cr_2O_7$	solid phase	ρ/kg·dm^{-3}
31.15	0.00	KNO_3	1.180
30.92	3.78	KNO_3	1.198
30.78	6.28	KNO_3	1.207
30.83	6.90	$KNO_3 + K_2Cr_2O_7$	1.212
28.08	7.15	$K_2Cr_2O_7$	1.197
21.12	7.58	$K_2Cr_2O_7$	1.166
10.74	8.60	$K_2Cr_2O_7$	1.123
5.09	10.03	$K_2Cr_2O_7$	1.106
0.00	11.45	$K_2Cr_2O_7$	1.074

Table 6. Solubility Data for the Ternary System $K_2Cr_2O_7$ + KNO_3 + H_2O at 30 °C

b/(kg/100 kg of H_2O)			
KNO_3	$K_2Cr_2O_7$	solid phase	ρ/kg·dm^{-3}
44.60	0.00	KNO_3	1.219
44.18	1.92	KNO_3	1.226
44.10	2.96	KNO_3	1.229
45.45	5.55	KNO_3	1.229
45.98	8.00	KNO_3	1.253
46.43	8.22	KNO_3	1.257
45.97	10.82	$KNO_3 + K_2Cr_2O_7$	1.260
36.77	11.93	$K_2Cr_2O_7$	1.185
32.60	11.64	$K_2Cr_2O_7$	1.169
23.65	12.31	$K_2Cr_2O_7$	1.151
17.99	13.49	$K_2Cr_2O_7$	1.116
12.68	14.51	$K_2Cr_2O_7$	1.114
5.89	15.78	$K_2Cr_2O_7$	1.110
3.70	17.52	$K_2Cr_2O_7$	1.107
0.75	18.82	$K_2Cr_2O_7$	1.105
0.00	19.93	$K_2Cr_2O_7$	1.103

each saturation curve, the solid phases were identified by X-ray analysis using a PW 1050/70 Philips X-ray diffractometer.

The density of the aqueous solutions was determined with a pycnometer. The accuracy of the method is ±0.1%, and the reproducibility is ±0.05%.

Analytical Methods. The concentration of the dichromate ion was determined by titration against Mohr's salt (Furman, 1968). About 8 g of sample solution was used. The precision of the method is ±0.5%, and the reproducibility is ±0.3%. The water content was determined by evaporating weighed samples of about 8 g in an oven at 150 °C for 12 h (precision ±0.2% and reproducibility ±0.1%). The concentration of potassium nitrate was determined by mass balance calculation.

Results and Discussion

Comparison of the literature data for the binary systems KNO_3 + H_2O and $K_2Cr_2O_7$ + H_2O and for the ternary system $K_2Cr_2O_7$ + KNO_3 + H_2O at the temperature range (10 to 40) °C with our results is given in Tables 1−3. For the solution compositions of the isobaric isothermal invariant equilibrium (eutonic) points of the ternary system, the difference in solubility is less than 0.5 kg/100 kg of H_2O for KNO_3 and less than 4.78 kg/100 kg of H_2O for $K_2Cr_2O_7$.

The experimental results for the ternary system $K_2Cr_2O_7$ + KNO_3 + H_2O at (10, 20, 30, and 40) °C are given in Tables 4−7, respectively. The results show that at the temperatures (10, 20, 30, and 40) °C, only anhydrous potassium nitrate and potassium dichromate exist as solid phases. The isotherms for the four cases are presented in Figure 1. The figure shows that the solubility of KNO_3 is almost independent of the $K_2Cr_2O_7$ concentration, whereas the solubility of $K_2Cr_2O_7$ decreases sharply with increases of KNO_3 concentration.

Table 7. Solubility Data for the Ternary System $K_2Cr_2O_7$ + KNO_3 + H_2O at 40 °C

b/(kg/100 kg of H_2O)			
KNO_3	$K_2Cr_2O_7$	solid phase	ρ/kg·dm^{-3}
67.70	0.00	KNO_3	1.278
67.52	4.97	KNO_3	1.283
67.44	10.58	KNO_3	1.290
67.00	15.78	$KNO_3 + K_2Cr_2O_7$	1.295
60.13	15.80	$KNO_3 + K_2Cr_2O_7$	1.295
59.72	16.67	$KNO_3 + K_2Cr_2O_7$	1.292
43.62	16.99	$K_2Cr_2O_7$	1.227
38.56	17.62	$K_2Cr_2O_7$	1.226
32.38	18.36	$K_2Cr_2O_7$	1.200
26.23	18.15	$K_2Cr_2O_7$	1.186
21.73	19.50	$K_2Cr_2O_7$	1.182
13.10	20.59	$K_2Cr_2O_7$	1.175
8.79	22.60	$K_2Cr_2O_7$	1.173
2.82	24.60	$K_2Cr_2O_7$	1.131
0.00	25.00	$K_2Cr_2O_7$	1.139

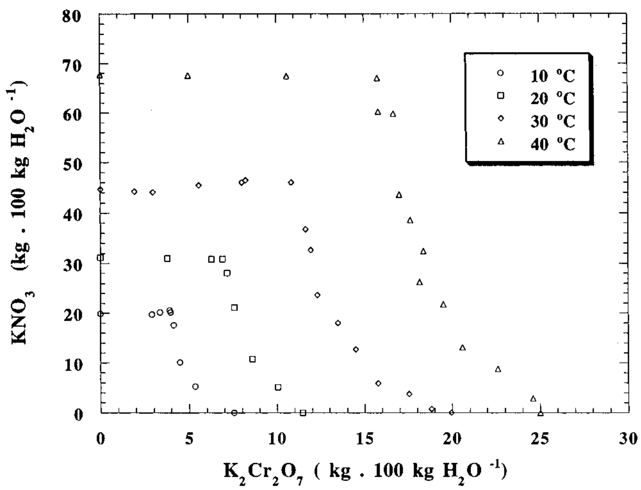

Figure 1. Phase diagram of the ternary system $K_2Cr_2O_7$ + KNO_3 + H_2O at 10, 20, 30, and 40 °C.

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