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Solubility of Potassium Dichromate in Dilute Aqueous Ethanol Solutions in the Temperature Range 283 K to 303 K

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Solubility data for potassium dichromate in dilute aqueous ethanol solutions were determined at five temperatures (283, 288, 293, 298, and 303) K. The densities of the saturated solutions were also measured. The solubility data (283, 288, 293, and 298) K correlated well with the empirical equation ln $x_1 = A + Bx_2 + Cx_2^2$ with an precision of ±1.5% where x_1 and x_2 are the mole fraction of potassium dichromate and ethanol in salt-saturated solutions and *A*, *B*, and *C* are fitted empirical constants depending on the temperature. The results indicate that at ambient temperatures of about 283 to 303 K, addition of less than 0.01 mass fraction of ethanol to an aqueous saturated solution of potassium dichromate caused "salting out" in the range between 33 and 43% of the mass of the salt.

Introduction

The salting-out precipitation/crystallization process is an important separation technique that finds application in many chemical and biochemical industrial processes. The method is based on adding to saturated solution a component that reduces the solubility of the solute and thus causes precipitation/crystallization of the solute from the solution. Salting out, which may thus be performed at ambient temperatures, is therefore considered particularly attractive in processes in which the material is sensitive to high temperatures, such as biochemical reactions, or when the crystallization by common methods of cooling or evaporation involve high energy costs. The salting out of a solute from an aqueous solution may be performed by one of two methods (Mullin, 1993): (a) adding a solid component such as inorganic salt having a common ion with the solute or (b) adding an organic solvent that is miscible in water to reduce the solubility of the solute. The latter method is used extensively in biochemical industrial separation processes; for example, ethanol, acetone, or polyethylene glycol is added to precipitate proteins (Kula et al., 1982). This technique can also be used for salting-out of inorganic salts to improve yield and purity (Thompson and Molstad, 1945; Gee et al., 1947; Hoppe, 1968; Lozano, 1976; Alfassi and Ata, 1983). The main disadvantages of the salting-out technique for the production of inorganic salts are that the added solvent is usually much more expensive than the inorganic products and an additional separation process such as distillation is required for recovery of the solvent.

In the present work, we studied the possibility of applying the salting-out technique to increase the yield of potassium dichromate from an aqueous solution by adding a miscible organic solvent (MOS) as the precipitating agent. Since our aim was to develop the basis for an industrial process that would be economically viable, i.e., without the need for solvent recovery, we imposed certain restrictions on the choice of the organic solvent. The main condition was that only small amounts of the solvent should be necessary to cause a sharp decrease in the solubility of potassium dichromate in aqueous solution; in addition, the solvent should be relatively inexpensive and environmentally friendly. A phase diagram of the system $K_2Cr_2O_7$ + water + MOS is required as basic data for assessment of this method. The only relevant data available in the literature (Hertz and Lorentz, 1929) is that for 1,4-dioxane as the MOS at only one temperature (25 °C).

We chose ethanol as a solvent that meets the abovementioned demands as the MOS. The aim of this work was to determine the solubility of potassium dichromate in dilute ethanol aqueous solutions at five temperatures—(283, 288, 293, 298, and 303) K—and to measure the densities of the saturated solutions. The results can be used in the design of the optimal process for the precipitation of potassium dichromate by "salting out" from an aqueous solution in which ethanol is the MOS.

Experimental Section

Materials. Extra-pure potassium dichromate (DABG E251, 99.0%), absolute ethanol (GR ACS; purity min. 99.8%), 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 Corporation).

Apparatus and Procedure. A schematic description of the experimental apparatus is given in Figure 1. A saturated potassium dichromate aqueous solution at 308 K was prepared and used as the "mother solution" in all the experiments. The composition of the mother solution was determined analytically and checked by a gravimetric method. For each experiment, a weighed amount (about 300 g) of the mother solution plus a weighed amount of ethanol were charged into a 0.5-dm^3 glass beaker (B) to obtain the desired mass fraction of ethanol in the initial solution. The beaker was closed by cover (F) and immersed in a water bath (A) whose temperature was controlled by electrical thermostat (Haake Corp). The mixture was stirred continuously with a stirrer (E). The temperatures in the flask and in the water bath were measured by copper−constantan thermocouples (±0.2 K), which were calibrated by thermometer model Lauda R 42 (±0.01 K).

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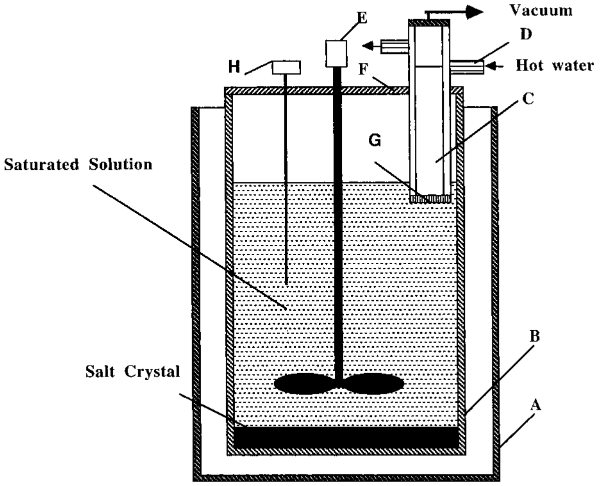

Figure 1. Schematic description of apparatus solubility measurement: (A) thermostated water bath, (B) glass beaker (0.5 dm^3), (C) sampling system, (D) heating jacket, (E) stirrer, (F) cover, (G) glass filter, (H) thermocouple.

The aqueous samples were sucked through a porous glass filter (G) into a sampling glass container (C) by means of a vacuum pump. The sampling system was heated to slightly more than the saturation temperature to prevent possible crystallization. Heating was accomplished by means of a heating jacket (D), in which hot water was circulated from the thermostatic bath. Preliminary tests showed that about 4 h were sufficient to reach equilibrium. In our experiments, sampling was performed after a minimum of 8 h. The system was left unstirred for 60 min before sampling to enable all the suspended crystals to settle. Sampling lasted about 2 s.

The density of the saturated aqueous solutions was measured at equilibrium temperature with a pycnometer. The accurancy of the method is ±0.1%, and the precision is ±0.05%.

Analytical Methods. The mass fraction of potassium dichromate was determined by titration of dichromate ion against Mohr's salt (Furman, 1968). About 8 g of sample solution was used. The accuracy of method is ±0.5%, and the reproducibility is ±0.3%. The results obtained by the analytical method were checked against a gravimetric method by evaporating a sample of known mass of about 8 g (accuracy ±0.0001 g) in an oven at 150 °C for 12 h. The difference between the results obtained by these two methods was less than 0.5%.

The solid phase was identified by X-ray analysis using a PW 1050/70 Philips X-ray diffractometer. The results of the X-ray analysis showed that in temperature ranges (283 to 303) K, potassium dichromate is the only solid phase in this system (Note, photochemical oxidation of the potassium dichromate might occur in this system. However, under the experimental conditions of this work—less than 1.5 mass % of ethanol, temperatures between 283 and 303 K, and the system maintained in a container opaque to light radiation—the reaction rate was very low and the effect after several days could be neglected.) These results indicate that the ratio between mass fraction of ethanol and mass fraction of water in the saturated solution has to be equal to this ratio in the initial solution. Considering that the composition of the initial solution and the mass fraction of potassium dichromate in the saturated solution are known, we could determine the mass fraction of each component in the saturated solution by simple mass balance equations.

Table 1. Mole (x_1) Fraction of $K_2Cr_2O_7$ and Density (ρ) of the Saturated Solution as a Function of Mole (x_2) Fraction of Ethanol at the Temperatures (283, 288, 293, 298, and 303) K

$1000x_1$	$1000x_2$	ρ/kg·dm^{-3}
	T = 283 K	
4.59	0.00	1.058
4.01	0.21	1.057
3.91	0.42	1.056
3.66	1.04	1.055
3.35	2.08	1.045
2.86	3.10	1.038
2.32	4.10	1.021
	T = 288 K	
5.32	0.00	1.067
5.26	0.21	1.066
5.08	0.43	1.064
4.39	1.05	1.061
4.28	2.11	1.057
3.86	3.14	1.046
3.13	4.16	1.035
	T = 293 K	
6.49	0.00	1.074
6.42	0.22	1.073
6.31	0.43	1.071
6.15	1.08	1.068
5.38	2.14	1.055
5.09	3.20	1.046
4.15	4.22	1.035
	T = 298 K	
8.69	0.00	1.120
8.21	0.22	1.115
8.09	0.44	1.099
7.58	1.10	1.091
6.59	2.17	1.079
5.98	3.24	1.065
5.60	4.31	1.057
	T = 303 K	
12.06	0.00	1.103
10.81	0.23	1.101
10.32	0.45	1.100
9.48	1.13	1.097
8.33	2.23	1.092
8.11	3.33	1.080
7.21	4.40	1.072

Results and Discussion

Solubility data for potassium dichromate in water are available in a number of papers (Tilden and Shenstone 1884; Bogoyavlenskii, 1949, 1952; Kearly,1964). A comparison of the literature values with the experimental results measured with our experimental system for the binary system $K_2Cr_2O_7 + H_2O$ at (283, 293, 303, and 313) K is given in our previous paper (Korin and Soifer, 1997). The literature values at (283, 293 , 298, 303, and 313) K are in the ranges of (7.4 to 7.5, 11.0 to 11.1, 13.8, 15.4 to 15.7, and 20.6) mass %, respectively. Our experimental results at these temperatures are (7.0, 9.6, 13.0, 16.6, and 20.0) mass %. It can be seen that our result at 303 is slightly lower than the literature values, while at 283 and 313 K, our measurements fall within these ranges.

The experimental results on the solubility of potassium dichromate in dilute ethanol aqueous solutions and the density of the saturated solutions at the temperatures (283, 288, 293, 298, and 303) K are presented in Table 1.

Figure 2 presents the plots of ln x_1 against x_2 at constant temperature, where x_1 and x_2 are the mole fraction of potassium dichromate and ethanol in salt-saturated solution. The data fit the empirical equation:

$$\ln x_1 = A + Bx_2 + Cx_2^{\,2} \qquad (1)$$

where A, B, and C are adjustable empirical coefficients that

Table 2. Coefficients *A*, *B*, and *C* and the Standard Error of Estimate (σ) for Equation 1 at the Temperatures (283, 288, 293, 298, and 293) K

T/K	*A*	*B*	*C*	*s*
283	−5.4571	−112.29	−7799	0.1123
288	−5.2479	−93.366	−6086	0.1034
293	−5.0409	−38.661	−14983	0.0522
298	−4.7546	−141.94	+9587	0.0316
303	−4.4671	−178.15	+17703	0.0905

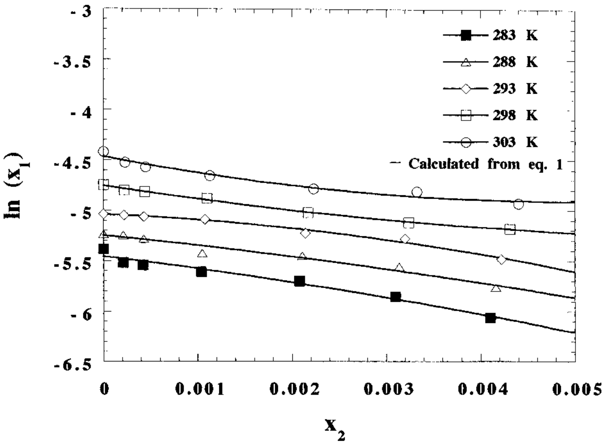

Figure 2. Logarithms of mole fraction of $K_2Cr_2O_7$ (x_1) versus mole fraction of ethanol (x_2) at various constant temperatures.

depend on the temperature. The values of these coefficients are presented in Table 2. The standard error of estimate σ is given by

$$\sigma = \{\sum[\ln x_1^{\mathrm{calc}} - \ln x_1^{\mathrm{exp}}]^2/(n - m)\}^{1/2} \tag{2}$$

where *n* and *m* are the number of data points and the number of empirical coefficients, respectively. ln x_1^{exp} is determined directly from the analytical measurements and ln x_1^{calc} from eq 1.

Note, the calculated standard error of estimate shows that in all isotherms, three coefficients are required for best representing the exprimental data. The deviations of ln x_1, calculated from measured data, from the values obtained from the fitted correlations are presented in Figure 3. The correlation reproduced the experimental data with an precision of ±1.5%.

On the basis of the experimental data, calculation of the mass fractions of potassium dichromate precipitated from saturated aqueous solutions by "salting out" with ethanol showed that at ambient temperature of approximately 283 to 303 K, addition of less than 0.01 mass fraction of ethanol to an aqueous saturated solution of potassium dichromate caused "salting out" in the range between 33 and 43% of the mass of the salt. This finding is of significant importance in the assessment of this method as a means of improving the yield of the industrial process for crystallization of potassium dichromate.

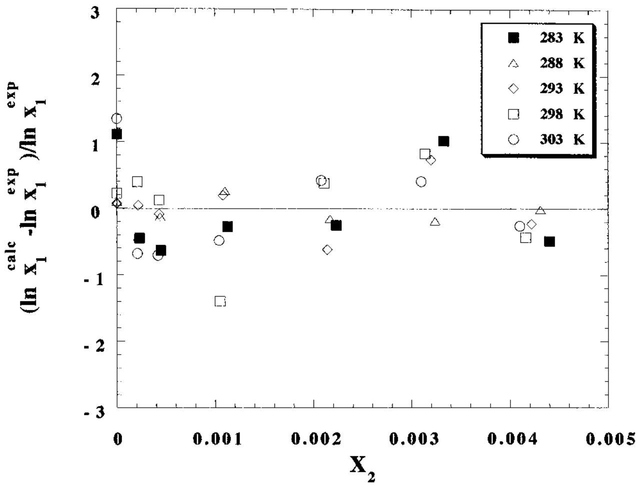

Figure 3. Deviation of experimental ln x_1 from the values derived from the fitted correlations.

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