

# Solubility of Potassium Dichromate in Dilute Aqueous Methanol and 2-Propanol Solutions in the Temperature Range 283 K to 303 K

Eli Korin\* and Leonid Soifer

Department of Chemical Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel

Solubility data for potassium dichromate in dilute aqueous methanol and 2-propanol solutions and the densities of the saturated solutions at the equilibrium temperature were determined at five temperatures (283, 288, 293, 298, and 303) K. The solubility data were correlated with the empirical equation  $\ln x_1 = A + Bx_i$  at temperatures (283, 288, 293, and 298) K and  $\ln x_1 = A + Bx_i + Cx_i^2$  at 303 K, where  $x_1$  are the mole fraction of potassium dichromate and  $x_i$  the mole fraction of methanol or 2-propanol in salt-saturated solutions and  $A$ ,  $B$ , and  $C$  are fitted empirical constants depending on the temperature. The precision of the fitted correlations are less than  $\pm 0.7\%$  for both methanol and 2-propanol aqueous systems.

## Introduction

Adding of a miscible organic solvent (MOS) to reduce the solubility of the solute in an aqueous solution is an important separation technique in many industrial processes. The method is considered particularly attractive, in cases that appropriate MOS is found to be suitable precipitating agents at ambient temperature, for material that are sensitive to high temperature such as pharmaceutical products (Kula et al., 1982). The method has been also investigated for improve the yield and purity for precipitation of inorganic salts from aqueous solutions (Lozano, 1976). Usually this method is too expensive for application separation of inorganic materials because of the relatively high cost of recovery process such as distillation in production of relatively inexpensive product. However, in cases that adding a small amount of inexpensive MOS is enough to cause drowning out of a significant percent of the solute, the method might pay off without recovery of the MOS. To examine the possibility of using this approach to increase the yield of crystallization of potassium dichromate by adding a small percent of alcohol solvent (AS), solubility data for the potassium dichromate in dilute aqueous alcohol solutions is needed.

In the present work, we have determined the solubility of the potassium dichromate in dilute aqueous alcohol solutions. This data is needed to study the possibility of applying the salting-out technique to increase the yield of potassium dichromate crystallization from an aqueous solution by adding alcohol solvent (AS) as the precipitating agent without the need for solvent recovery.

Solubility data for potassium dichromate in dilute aqueous ethanol solutions at five temperatures (283, 288, 293, 298, and 303) K was reported in our previous paper (Korin and Soifer, 1997). The aim of this paper is to report on the solubility data of potassium dichromate in dilute methanol and 2-propanol aqueous solutions at five temperatures—(283, 288, 293, 298, and 303) K—and the densities of the saturated solutions at the equilibrium temperature.

## Experimental Section

**Materials.** Extra-pure potassium dichromate (DABG E251, 99.0%), methanol (GR ACS ISO; purity minimum 99.8%), 2-propanol (GR ACS ISO; purity minimum 99.7%), and Mohr's salt [extra-pure  $(\text{NH}_4)_2(\text{FeSO}_4)_2 \cdot 6\text{H}_2\text{O}$ , >99%] were supplied by Merck. Deionized water was obtained by means of a Modulab Mode Pure Plus system (Continental Water System Corporation, U.S.).

**Apparatus and Procedure.** A description of the apparatus and the experimental procedure is described in detail in our previous paper (Korin and Soifer, 1997). A saturated potassium dichromate aqueous solution at 308 K was prepared and used as the "mother solution" in all experiments. The composition of the mother solution was determined analytically and checked by a gravimetric method.

For each experiment, a weighted amount (about 300 g) of the mother solution ( $\pm 0.001$  g) plus a weighted amount of alcohol, methanol or 2-propanol ( $\pm 0.0001$  g), was charged into a 0.5 dm<sup>3</sup> glass beaker. The loaded beaker was closed and maintained in thermostatic water bath. The temperatures in the flake and the water bath were measured by copper–constantan thermocouples ( $\pm 0.2$  °C), which were calibrated by thermometer model Lauda R42 ( $\pm 0.01$  °C). Preliminary experiments showed that about 4 h is sufficient to reach equilibrium. The samples were withdrawn from the solution through a glass filter after at least 8 h. The solid phase was identified by X-ray analysis using a PW 1050/70 Philips X-ray diffractometer. The density of the saturated solution was measured at the equilibrium temperature with a pycnometer. The accuracy is  $\pm 0.1\%$  and precision  $\pm 0.01\%$

**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 a sample solution was used. The accuracy of method is  $\pm 0.5\%$ , and the reproducibility is  $\pm 0.3\%$ . 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  $\pm 0.0001$  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%.

\* Corresponding author. E-mail: ekorin@bgumail.bgu.ac.il.

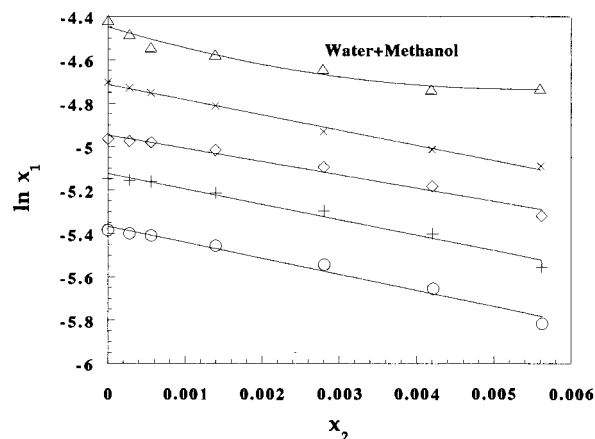
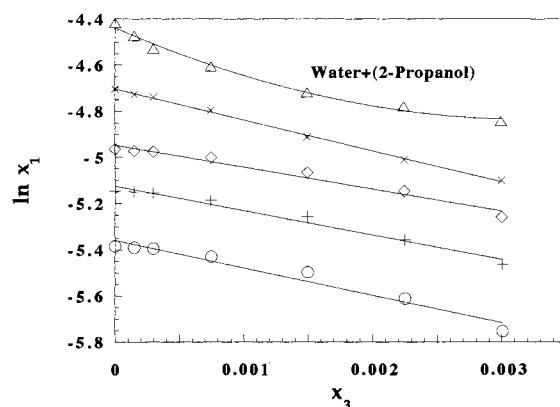
**Table 1. Mole ( $x_1$ ) Fraction of  $K_2Cr_2O_7$  and Density ( $\rho$ ) of the Saturated Solution as a Function of Mole ( $x_2$ ) of Methanol at the Temperatures (283, 288, 293, 298, and 303) K**

$1000x_1$	$1000x_2$	$\rho/\text{kg}\cdot\text{dm}^{-3}$	$1000x_1$	$1000x_2$	$\rho/\text{kg}\cdot\text{dm}^{-3}$
$T = 283 \text{ K}$					
4.59	0.00	1.058	3.91	2.80	1.049
4.51	0.28	1.057	3.50	4.21	1.043
4.47	0.56	1.056	2.97	5.67	1.031
4.26	1.40	1.054			
$T = 288 \text{ K}$					
5.82	0.00	1.067	5.01	2.80	1.060
5.77	0.28	1.067	4.51	4.21	1.053
5.74	0.56	1.066	3.87	5.62	1.040
5.45	1.40	1.063			
$T = 293 \text{ K}$					
6.98	0.00	1.074	6.13	2.80	1.058
6.91	0.28	1.074	5.61	4.20	1.049
6.87	0.56	1.072	4.90	5.62	1.039
6.63	1.40	1.068			
$T = 298 \text{ K}$					
9.07	0.00	1.120	7.22	2.80	1.083
8.82	0.28	1.117	6.64	4.20	1.070
8.64	0.55	1.108	6.16	5.61	1.060
8.13	1.40	1.102			
$T = 303 \text{ K}$					
12.06	0.00	1.103	9.63	2.79	1.095
11.29	0.28	1.102	8.77	4.19	1.092
10.64	0.56	1.100	8.80	5.59	1.088
10.30	1.38	1.098			

**Table 2. Mole ( $x_1$ ) Fraction of  $K_2Cr_2O_7$  and Density ( $\rho$ ) of the Saturated Solution as a Function of Mole ( $x_3$ ) of 2-Propanol at the Temperatures (283, 288, 293, 298, and 303) K**

$1000x_1$	$1000x_2$	$\rho/\text{kg}\cdot\text{dm}^{-3}$	$1000x_1$	$1000x_2$	$\rho/\text{kg}\cdot\text{dm}^{-3}$
$T = 283 \text{ K}$					
4.59	0.00	1.058	4.10	1.50	1.052
4.56	0.15	1.058	3.66	2.25	1.044
4.54	0.30	1.057	3.17	3.01	1.038
4.39	0.75	1.056			
$T = 288 \text{ K}$					
5.82	0.00	1.067	5.21	1.50	1.061
5.80	0.15	1.066	4.72	2.25	1.054
5.78	0.30	1.065	4.25	3.00	1.046
5.59	0.75	1.063			
$T = 293 \text{ K}$					
6.98	0.00	1.074	6.31	1.49	1.062
6.93	0.15	1.073	5.82	2.25	1.053
6.91	0.30	1.072	5.20	3.00	1.040
6.73	0.75	1.069			
$T = 298 \text{ K}$					
9.07	0.00	1.120	7.36	1.49	1.084
8.85	0.15	1.116	6.68	2.24	1.071
8.75	0.30	1.110	6.10	3.00	1.059
8.23	0.74	1.103			
$T = 303 \text{ K}$					
12.06	0.00	1.103	8.92	1.49	1.090
11.40	0.15	1.102	8.39	2.24	1.082
10.79	0.30	1.101	7.88	2.99	1.075
9.99	0.74	1.008			

The results of the X-ray analysis showed that in temperature range (283 to 303) K potassium dichromate is the only solid phase in this system. These results indicate that the ratio between mass fraction of alcohol (methanol or 2-propanol) to 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, the mass fraction of each component

**Figure 1.** Logarithms of mole fraction of  $K_2Cr_2O_7$  ( $x_1$ ) versus mole fraction of methanol ( $x_2$ ) at various temperatures: (○) 283 K, (+) 288 K, (◇) 293 K, (×) 295 K, (△) 303 K.**Figure 2.** Logarithms of mole fraction of  $K_2Cr_2O_7$  ( $x_1$ ) versus mole fraction of 2-propanol ( $x_3$ ) at various temperatures: (○) 283 K, (+) 288 K, (◇) 293 K, (×) 295 K, (△) 303 K.**Table 3. Coefficients  $A$ ,  $B$ , and  $C$  and the Standard Error of Estimate ( $s$ ) for Eqs 1 and 2 at the Temperatures (283, 288, 293, and 298) K and 303 K, Respectively**

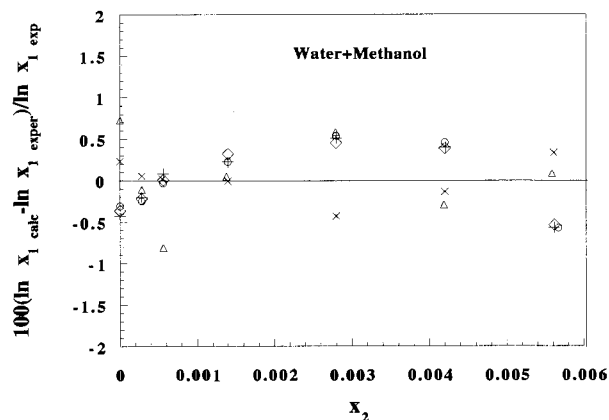
$T/\text{K}$	$A$	$B$	$C$	$s$
Water + Methanol				
283	-5.37	-73.81		0.0896
288	-5.12	-70.86		0.0242
293	-4.95	-61.05		0.0222
298	-4.71	-70.01		0.0135
303	-4.45	-106.16	9817	0.0258
Water + (2-Propanol)				
283	-5.36	-118.98		0.0342
288	-5.13	-105.21		0.0197
293	-4.95	-95.19		0.0209
298	-4.70	-134.01		0.0060
303	-4.44	-243.79	37248	0.0161

in the saturated solution could be determined by simple mass balance equations.

## Results

The experimental results on the solubility of potassium dichromate in dilute methanol and 2-propanol aqueous solutions and the density of the saturated solutions at the temperatures (283, 288, 293, 298, and 303) K are presented in Tables 1 and 2, respectively.

Figures 1 and 2 present the plots of  $\ln x_1$  against  $x_2$  or  $x_3$ , at constant temperature, where  $x_1$ ,  $x_2$ , and  $x_3$  are the mole fraction of potassium dichromate, methanol, and 2-propanol in salt-saturated solution. The data were fitted



**Figure 3.** Percentage deviations of experimental  $\ln x_1$  from the values derived from the fitted correlations for dilute aqueous methanol solutions: (O) 283 K, (+) 288 K, (◇) 293 K, (x) 295 K, (Δ) 303 K.

to the linear empirical eq 1 at the temperatures (283, 288, 293, and 298) K

$$\ln x_1 = A + Bx_i \quad (1)$$

and to second-order empirical equation at 303 K

$$\ln x_1 = A + Bx_i + Cx_i^2 \quad (2)$$

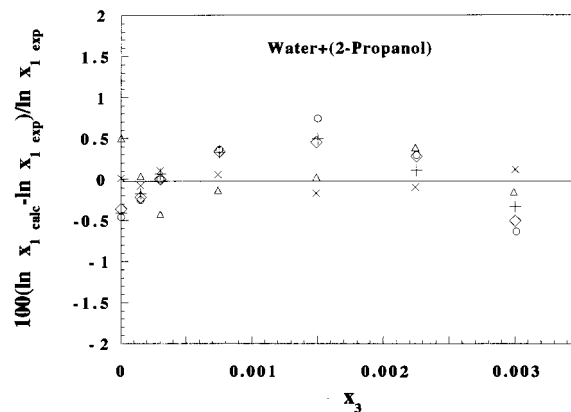
where  $x_1$  are the mole fraction of potassium dichromate and  $x_i$  the mole fraction of methanol or 2-propanol in salt-saturated solutions and  $A$ ,  $B$ , and  $C$  are fitted empirical constants depending on the temperature. The values of these coefficients are presented in Table 3.

The standard error of estimate  $s$  is given by

$$s = \left\{ \sum [\ln x_{1 \text{ calc}} - \ln x_{1 \text{ exp}}]^2 / (n - m) \right\}^{1/2} \quad (3)$$

where  $n$  and  $m$  are the number of data points and the number of empirical coefficients, respectively.  $\ln x_{1 \text{ exp}}$  is determined directly from the analytical measurements and  $\ln x_{1 \text{ calc}}$  from eq 1 or 2.

The percentage deviations of experimental  $\ln x_1$ , from the values derived from the fitted correlations, are less than  $\pm 0.7\%$  for both dilute methanol or 2-propanol saturated solutions and are presented in Figures 3 and 4, respec-



**Figure 4.** Percentage deviations of experimental  $\ln x_1$  from the values derived from the fitted correlations for dilute aqueous 2-propanol solutions: (O) 283 K, (+) 288 K, (◇) 293 K, (x) 295 K, (Δ) 303 K.

tively. On the basis of these experimental data, it could be showed that at ambient temperatures of about 283 to 303 K addition of less than 0.01 mass fraction of methanol or 2-propanol to an aqueous saturated solution of potassium dichromate caused "salting out" in the range between 1.6 and 10.9% or 0.9 to 9.8% of the mass of the salt, respectively.

#### Acknowledgment

The authors thank Ms. Miri Mamana for her assistance in the experimental work.

#### Literature Cited

- Furman, N. H. *Standard Methods of Chemical Analysis*, 6th ed; D. Van Nostrand Inc.: Princeton, NJ, 1968.
- Korin, E.; Soifer, L. Solubility of Potassium Dichromate in Dilute Aqueous Ethanol Solution in the Temperature Range 283 K to 303 K *J. Chem. Eng. Data* **1997**, *42*, 1251–1253.
- Kula, M. R.; Kroner, K. H.; Hustedt, H. *Advances in Biochemical Engineering*; Springer-Verlag: New York, 1982; Vol. 24, p 73.
- Lozano, J. A. F. Recovery of Potassium Magnesium Sulfate Double Salt from Seawater Bittern. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15*, 445–449.

Received for review February 11, 1998. Accepted June 4, 1998.

JE980043J