

DISTRIBUTION OF ISOMORPHOUS SALTS BETWEEN AQUEOUS AND SOLID PHASES IN FRACTIONAL CRYSTALLIZATION-V

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The theory given in Part I [1] for fractional crystallization has been tested for two systems. One is an alum system, while the second contains two isomorphous picromerite salts. The correlation between the distribution coefficient K and the ratio of the solubilities of the components in each system has been discussed. Finally, the Roozeboom square diagram has been also investigated.

INTRODUCTION

For ternary systems containing pairs of isomorphous salts and water, Abu-Elamayem [1-4] showed that the distribution of salts between Liquid and solid solutions in equilibrium and non-equilibrium states obeys equations 1 and 2 respectively:

$$Y^2W(K-1) - Y[1 + (K-1)(W+a)] + Ka = 0 \quad (1)$$

$$-dY/dW = \frac{1}{W} \frac{1}{[1 + (1-W - (a-Wy)l/m) - Y]} \frac{1}{K(a-Wy)} \quad (2)$$

The terms in these equations have been already defined [1, 2].

We are interested in gaining wide application for this theory. In the present investigations the validity of this theory has been tested for another alum system composed of $(\text{NH}_4)_2\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. It was also found useful to choose another system from the picromerite (Schoenite) type, $\text{Mg}/\text{Ni}(-\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, for more confirmation.

The solubilities of the two alum salts were determined [5] while those for the two picromerite salts have been consulted from the literature [6].

EXPERIMENTAL

Ammonium chromium sulphate, ammonium aluminium sulphate, nickel ammonium sulphate and magnesium

ammonium sulphate were of the Analar type. Details for the experimental steps have been provided elsewhere [1, 2]. Analysis of the mixed alum crystals was achieved by determining the chromium ion concentration volumetrically [7], while that for the picromerite system was performed by the gravimetric determination of nickel ion concentration [7] through precipitation with dimethyl glyoxime.

RESULTS AND DISCUSSION

1. *The alum system, chrome alum-ammonium alum- H_2O .* At 0° , the experimental points for equilibrium condition (Fig. 1), were found to lie on the theoretical curves with $K = 1.5$.

At 15 and 35° , as shown in Fig. 2, the experimental results for equilibrium conditions coincided with the theoretical curves for $K = 2.1$ and 11 respectively.

Since both solubility and K increases with temperature, it becomes necessary to correlate K with solubility.

From Table 1, it is seen that the values of $(\frac{s_1}{s_2})^{1.43}$ at any temperature are close to the value of K at the same temperature, i.e. $K = (\frac{s_1}{s_2})^{1.43}$.

Table 1. Test for the empirical equation $K = (\frac{s_1}{s_2})^n$

($^\circ\text{C}$)	S_1	S_2	$1.43 \log(\frac{s_1}{s_2})$	$K_{\text{calc.}}$	$K_{\text{exp.}}$
0	5.17	3.90	0.1750	1.49	1.5
15	16.22	9.55	0.3289	2.13	2.1
35	57.54	28.84	0.4288	2.68	11

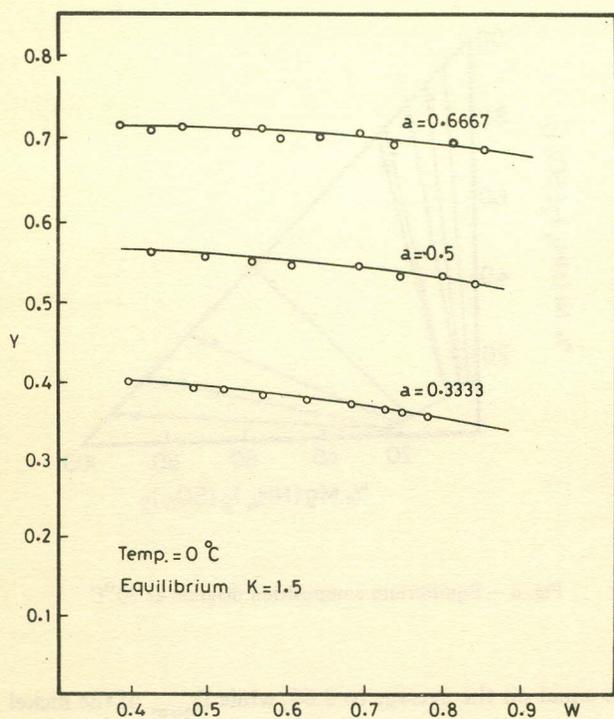


Fig. 1

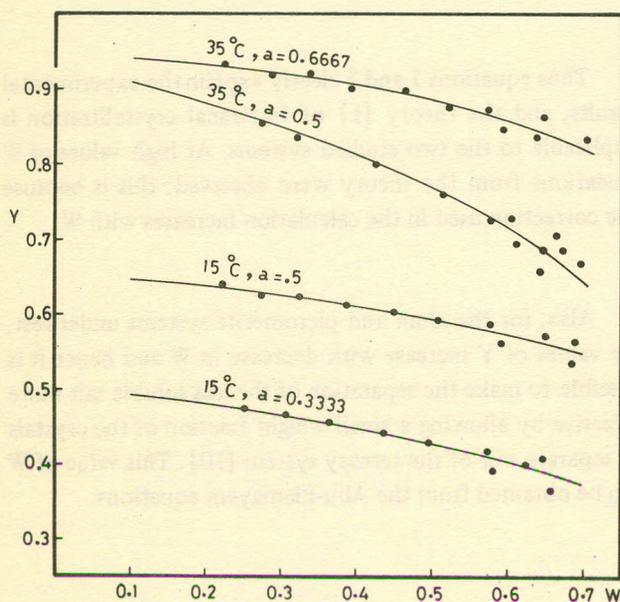


Fig. 2

Deviation from the empirical relation, $K = \left(\frac{s_1}{s_2}\right)^{1.43}$, and the theory of crystallization at 35° was noticed. This may be explained being due to the existence of the two forms of chromium salt (green and violet) at such temperatures. In this way, the system is quaternary [8].

2. The picromerite system: $Mg(NH_4)_2(SO_4)_2 - Ni(NH_4)_2(SO_4)_2 - H_2O$. The validity of equations 1 and 2 for this system can be seen from Fig. 3. The experimen-

tal results at 0° agreed with the theoretical curve with $K=5$ for non-equilibrium conditions and $K=14.5$ for the equilibrium conditions.

The data at 20 and 30° (Fig. 4) for equilibrium condition are fitted with the theoretical curve with $K = 8.2$ and 7.7 respectively.

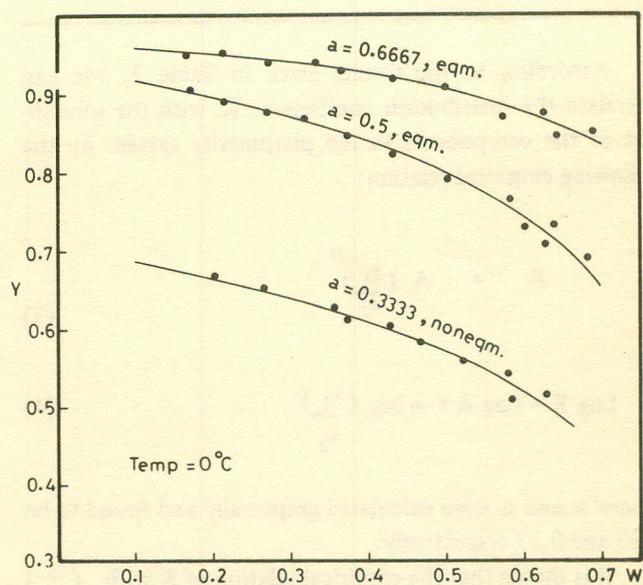


Fig. 3

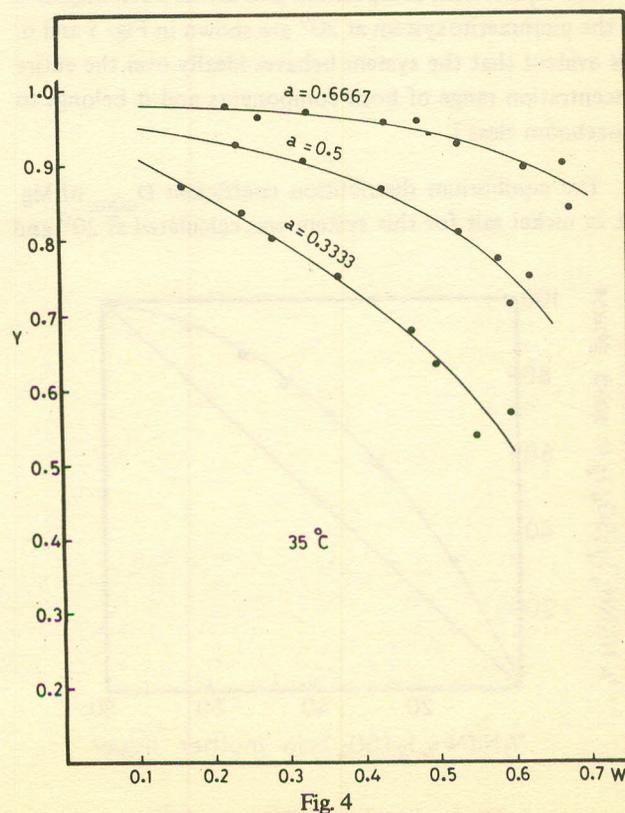


Fig. 4

Table 2. Test for empirical relation

(°C)	S ₁	S ₂	$K=A\left(\frac{s_1}{s_2}\right)^n$	K _{exp.}
0	10.58	1.00	14.46	14.5
20	15.23	6.5	8.24	8.2
30	17.84	9.0	7.74	7.7

According to the results given in Table 2, one can correlate the distribution coefficient, K, with the solubilities of the components in the picromerite system by the following empirical relation:

$$K = A \left(\frac{s_1}{s_2}\right)^n \quad (3)$$

$$\text{or } \log K = \log A + n \log \left(\frac{s_1}{s_2}\right) \quad (4)$$

where A and n were calculated graphically and found to be 6.03 and 0.37 respectively.

It is shown that the empirical relation of K with $\left(\frac{s_1}{s_2}\right)$ takes a different form from that of the alum system.

The equilibrium composition and distribution diagrams for the picromerite system at 20° are shown in Fig. 5 and 6. It is evident that the system behaves ideally over the entire concentration range of both components and it belongs to Roozeboom class I.

The equilibrium distribution coefficient D_{eqm} of Mg salt in nickel salt for this system was calculated at 20° and

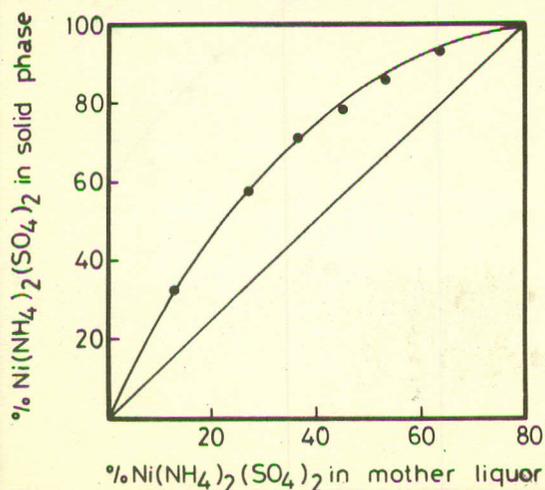


Fig. 5 - Distribution diagram at 20°C

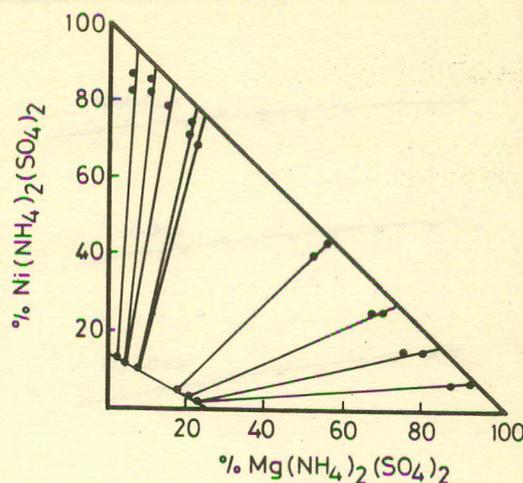


Fig. 6 - Equilibrium composition diagram at 20°C

was equal on the average to 0.64, while D_{eqm} of the nickel salt in magnesium salt was found to be 1.32. Similar values were previously reported by Gorstein [9].

Thus equations 1 and 2 clearly explain the experimental results, and the theory [1] of fractional crystallization is applicable to the two studied systems. At high values of W deviations from the theory were observed; this is because the correction used in the calculation increases with W.

Also, for the alum and picromerite systems under test, the values of Y increase with decrease in W and hence it is possible to make the separation of the less soluble salt more effective by allowing a small weight fraction of the crystals to separate out of the ternary system [10]. This value of W can be obtained from the Abu-Elamayem equations.

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