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

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### ABSTRACT

The theory given earlier for fractional crystallization has been tested for a new system containing double salts of the picromerites (Schoenite) type. The experimental results of the system—cobalt ammonium sulphate—nickel ammonium sulphate agree with the theory. The empirical relation between  $K$  and the solubilities of the two salts was investigated. The system was found to be of Roozeboom type I. The equilibrium distribution coefficient  $D_{eqm}$  was also calculated.

### INTRODUCTION

HILL *et al.*<sup>1</sup> derived a theoretical relation correlating the concentrations of pairs of isomorphous salts in aqueous phase with those in the solid phase when equilibrium is established.

Recently, a theory<sup>2</sup> accounting for fractional crystallization of isomorphous salts under both equilibrium and non-equilibrium conditions was formulated as given in equations (1) and (2) respectively.

$$y^2 W (k-1) - y \{1 + (k-1) (W+a)\} + a = 0 \quad (1)$$

$$-\frac{dy}{dw} = \frac{1}{W} \left[ 1 / \left\{ 1 + \frac{1}{k} \left( \frac{1-w}{a-wy} - 1 \right)^{1/m} \right\} \right] \quad (2)$$

Earlier investigations<sup>2-6</sup> were focussed on the validity of the above theory on only the alum systems. For further confirmation of this theory, which is the main objective of the present paper, results for a system of the picromerites type are presented.

Double salts of the picromerites (Schoenite) type are usually truly isomorphic and for a continuous series of solid solutions. Accordingly, the study of such systems presents considerable interest for the elucidation of the laws governing the distribution of isomorphic components between the solid and liquid phases.

### EXPERIMENTAL

Cobalt ammonium sulphate and nickel ammonium sulphate were of Analar grade. The experimental procedures described earlier<sup>2-6</sup> were carried out at 0, 20 and 30°C under equilibrium and non-equilibrium conditions.

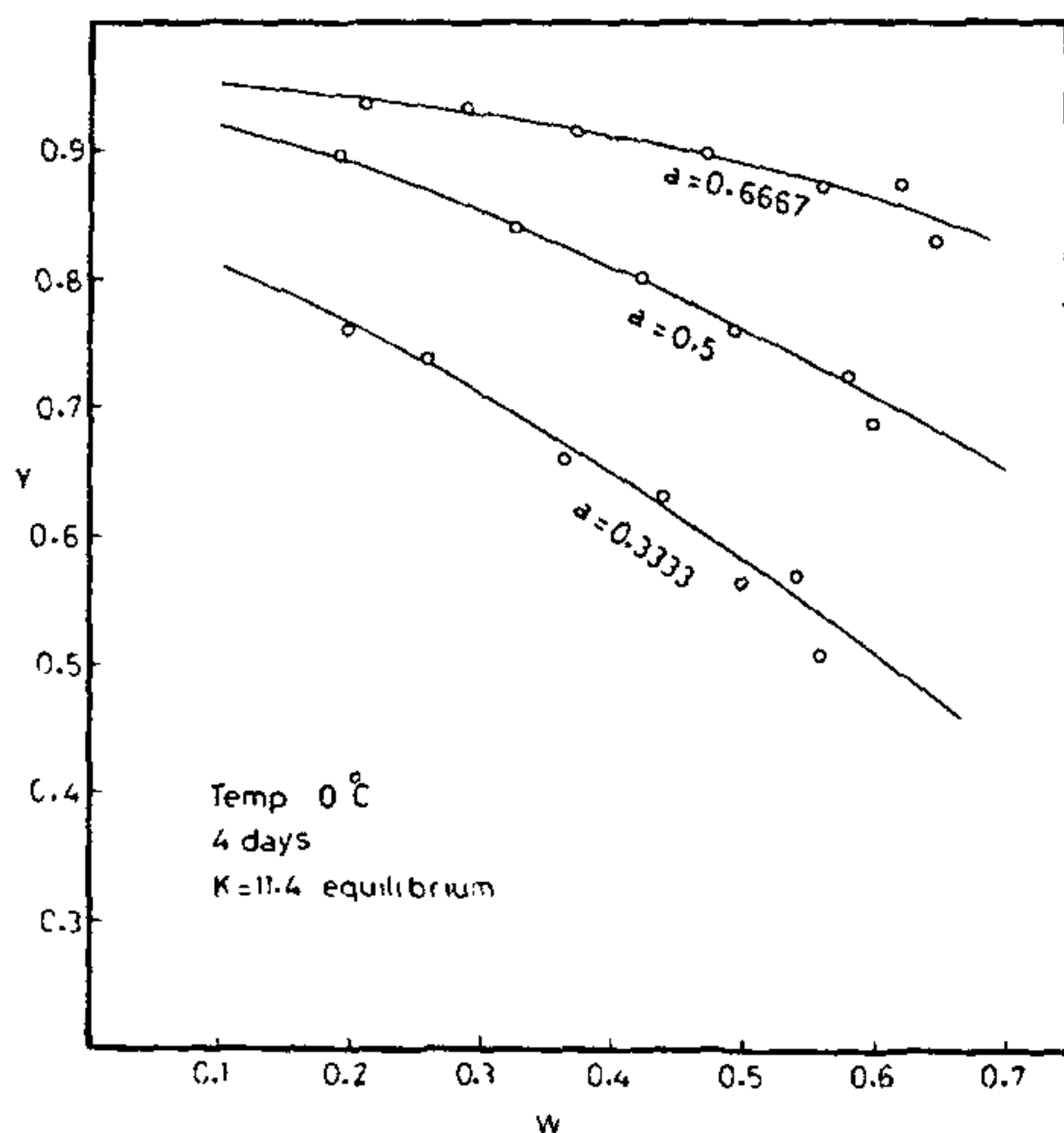
The concentration of cobalt in the crystals was determined by potentiometric titration with potassium ferricyanide in an ammoniacal medium.

### RESULTS AND DISCUSSION

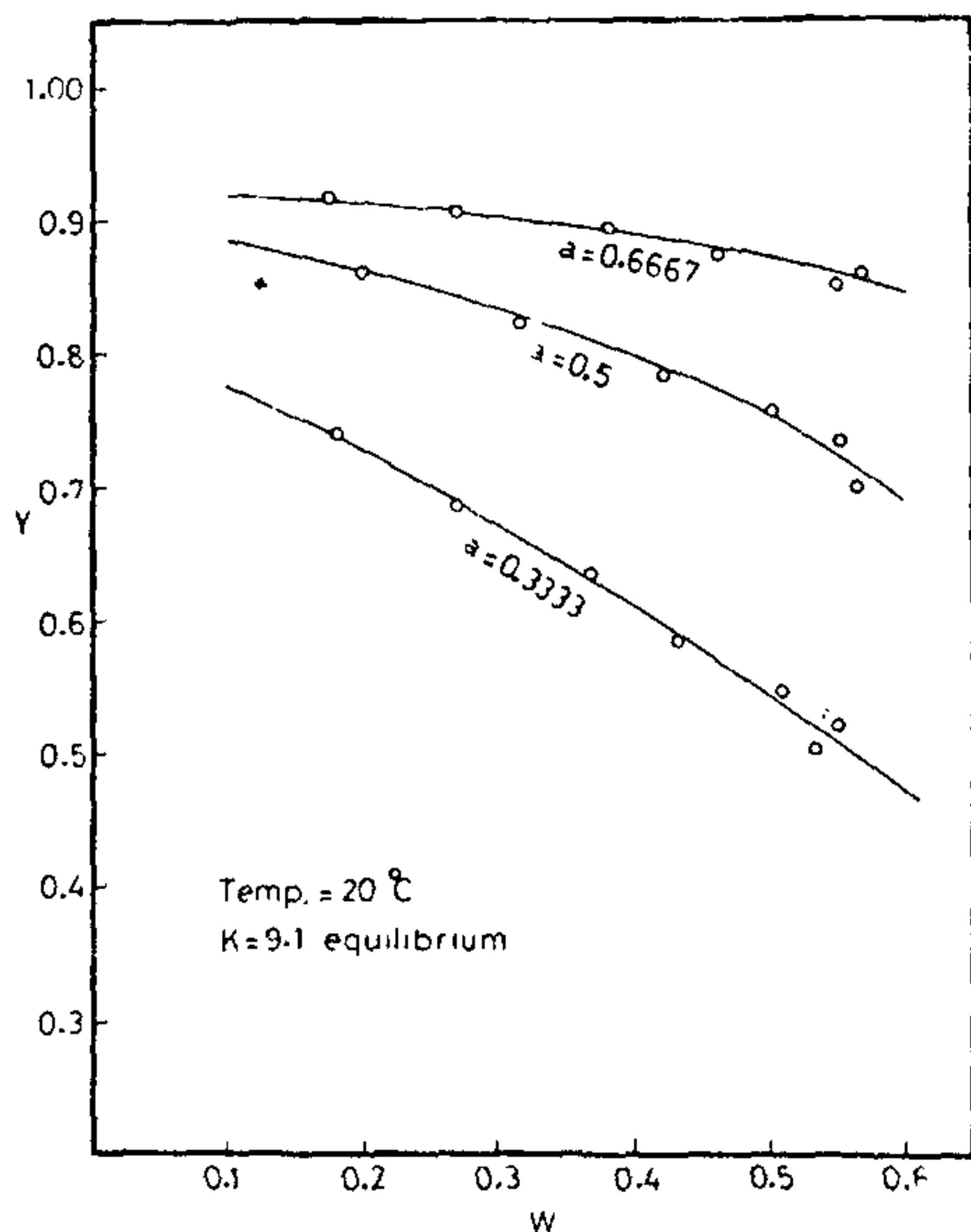
To verify the theory given above, the  $Y$  values corresponding to different amounts of  $W$  for equilibrium and non-equilibrium were calculated from equations (1) and (2) and the theoretical  $Y-W$  curves were drawn. The experimental results were plotted on the above curves to test the theory.

At 0°C, the  $Y$  vs.  $W$  plot throw some light on the crystallization process which varies according to the period of crystallization. When the period of crystallization is short (6 hr) no equilibrium is attained. Hence, equation (2) can be employed to explain the experimental results. Actually, the results lie on the theoretical curve for  $K = 4$ . A period of four days is sufficient for equilibrium and the experimental data agree with  $K = 11.4$  as shown in figure 1.

At 20 and 30°C, in contrast to that at 0°C, the results at 6 hr coincide with those at four days indicat-



**Figure 1.** Relation between  $W$ - $Y$  for the system cobalt ammonium sulphate—nickel ammonium sulphate at  $0^{\circ}\text{C}$ .



**Figure 2.** Relation between  $W$ - $Y$  for the system cobalt ammonium sulphate—nickel ammonium sulphate at  $20^{\circ}\text{C}$ .

ing that the equilibrium between solid and liquid phases is attained more quickly at a higher temperature.

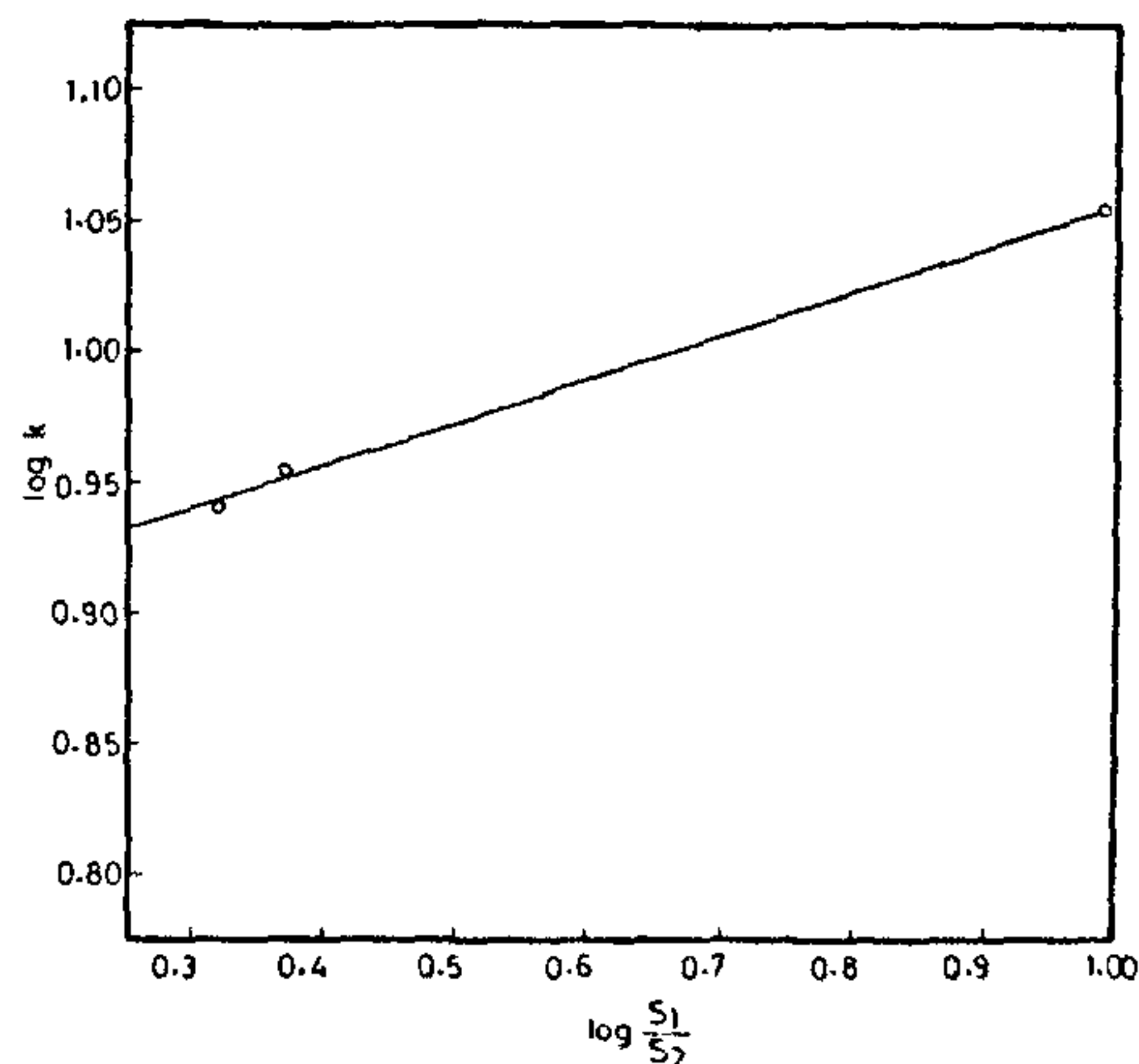
The theoretical values at equilibrium with  $K \approx 9.1$  (figure 2) and 8.8 fitted the experimental results at  $20^{\circ}\text{C}$  and  $30^{\circ}\text{C}$  respectively. The results at  $20^{\circ}\text{C}$  and  $30^{\circ}\text{C}$  show only approximate values of  $K$ , this can be explained as due to the approximate ratio of the solubilities of the two salts at the two temperatures as shown in table 1.

The above data at  $0^{\circ}\text{C}$ ,  $20^{\circ}\text{C}$  and  $30^{\circ}\text{C}$  show close agreement between theory and experiment. The deviation only becomes considerable for larger  $W$  values since the correction used in the calculation increases with  $W$ .

As reported earlier<sup>7</sup>, the importance of the above theory<sup>2</sup> lies in the fact that it is possible to calculate theoretically the amount of the less soluble salt in the system (expressed as weight fraction) that will be present in a given weight of crystals (expressed as weight fraction  $W$ ) that separate during crystallization.

The  $Y$  values increase with decrease in  $W$  and it is possible to separate the less soluble salt more effectively by allowing a small weight fraction of the crystals to separate out of the ternary system. This value of  $W$  can be obtained from Abu-Elamayem's equations<sup>2</sup>.

The correlation of the distribution coefficient  $K$  with the solubilities<sup>8</sup>  $S_1$  and  $S_2$  for the more and less soluble components respectively, has been investigated for this system. The results are shown in table 1 and represented in figure 3.



**Figure 3.** Relation between  $K$  and the solubilities of the two salts.



TABLE I

$t^{\circ}\text{C}$	$S_1^{(a)}$	$S_2$	$\text{Log } S_1/S_2$	$K_{\text{exp}}$
0	9.8	1.0	0.9912	11.35
20	15.5	6.5	0.3774	9.08
30	19.0	9.0	0.3245	8.78

<sup>(a)</sup>  $S_1$  for cobalt ammonium sulphate.

From figure 3, one can deduce

$$\text{Log } K = \log A + n \log S_1/S_2$$

The two constants  $A$  and  $n$  were calculated and were found to be 8.61 and 0.17 respectively.

The system is found to be of Roozeboom class I and behaves ideally over the entire concentration range of both the components.

The magnitude of the equilibrium distribution coefficient  $D_{\text{eqm}}$  of cobalt salt in nickel salt  $D_{\text{eqm}}(\text{Co}, \text{Ni})$

is calculated and is equal on the average to 0.31; the magnitude of the  $D_{\text{eqm}}(\text{Ni}, \text{Co})$  is equal on the average to 3.15

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## MODIFICATION OF SUSCEPTIBILITY IN RICE TO BACTERIAL LEAF BLIGHT BY PHENOLS AND RELATED SUBSTANCES

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### ABSTRACT

DL-Phenylalanine enhanced resistance of rice plants to *Xanthomonas campestris* pv. *oryzae* more effectively than shikimic acid, L-isomers of both phenylalanine and tyrosine, *p*-hydroxybenzoic, cinnamic, *p*-coumaric, caffeic, ferulic, vanillic and chlorogenic acids which are known to be present in rice plants when administered through the roots of seedlings.

### INTRODUCTION

**R**ICE cultivars reacting incompatibly to *Xanthomonas campestris* pv. *oryzae* (XCO) display brown discolouration of the tissue<sup>1</sup>. Although this bacterium is a typical vascular colonizer, microscopic examination of the diseased tissue revealed that the discolouration occurred not only in the vascular system, but also in the adjoining parenchymatous tissue<sup>1</sup>. This led to the postulation<sup>2</sup> that browning reaction is involved in the localization of the inoculum at the site of penetration.

Levels of phenols in XCO-infected rice leaves increased compared to healthy leaves<sup>3,4</sup>. This response is active especially in the resistant host-

parasite combinations caused by genetic make-up of the host and/or due to certain environmental factors like potassium nutrition of the host<sup>3</sup> and light intensity<sup>4</sup>. Paradoxically, in our earlier experiments, we found that the healthy leaves of bacterial blight susceptible rice cultivar possessed higher amounts of phenols than the less-susceptible and resistant cultivars. Since phenolic metabolism is associated with tissue discolouration leading to necrosis and disease resistance<sup>5,6</sup>, one major question is whether or not phenols are involved in bacterial blight resistance of rice. We therefore, investigated the effect of some of the native phenols of rice and their precursors on the development of bacterial leaf blight in rice plants.