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DISTRIBUTION COEFFICIENTS OF SOME DIVALENT IMPURITIES IN NaCl*

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ABSTRACT: The distribution coefficient of divalent impurities such as Mn^{2+}, Ca^{2+}, Cu^{2+} and Cd^{2+} in sodium chloride single crystals grown from the melt are determined by atomic absorption spectrophotometry. The crystals were grown by a method similar to that described by Kyropoulos. Graphs were obtained that show the dependence of the fractional impurity concentration as a function of the fraction of melt which has been solidified. From these graphs a value for the distribution coefficient for each impurity is obtained.

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INTRODUCTION

Until now general different analytical methods have been utilized for the determination of the distribution coefficients of metal impurities in NaCl crystals. Among these we have Chemical[1], Optical[2] as well as EPR[3] methods In this paper we report the use of atomic absorption spectrophotometry techniques to determine the distribution coefficients of the following divalent impurities: Mn^{2+}, Ca^{2+}, Cu^{2+} and Cd^{2+} in NaCl single crystals. This method of analysis was selected in view of the advantages it presents. The most important being its greatest sensibility in comparison with the methods previously cited.

EXPERIMENTAL

The method of Kyropoulos[4] in the open atmosphere (with some modifications[5] was used to grow the single crystals, starting with 200 gs of sodium chloride of reagent grade (J.T. Baker Chemical Co.). The impurities $MnCl_2$, $CaCl_2$, $CuCl_2$ and $CdCl_2$ were added in 1.04, 1.18, 2.25 and 1.45 1.45 wt%, respectively. When the desired crystal diameter was attained (about 3 cm), the growing conditions were regulated to keep the diameter uniform for the rest of the crystallization; condition considered to be representative of a steady state. Once the crystal is grown, it is allowed to cool slowly down to room temperature (in about 20 h). The crystals obtained were single and nearly cylindrically shaped.

The samples required for the atomic absorption analysis were prepared by cleaving slices perpendicular to the cylinder axis, at 3 mm intervals. The concentration of impurity in a sample was taken to represent the concentration at the average height of the sample in the crystal. The determination of the impurity concentration in each region of the analyzed crystal was made with a Perkin-Elmer, model 303, atomic absorption spectrophotometer. The disolution methods for the sample preparation are well known and are reported in the literature[6].

The crystallization conditions are such that we can make the following assumptions:

a) The rate of growth remains constant throughout the crystallization process.

b) The impurities are distributed uniformly throughout the melt.

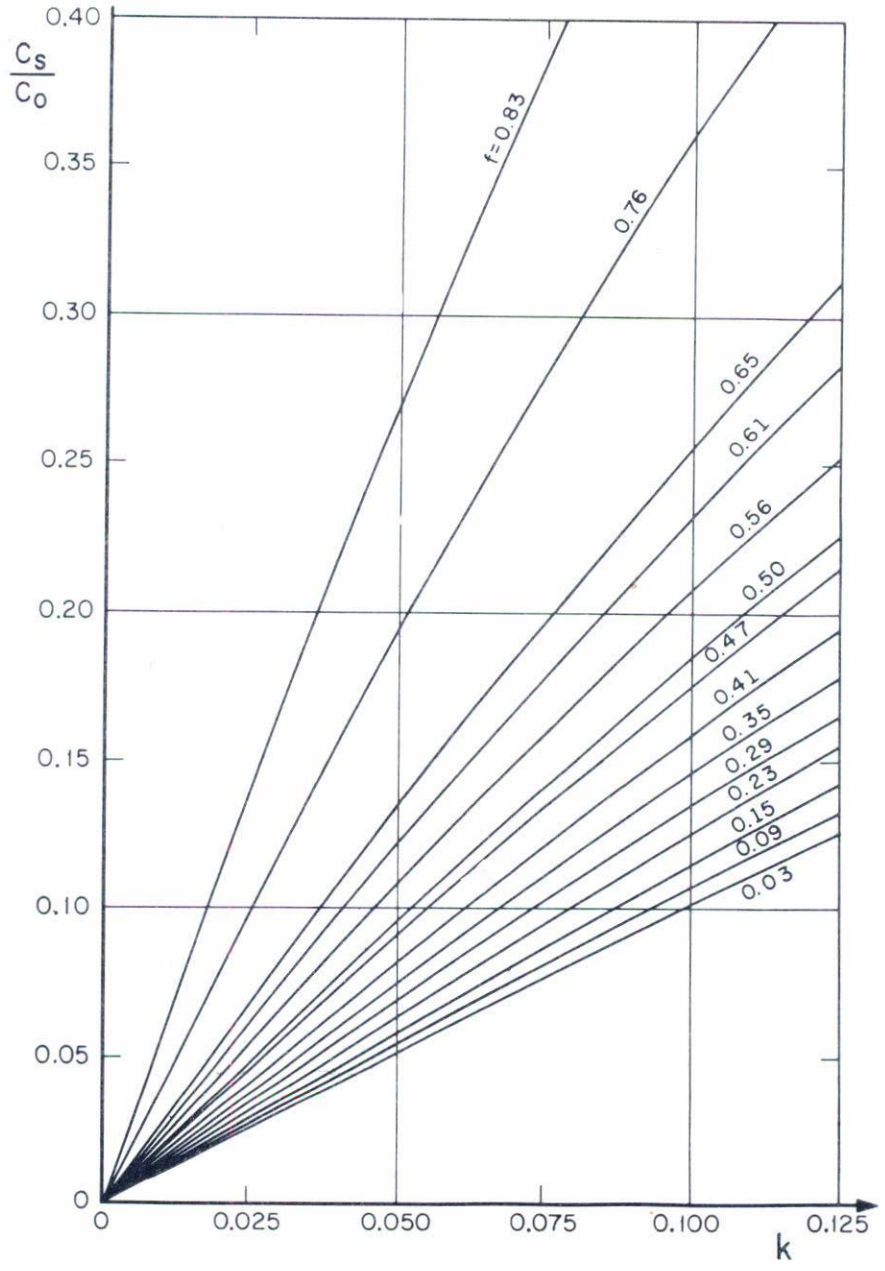

Fig. 1 Fractional impurity concentration as a function of the distribution coefficient for a series of values of the fraction of melt solidified.

Under these conditions the distribution of impurities in the crystal obeys Pfann's[7] equation:

$$\frac{C_s(x)}{C_0} = k\,[1 - f(x)]^{k-1}$$

were $C_s(x)$ is the impurity concentration in the solid at height x, measured from the seed along the crystallization axis; C_0, is the initial concentration in the melt, $f(x)$ is the ratio of the volume of the crystal of height x to the initial volume of melt and k the distribution coefficient.

Using this equation, we can make a plot of the fractional impurity concentration C_s/C_0 as a function of the distribution coefficient k for a series of values of the fraction of melt solidified $f(x)$. This is shown in Fig. 1. From this graph we obtain the values of the distribution coefficient corresponding to the fractional impurity concentrations measured for each fraction of melt solidified. The value of k for each crystal is taken as the average value for the various sample from a single crystal.

RESULTS AND CONCLUSIONS

The fractional impurity concentration as a function of the fraction of melt solidified for each crystal is shown in Fig. 2. In this graph, the points represent the experimental data, and the curves the average value of the distribution coefficient for each crystal.

The distribution coefficients for the four crystals grown are given in table 1, where the errors quoted correspond to one standard deviation.

The results show very good agreement between the theoretical curves and the experimental data, indicating that growth conditions approached the ones required by Pfann's theory. Moreover, in the case of Mn^{2+} our results agree (within the limits of the experimental error) with the value found by electron paramagnetic resonance[3]; in the case of the other impurities analized, the comparison with the results obtained by other authors[1] is difficult because they use both different growth rates and initial concentrations.

It may be argued that the background impurities present in the pure salt can affect our results. However, at this point we can only say that recently[8] the pure salt used has been analized using atomic absorption spectrophotometry and the impurity levels in almost every case is 3 orders of magnitude below the concentrations used in this work.

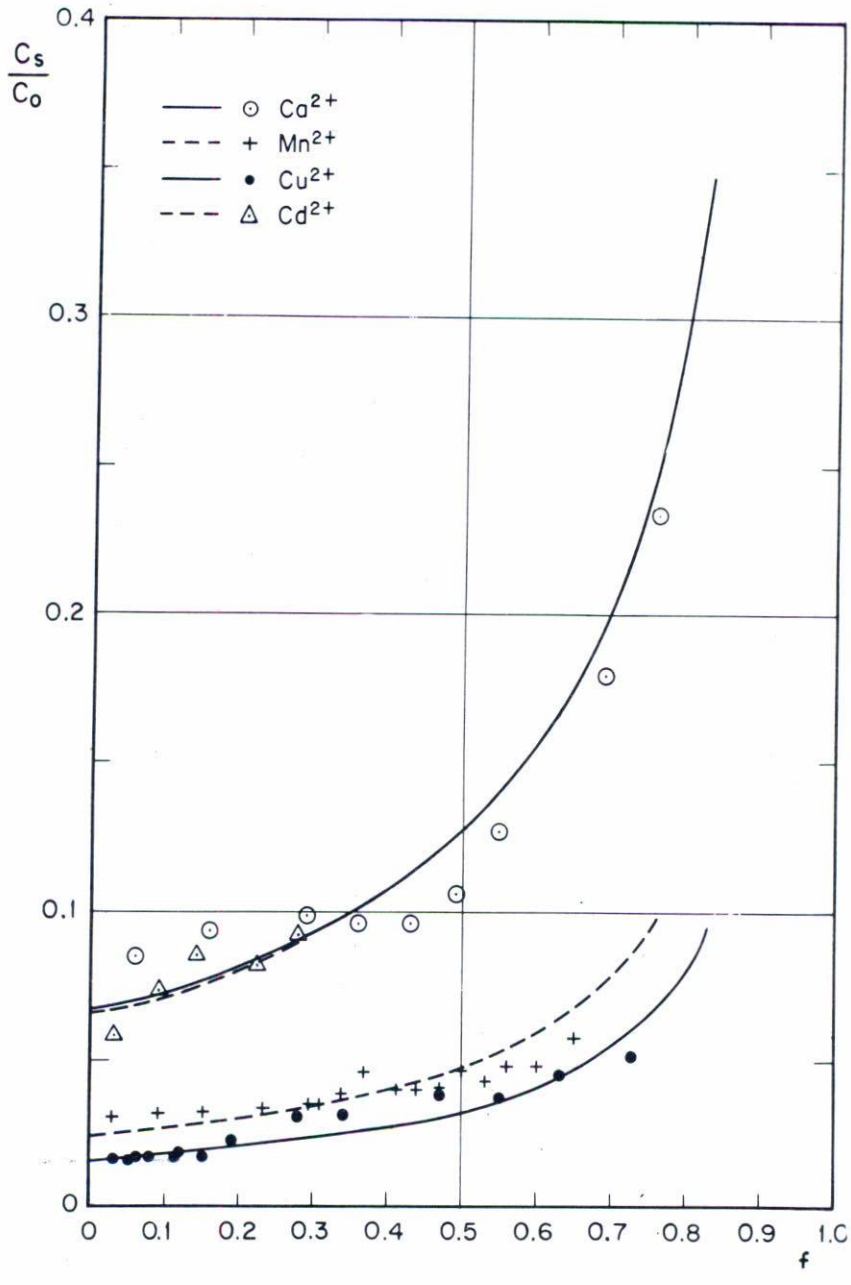

Fig. 2 Distribution of the impurities studied in sodium chloride crystals.

Impurity	Rate of growth (mm/h)	Initial concentration wt.%	$\langle k \rangle$
Mn^{2+}	13.2	1.04	.0248 ± .0007
Ca^{2+}	9.9	1.18	.0663 ± .0037
Cu^{2+}	10	2.25	.0171 ± .0006
Cd^{2+}	9.3	1.45	.0658 ± .0029

Table 1. The distribution coefficients for the impurities studied, the errors quoted correspond to one standard deviation.

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RESUMEN

En este trabajo se determinan los coeficientes de distribución de impurezas divalentes tales como Mn^{2+}, Ca^{2+}, Cu^{2+} y Cd^{2+} en monocristales de NaCl obtenidos a partir del fundente. Los cristales fueron crecidos por un método similar al descrito por Kyropoulos. De ellos se analizan muestras cortadas a niveles diferentes, perpendicularmente a la dirección de cristalización. Para el análisis de las muestras se utiliza la técnica de espectrofotometría por absorción atómica. Los resultados se grafican mostrando la relación de concentraciones en función de la fracción solidificada y de ellos se propone un valor para el coeficiente de distribución.