

SALT PURIFICATION BY RECRYSTALLIZATION. APPLICATION OF THE HOMOGENEOUS DISTRIBUTION LAW

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In a recently published series of papers on mathematical modelling of salt purification by recrystallization, the microcomponent distribution was assumed to follow the homogeneous distribution law $\bar{Y} = k_H \bar{X}$, where \bar{X} and \bar{Y} are the mean masses of the microcomponent *per* unit mass of the macrocomponent in the liquid and solid phases, respectively, and k_H is the analytically determined distribution coefficient of the microcomponent. From the physical point of view, it is more rigorous to assume the validity of an equation of the form $Y = k_H^* X$, where Y and X are the masses of the microcomponent *per* unit mass of the macrocomponent at the surface of the solid phase and in the solution, respectively, and k_H^* is the homogeneous distribution coefficient relating to the equilibrium between the microcomponent and macrocomponent in the solution and at the crystal surface (whereas the analytically determined k_H relates to the equilibrium with respect to the bulk of the crystals). This paper presents a simple relationship between the empirical coefficients of the two equations, permitting the recrystallization process to be described by means of the original simple equation using analytically determined component concentrations.

In crystallization of salts from multicomponent systems, microcomponents always become entrapped in the macrocomponent crystals. This is an undesirable phenomenon because of increasing requirements for the product purity. Crystal contamination can arise from a number of causes: the adherence of the mother liquor to the crystal surface; incorporation of the microcomponent into the crystal lattice, which may occur by various mechanisms¹⁻³; and enclosure of the contaminated solution in the bulk of the crystal. Although different mechanisms may operate, the microcomponent distribution can frequently be approximated by the so-called homogeneous distribution law**

$$Y = k_H^* X, \quad (1)$$

where $X = (w_2/w_1)_l$ and $Y = (w_2/w_1)_c$ are the masses of the microcomponent (2) *per* unit mass of the macrocomponent (1) in the liquid phase and at the surface of the solid phase, respectively, and k_H^* is the homogeneous distribution coefficient.

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** If the relative mole fractions are used in place of X and Y in Eqs (1) and (2), the coefficients k_H^* and k_H have the same numerical values.

In previous papers⁴⁻⁸ we developed mathematical models of salt purification by recrystallization. The microcomponent distribution was formally described in terms of Eq. (1) in the form

$$\bar{Y} = k_H \bar{X}, \quad (2)$$

where \bar{X} and \bar{Y} are the mean masses of the microcomponent *per* unit of the macrocomponent in the liquid and solid phases, respectively, at the equilibrium temperature of crystallization. Equation (2) is strictly true only if the empirical parameter k_H is determined under the same conditions (especially the concentrations and the parameters of the mass balance) as those of the operating crystallizer. If this is not the case, the reliability of the models is reduced. The aim of the present work is to overcome the limitation imposed by this approximation by finding a transformation equation

$$k_H = k_H(k_H^*) \quad (3)$$

which would permit correction of the experimentally determined parameter k_H to that for different conditions, *i.e.* for different initial and/or equilibrium macrocomponent concentration in the system, thereby increasing the reliability of the application of the models derived previously⁴⁻⁸.

THEORETICAL

We shall derive transformation equations (3) for a well stirred continuous crystallizer and a batch crystallizer.

For a well stirred continuous crystallizer operating in a steady-state regime, we have

$$\bar{X} = X, \quad \bar{Y} = Y, \quad (4)$$

and hence we obtain the trivial solution

$$k_H = k_H^*. \quad (5)$$

A more complicated situation is found with a batch crystallizer, where the compositions of both phases are functions of time. The mass balance for the microcomponent over the time interval $\langle 0, t_c \rangle$, where t_c is the batch time, yields

$$w_{o1} X_o = (w_{o1} - w_{f1}) \bar{Y} + w_{f1} X_f, \quad (6)$$

where w_{o1} and w_{f1} are the macrocomponent concentrations in kg/kg of solvent at the beginning and at the final temperature of crystallization, respectively; X_o and X_f are the masses of the microcomponent *per* unit mass of macrocomponent in the

liquid phase at the beginning and the end of crystallization, respectively; and \bar{Y} is the mean mass of the microcomponent *per* unit mass of macrocomponent in the solid phase. On the basis of Eq. (2), we can write

$$\bar{Y} = k_H \bar{X}_f = k_H X_f. \quad (7)$$

The mass balance equation for the microcomponent on a batch crystallizer at time t (expressed with respect to 1 m^3 of solvent) is

$$\dot{m}_c Y(t) + \rho_{\text{sol}} d(w_1 X)/dt = 0, \quad (8)$$

where \dot{m}_c is the amount of macrocomponent which crystallizes in unit time from unit volume of solvent, and ρ_{sol} is the solvent density. The product $\dot{m}_c Y(t)$ is the rate of increase of the microcomponent amount (*per* 1 m^3 of the solvent) in the crystal mass. The second term in Eq. (8) represents the accumulation of the microcomponent in solution.

From Eq. (8), we obtain

$$Y dm_c + \rho_{\text{sol}}(X dw_1 + w_1 dX) = 0. \quad (9)$$

The mass balance equation for the macrocomponent at time t (expressed with respect to 1 m^3 of the solvent) is of the form

$$m_c = \rho_{\text{sol}}(w_{o1} - w_1).$$

Hence,

$$dm_c = -\rho_{\text{sol}} dw_1. \quad (10)$$

Combining Eqs (9) and (10) and integrating within the limits $\langle w_{o1}, w_{f1} \rangle$ and $\langle Y_o, Y_f \rangle$, we get

$$\ln(w_{o1}/w_{f1}) = - \int_{Y_o}^{Y_f} (Y - X)^{-1} dX. \quad (11)$$

Taking into account Eq. (1), we can rewrite Eq. (11) as

$$\ln(w_{o1}/w_{of}) = (1 - k_H^*)^{-1} \ln(Y_f/Y_o)$$

or

$$Y_f = Y_o(w_{o1}/w_{f1})^{1-k_H^*}.$$

Since, on the basis of Eq. (1),

$$Y_o = k_H^* X_o,$$

it follows that

$$Y_f = k_H^* X_o (w_{o1}/w_{f1})^{1-k_H^*}. \quad (12)$$

Equation (1) may also be written in the form

$$X_f = Y_f/k_H^*. \quad (13)$$

Using Eqs (7), (12), and (13), Eq. (6) can be transformed to the form

$$(w_{o1}/w_{f1})^{k_H^*} = (w_{o1}/w_{f1} - 1) k_H + 1 \quad (14)$$

or

$$k_H^* = \ln [(w_{o1}/w_{f1} - 1) k_H + 1] / \ln (w_{o1}/w_{f1}) \quad (15a)$$

or, alternatively,

$$k_H = [(w_{o1}/w_{f1})^{k_H^*} - 1] / (w_{o1}/w_{f1} - 1). \quad (15b)$$

Equations (14) and (15) are the final forms of transformation equation (3) for a well stirred batch crystallizer. The $k_H(k_H^*)$ dependence expressed by Eq. (14) or (15) is represented in Fig. 1 for various values of w_o/w_f . The graph is confined to the range of validity of the model of recrystallization realized in a countercurrent cascade⁴, i.e. to $w_o/w_f \geq 2$.

EXPERIMENTAL

Calculation of the Distribution Coefficient from Experimental Data for a Batch Crystallizer

A saturated solution of $\text{NH}_4\text{Al}(\text{SO}_4)_2$ in distilled water was prepared in a laboratory crystallizer at $T_0 = 60^\circ\text{C}$ and then cooled down to $T_f = 20^\circ\text{C}$. Before crystallization the salt contained $y_0 = 7.8 \cdot 10^{-5} \text{ Fe}^{2+}$. The separated product crystals contained $y_f = 2.4 \cdot 10^{-5} \text{ Fe}^{2+}$. The quantities y_o and y_f are the mass fractions of the microcomponent before and after crystallization, respectively. The solubilities have been tabulated⁹ as $w_o(60^\circ\text{C}) = 0.5217 \text{ kg of hydrate/kg of free solvent}$, and $w_f(20^\circ\text{C}) = 0.1107 \text{ kg of hydrate/kg of free solvent}$. From the definitions of the concentrations, it follows that

$$\begin{aligned} \bar{Y}_o &= y_o / (1 - y_o) \\ \bar{Y}_f &= y_f / (1 - y_f). \end{aligned} \quad (16)$$

The mass balance equation for the microcomponent in a batch crystallizer (Eq. (6)) can be rearranged to give

$$\bar{X}_f = [w_o \bar{Y}_o - (w_o - w_f) Y_f] / w_f. \quad (17)$$

On the basis of Eq. (2), we can write

$$k_H = \bar{Y}_f / \bar{X}_f. \quad (18)$$

From Eqs (16) to (18), we obtain $k_H = 0.039$. In our case, the distribution coefficient k_H was determined for a batch crystallizer with $w_o/w_f = 4.71$.

Correction of the Distribution Coefficient to That for Different Conditions

In the preceding section, we determined the distribution coefficient for $w_o/w_f = 4.71$. Now we shall calculate its value for changed conditions, $w_o/w_f = 3.0$.

From Eq. (14) with $k_H = 0.039$ and $w_o/w_f = 4.71$, we find $k_H^* = 0.0872$. Substituting this value and the new ratio $w_o/w_f = 3.0$ into Eq. (15) yields $k_H = 0.050$. With this value of k_H and the ratio $w_o/w_f = 3.0$, we can apply the models derived previously⁴⁻⁸.

Calculation of the Distribution Coefficient k_H^* from Experimental Data for a Well Stirred Continuous Crystallizer

A solution of $\text{NH}_4\text{Al}(\text{SO}_4)_2$ saturated at 35°C was cooled in a laboratory continuous crystallizer to 25°C . Before and after crystallization the salt contained $y_o = 7.8 \cdot 10^{-5} \text{Fe}^{2+}$ and $y_f = 3.1 \cdot 10^{-5} \text{Fe}^{2+}$, respectively. In solubility tables⁹ we find $w_o(35^\circ\text{C}) = 0.1932$ and $w_f(25^\circ\text{C}) = 0.1342$ kg of hydrate/kg of free solvent. The values of \bar{Y}_o and \bar{Y}_f are obtained from Eq. (16). The mass balance equation for the microcomponent on the continuous crystallizer, coupled with Eqs (4) and (5), yields

$$k_H^* = \frac{w_f \bar{Y}_f}{w_o \bar{Y}_o - (w_o - w_f) \bar{Y}_f} = 0.314.$$

Since Eq. (5) is valid, the coefficient k_H^* need not be corrected if the continuous crystallization is operated at different values of w_o and w_f . If, however, data from a continuous crystallizer are to be applied to batch crystallization, recalculation using Eq. (15) is necessary. When applying

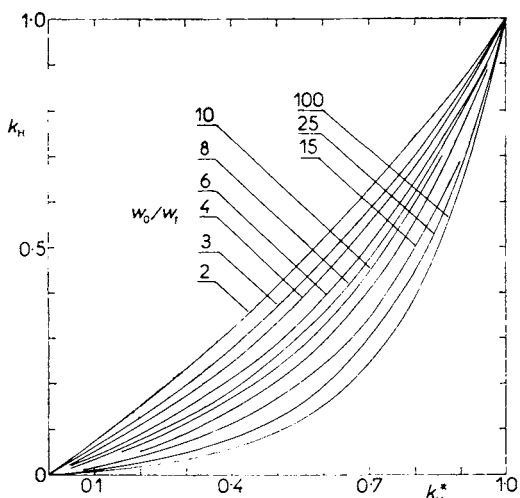


FIG. 1

The $k_H(k_H^*)$ dependence for various concentration ratios w_o/w_f . The figure on each curve indicates the relevant w_o/w_f value

data obtained in this way, we must bear in mind that, under otherwise the same conditions, the coefficients k_H and k_H^* depend largely on the cooling rate. When the previously derived models⁴⁻⁸ are used, it is therefore advisable to determine the coefficient k_H or k_H^* under conditions close to those of the actual operational regime and to use Eq. (14) or (15) only to correct the value for a different w_o/w_f ratio.

LIST OF SYMBOLS

k_H	distribution coefficient of microcomponent determined analytically from phase compositions
k_H^*	homogeneous distribution coefficient
m_c	mass of suspension
\dot{m}_c	instantaneous specific output of crystallizer
t	time
t_c	batch time
T	temperature, °C
w_1	concentration of macrocomponent, kg/kg of solvent
X	mass of microcomponent <i>per</i> unit mass of macrocomponent in the liquid phase
\bar{X}	mean mass of microcomponent <i>per</i> unit mass of macrocomponent in the liquid phase
Y	mass of microcomponent <i>per</i> unit mass of macrocomponent at the surface of the solid phase
\bar{Y}	mean mass of microcomponent <i>per</i> unit mass of macrocomponent in the bulk of the solid phase
y	mass fraction of microcomponent in the solid phase
ρ_{sol}	solvent density, kg m ⁻³

Subscripts

1	macrocomponent
2	microcomponent
o	at the start of crystallization
f	at the end of crystallization

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