

## EFFECT OF IMPURITIES ON THE WIDTH OF THE METASTABLE REGION OF POTASSIUM SULFATE

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The width of the metastable region of potassium sulfate was measured in the presence of various concentrations of chromate, copper(II) and aluminium ions. The dependence of the metastable region width on the impurity concentration is generally nonlinear and in some cases even changes its nature: while in low concentrations some impurities make the metastable region narrower, they make it broader if present in higher concentrations. The effect of the impurities increases in order  $\text{K}_2\text{Cr}_2\text{O}_7 - \text{CuSO}_4 - \text{Al}_2(\text{SO}_4)_3$ .

Published data concerning the effect of impurities on the kinetics of nucleation and the associated supercoolability of solutions are rather inconsistent<sup>1,2</sup>. Inorganic impurities can generally be divided into highly active and little active. Highly active impurities include mainly polyvalent metal cations such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cd}^{2+}$  and some anions, e.g.  $\text{WO}_4^{2-}$  and  $\text{PO}_4^{3-}$ . Such substances are able to cause appreciable changes in the crystallization parameters if present in concentrations even as low as thousandths to hundredths per cent, whereas units to tens per cent concentrations are necessary in the case of little active substances.

The effect of concentration of the impurity has been dealt with only scarcely in the literature. The effect of  $\text{Pb}^{2+}$  ions on the crystallization of KCl is an exception (an overview of papers is given, e.g., in ref.<sup>3</sup>). It is reported that lead ions widen the metastable region monotonically following the relation

$$S = \text{const } c_{\text{Pb}^{2+}}^{0.25} . \quad (1)$$

A direct proportionality between the attainable supercooling and the impurity concentration has also been reported by other authors<sup>2,4,5</sup>. The effect of  $\text{Mn}^{2+}$  ions on the width of the metastable region of ammonium sulfate<sup>6</sup> is somewhat more complex, the concentration dependence exhibiting a pronounced minimum in the 0.15% range.

From among impurities affecting the nucleation kinetics of potassium sulfate, the effect of  $\text{Pb}^{2+}$  has been studied in ref.<sup>7</sup> and of  $\text{Cr}^{3+}$  and other ions in refs<sup>8-11</sup>. The

majority of papers dealing with the effect of impurities on the crystallization of  $\text{K}_2\text{SO}_4$  were concerned with the crystal shape as affected by some inorganic anions<sup>12 - 14</sup>, whereas other papers report the effect of divalent and trivalent cations on the crystal size distribution<sup>15 - 24</sup>. The impurities investigated include, among others,  $\text{Cu}^{2+}$  (refs<sup>22,24</sup>),  $\text{Al}^{3+}$  (ref.<sup>24</sup>) and  $\text{K}_2\text{CrO}_4$  (refs<sup>14,25 - 28</sup>). Particular attention has been paid to the effect of trace quantities of  $\text{K}_2\text{CrO}_4$  or chromium(III) ions<sup>29 - 32</sup> because they seemed to significantly affect the solubility of the macrocomponent. Actually, however, this effect can be unambiguously ascribed to a marked slowing-down of the growth and dissolution of  $\text{K}_2\text{SO}_4$ . The above impurities, which apparently affect the crystallization of  $\text{K}_2\text{SO}_4$  appreciably, were chosen in this work to examine their effect on the width of the metastable region and hence, on nucleation behaviour, of potassium sulfate.

Various explanations of the effect of impurities on nucleation have been suggested<sup>1</sup>. One of them consists in an effect on the surface tension of the solution and thus on the crystal-solution interface tension. This effect is marked in the case of surfactants, which accelerate nucleation. In the case of inorganic impurities one can rather expect a slight increase in the surface tension bringing about slowed-down nucleation. Active inorganic impurities possessing a high ability to form coordination complexes reduce the nucleation rate; this effect is the more pronounced, the more stable the corresponding complex is. The complexes form so-called heteronuclei, whose number corresponds to the number of active ions into which the supersaturation redistributes and due to which the probability of nucleation of the macrosubstance in the bulk decreases. The inhibiting effect of some impurities is explained so that the impurity adsorbs on the surface of subcritical embryos, thereby preventing their growth to the critical size. In the case of high concentrations of low-activity impurities, the explanation can be sought in an increase in the solution viscosity and an associated decrease in the mobility of the ions of the macrosubstance, owing to which the probability of formation of critical nuclei is lowered. An accelerating effect on the nucleation can be expected in the case of impurities which are capable of forming lower soluble compounds with the macrosubstance. Impurities with a high hydrating power can reduce the number of water molecules available for the hydration of the macrosubstance ions and thereby also promote the nucleation. The above effects can play a still more marked part during heterogeneous nucleation on dust and colloid particles which are present in the solution, or during secondary nucleation as a result of formation of an adsorption layer on the surface of existing crystals. The mechanism of the impurity concentration gradient<sup>2</sup> on the crystal surface can play an additional role in systems where the impurity is easily entrained into the crystal lattice of the growing crystals: spontaneous nucleation does not occur in the solution bulk because the concentration of the inhibiting impurity is too high, while in the surface layer of the crystal the concentration of the impurity decreases due to its incorporation into the crystal, whereby its inhibiting effect is reduced also.

## EXPERIMENTAL

The following chemicals were used:  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  of reagent grade purity (Lachema, Brno, The Czech Republic) and  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  of technical purity (Lučební závody, Uhřetěves, The Czech Republic). Deionized water was employed to prepare the solutions. Solutions of  $\text{K}_2\text{SO}_4$  were saturated at  $50^\circ\text{C}$ , the data are given in Table I.

The apparatus and measuring procedure were as described previously<sup>3</sup>. Sample  $100 \text{ cm}^3$  volume was cooled from the temperature  $0.5 \text{ K}$  above the saturation temperature downwards until crystal bond was visually indicated at a temperature  $T$ , applying a rate of  $-\dot{T} = 20 \text{ K h}^{-1}$ . The difference between the saturation temperature  $T_{\text{eq}}$  and the above-mentioned temperature  $T$  gives the maximum supercooling  $\Delta T_{\text{max}}$ .

## RESULTS AND DISCUSSION

The results of measurement of the metastable region of potassium sulfate in the presence of  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$  cations and  $\text{Cr}_2\text{O}_7^{2-}$  anions are summarized in Table I and shown in Fig. 1. The metastable region width is nonlinear in all cases and can be described by the equation:

$$\Delta T_{\text{max}} = a + b \ln p + c \ln^2 p, \quad (2)$$

where  $p$  is the concentration (in wt.%) of the impurity, i.e.  $\text{CuSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , in the solution. The  $a$ ,  $b$  and  $c$  values are as follows:

$a = 21.22$ ,  $b = 2.743$ ,  $c = 0.2137$  for  $\text{CuSO}_4$ ,

$a = 28.05$ ,  $b = 4.937$ ,  $c = 0.3711$  for  $\text{Al}_2(\text{SO}_4)_3$ , and

$a = 16.54$ ,  $b = 0.684$ ,  $c = 0.0404$  for  $\text{K}_2\text{Cr}_2\text{O}_7$ .

The minimum for  $\text{Cu}^{2+}$  is  $12.42$  and lies at  $p = 0.00163\%$ , the minimum for  $\text{Al}^{3+}$  is  $11.62$  and lies at  $p = 0.00130\%$ , and the minimum for  $\text{Cr}_2\text{O}_7^{2-}$  lies deeply below the concentration of  $10^{-4}\%$ .

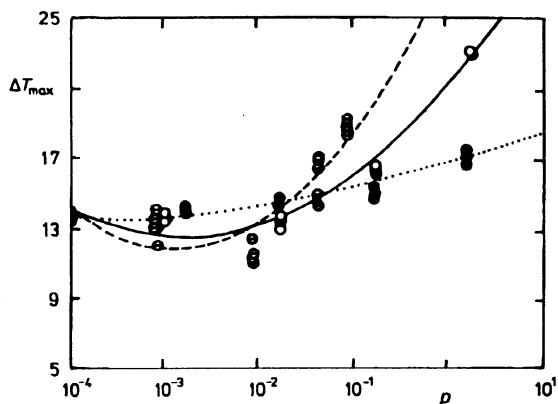


FIG. 1

Width of the metastable region of potassium sulfate in the presence of impurities: —  $\text{CuSO}_4$ , ---  $\text{Al}_2(\text{SO}_4)_3$ , ····  $\text{K}_2\text{Cr}_2\text{O}_7$ ;  $p$  is the impurity content (wt.%) in the solution

For the correlation it was assumed that pure  $K_2SO_4$  contains heavy metals in quantities corresponding to a concentration of  $1 \cdot 10^{-4}\%$  in solution.

Aluminium and copper ions form with potassium sulfate binary salts, viz.  $KAl(SO_4)_2$  and  $K_2Cu(SO_4)_2$ , respectively, which are less soluble than the starting components. With reference to the above considerations, it is plausible to assume that in the region of very low concentrations of the impurities there form subcritical heteronuclei or, rather, heteroembryos, which facilitate clustering of particles of the macrocomponent and thus promote the nucleation, that is, make the metastable region narrower. With its increasing concentration, the microimpurity either withdraws the ions of the macrosubstance, thereby lowering the effective supersaturation, or – which is more likely – adsorbs preferentially on the surface of embryos of the macrosubstance and so reduces the probability of nucleation, that is, makes the metastable region broader. Similar behaviour has been observed previously<sup>6</sup> in solutions of  $(NH_4)_2SO_4$  in the presence of  $Mn^{2+}$  ions: here, too, the binary sulfate  $(NH_4)_2Mn(SO_4)_2$  can form.

In the case of the  $Cr_2O_7^{2-}$  ions, or  $CrO_4^{2-}$  ions, only the mechanism of microimpurity adsorption on subcritical clusters is apparently involved, causing a slight hindering effect of the impurity on the nucleation of the macrocomponent.

TABLE I  
Width of the metastable region of potassium sulfate in the presence of impurities

Impurity	$T_{eq}$	Impurity concentration wt. %	$\Delta T_{max}^a$
–	51.3	–	$13.56 \pm 0.27$
$K_2Cr_2O_7$	52.0	0.0016	$14.02 \pm 0.08$
	51.8	0.016	$14.50 \pm 0.19$
	52.1	0.16	$15.05 \pm 0.26$
	55.1	1.6	$17.04 \pm 0.45$
$CuSO_4$	51.2	0.00165	$11.51 \pm 0.42$
	50.3	0.0166	$13.28 \pm 0.22$
	51.05	0.0166	$13.28 \pm 0.31$
	50.2	0.167	$16.31 \pm 0.23$
	47.8	1.68	$23.12 \pm 0.06$
$Al_2(SO_4)_3$	50.6	0.000826	$13.05 \pm 0.70$
	51.5	0.00824	$11.69 \pm 0.59$
	50.0	0.0411	$15.86 \pm 1.18$
	50.0	0.082	$18.58 \pm 0.38$

<sup>a</sup> Standard deviation of the  $\Delta T_{max}$  value calculated from 5 replicate measurements.

## CONCLUSIONS

Generally, the dependences of the metastable region width on the microimpurity concentration are not monotonous. In the case of microcomponents which can form stable complexes or binary salts with the macrocomponent, very low concentrations of the impurity bring about acceleration of the nucleation, whereas higher concentrations of the impurity cause inhibition to the nucleation through some different mechanism.

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