METASTABLE REGION OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE CONTAINING LEAD(II) IONS

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The method of cooling at a constant rate was applied to determine the width of the metastable region of aqueous solutions of potassium chloride saturated at approximately 40 °C and containing 0 to 0.1 wt.% $Pb(NO_3)_2$. Lead(II) ions widen the metastable region up to a $Pb(NO_3)_2$ concentration of about 0.01%, at which the solution is apparently saturated with the addition. Additional increase in the $Pb(NO_3)_2$ concentration rather makes the metastable region narrower. The experimental data are compared with published values and discussed in terms of theories. A plausible explanation of the observed dependences is based on Glasner's theory of nucleation of KCl in the presence of Pb^{2+} ions.

Crystallization of potassium chloride is affected appreciably by the presence of lead(II) ions. This effect was described quantitatively as early as 1939 by Yamamoto[1] and later by Sears[2], but it was not until 1962 that Kenat[3] started a number of studies dealing with this problem in detail. He found that in the presence of lead(II) ions, the maximum supersaturation of aqueous solutions of KCl, saturated at 35 °C, obeys the equation

$$S = 3.8\, c_{Pb^{2+}}^{0.25} \qquad (I)$$

(for lead concentrations in mol / 1 000 g H_2O). The problem was independently studied by Botsaris and coworkers[4], who also demonstrated that lead(II) ions suppress the nucleation of KCl; they suggested that lead poisons the heterogeneous germs or even inhibits the submicroscopic homogeneous embryos. Glasner and Skurnik[5] examined the nucleation and growth of KCl crystals in the presence of lead(II) ions and concluded that lead ions act as centres for the creation of embryos and thereby cause changes in their distribution. They suggested that the higher the lead concentration, the more embryos are created but the smaller they are in size. Only large embryos have a chance of growing to the size of crystal germs while small embryos play a role in the growth of crystals already present. This model has been criticised by Botsaris and Reid[6], who argue that lead ions affect not only the nucleation but also the growth of KCl crystals, which is hardly possible if they are embedded in embryos; crystal growth caused by embedding of whole clusters is improbable because lead slows down the growth of the

(100) and (111) planes but is embedded in the (100) planes solely. The authors draw attention to the fact that for a constant growth rate the equation

$$S/c_{Pb^{2+}}^{0.4} = \text{const.} \qquad (2)$$

is satisfied, which makes possible quantitative prediction of the effect of lead ions on the crystallization of potassium chloride. In a next work, where they examined the crystallization of KCl calorimetrically, Glasner and Kenat[7] found the maximum supersaturation to obey the relation

$$S = 76\, c_{Pb^{2+}}^{0.25} , \qquad (3)$$

the supersaturation being expressed as

$$S = 2.8\, (T_{eq} - T_{cr}) \qquad (4)$$

(in g KCl / 1 000 g H_2O). This result is interpreted by Glasner[8] as an evidence of heteronucleation and embedding of clusters in the growth mechanism. This concept was elaborated in more detail in ref.[9]. The relation between the nucleation rate and the growth of KCl crystals was later the concern of Seifert and Mersmann[10], who observed a high effect of pH: the effect of lead ions is eliminated at increasing pH.

The above papers, if dealing with the metastable region width, lack the definition of additional parameters relevant to the measurement, such as the cooling rate. Therefore, the aim of the present work was to determine the metastable region width for aqueous solutions of potassium chloride containing various amounts of lead(II) ions in dependence on the cooling rate, and to calculate nucleation parameters based on these data.

EXPERIMENTAL

The working solution was prepared from potassium chloride of reagent grade purity containing no more than 0.0005% heavy metals (lead) and from lead nitrate of reagent grade purity (both Lachema, Brno); distilled water was used. Lead salt solution was prepared by pipetting the requisite volume of 1% lead nitrate solution into a 1 000 cm^3 volumetric flask and diluting with water. In this solution, potassium chloride was dissolved in an amount corresponding to its tabulated solubility[11]. The lead nitrate concentration was increased by 0.0002% introduced into the solution by the used potassium chloride. Similar procedure has been employed up to the concentration of $Pb(NO_3)_2$ in the solution of 0.1%. Although the solubility product of $PbCl_2$ was then highly surpassed, no precipitation of this salt was observed. In the working solution so obtained, the temperature of saturation with KCl was determined by the last crystal dissolution method.

The metastable region width for the aqueous KCl solutions was measured by the method of cooling at a constant rate[12]: 100 cm^3 sample was cooled from a temperature 0.5 °C above the saturation temperature, applying a rate of $-\dot{T}$ = 5 or 20 °C / h until the first crystals could be observed visually. Temperature was measured with a platinum resistance thermometer and decreased by means of a digital programmable regulator. The difference between the temperature at which first crystals were observed and the temperature of saturation is the undercooling ΔT_{max}. The results of measurement are given in Table I.

RESULTS AND DISCUSSION

Observed data were fitted by the equation[12,13]

$$\log \Delta T_{max} = A + B \log (-\dot{T}) \tag{5}$$

using the least squares method. The constants A and B can be assigned the physical meaning of

$$A = [(1 - m) / m] \log (dw_{eq} / dT) - [(\log k_N) / m] \tag{6}$$

and

$$B = 1 / m , \tag{7}$$

where dw_{eq} / dT is the temperature solubility coefficient, m is the apparent nucleation order and k_N is the rate constant of nucleation in the power formula

$$\dot{N}_N = k_N \Delta w^m . \tag{8}$$

TABLE I
Observed metastable region widths for KCl solutions saturated at 41 – 42 °C

% $Pb(NO_3)_2$	$-\dot{T}$	Number of measurements	Average ΔT_{max}
0.0002	5	5	3.36 ± 0.12
	20	5	4.39 ± 0.13
0.0003	5	12	7.20 ± 0.09
	20	21	9.17 ± 0.17
0.0008	5	7	7.29 ± 0.07
	20	7	8.75 ± 0.14
0.0012	5	6	7.95 ± 0.16
	20	9	8.91 ± 0.10
0.0052	5	7	11.64 ± 0.10
	20	8	13.25 ± 0.16
0.01	5	7	13.17 ± 0.10
	20	14	14.82 ± 0.54
0.05	5	9	10.43 ± 0.95
	20	3	12.47 ± 0.32
0.1	5	8	9.95 ± 0.08
	20	10	12.24 ± 0.20

The results of calculation are given in Table II, the fitted undercooling values back-calculated from Eq. (5) are given in Table III. The straight lines expressed by Eq. (5) are shown in Fig. 1 for the various lead nitrate concentrations; in a nomographic representation enabling interpolation they are shown in Fig. 2.

Figure 3 shows the dependence of the apparent nucleation exponent m on the concentration of the lead salt. This dependence is nonlinear and exhibits a pronounced maximum at lead nitrate concentrations about $5 \cdot 10^{-3}$%. Such behaviour has been observed in other systems as well[14]. In this case it can be supposed that at the above

TABLE II
Evaluation of experimental data of the metastable region width

% $Pb(NO_3)_2$	A	B	m	k_N
0.0002	0.39098	0.19333	5.17	99 240
0.0003	0.73468	0.17500	5.71	15 633
0.0008	0.77016	0.13205	7.57	$1.86 \cdot 10^7$
0.0012	0.84248	0.08245	12.13	$2.71 \cdot 10^{14}$
0.0052	1.00073	0.09345	10.70	$2.10 \cdot 10^{10}$
0.01	1.05994	0.08512	11.75	$1.72 \cdot 10^{11}$
0.05	0.92544	0.13083	7.64	1 618 491
0.1	0.89542	0.14773	6.77	101 124

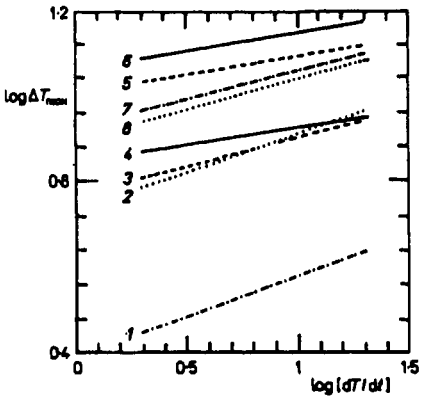

FIG. 1
Linearized dependence of maximum undercooling ΔT_{max} on cooling rate $-\dot{T}$. Lead nitrate concentration (in %): *1* 0.0002, *2* 0.0003, *3* 0.0008, *4* 0.0012, *5* 0.0052, *6* 0.01, *7* 0.05, *8* 0.1

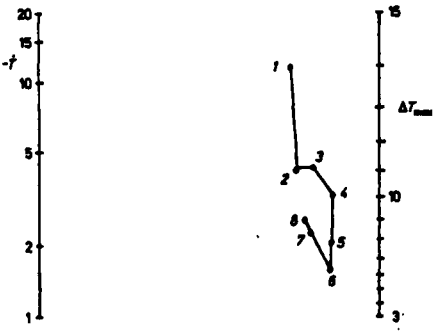

FIG. 2
Nomographic representation of the metastable region. Numbering as in Fig. 1. The line connecting the cooling rate value and the corresponding point passes the point of resulting undercooling

concentration of $Pb(NO_3)_2$, the solubility product of $PbCl_2$ was surpassed (the solubility product value is $1.327 \cdot 10^{-4}$) although its precipitation was not observed visually.

Using the relations reported previously[15,16], data calculated from metastable region width measurements can be employed to estimate the classical nucleation parameters, i.e. the number of particles constituting a critical nucleus,

$$N^* = (4m - 3g - 4)\,\overline{\Delta w} / w_{eq} \qquad (9)$$

TABLE III
Fitted values of maximum undercooling

% $Pb(NO_3)_2$	ΔT_{max} for $-\dot{T}$ =			$\delta(\Delta T_{max})$
	2 K/h	5 K/h	20 K/h	
0.0002	2.81	3.36	4.39	±0.12
0.0003	6.13	7.19	9.17	±0.14
0.0008	6.46	7.29	8.75	±0.11
0.0012	7.37	7.95	8.91	±0.12
0.0052	10.69	11.64	13.25	±0.13
0.01	12.18	13.17	14.81	±0.44
0.05	9.22	10.40	12.46	±0.82
0.1	8.71	9.97	12.24	±0.16

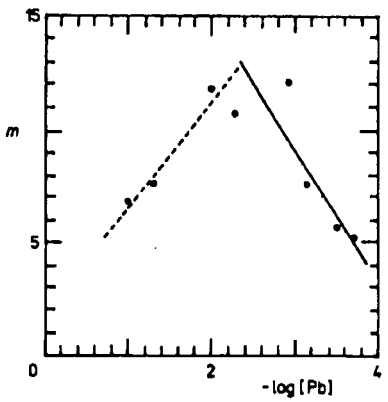

FIG. 3
Dependence of the apparent nucleation exponent m on the lead nitrate concentration

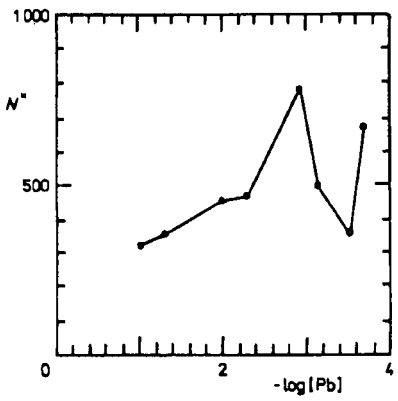

FIG. 4
Dependence of the number of particles constituting a critical nucleus on the lead nitrate concentration

or the critical nucleus size

$$L^* = [N^* M / (1\ 000\ \alpha \rho_c N_A)]^{1/3} \qquad (10)$$

and the specific surface energy

$$\sigma_{12}^* = 1\ 500\ [(\alpha\ \rho_c N_A k\ T) / (\beta M)]\ L^*\ \overline{\Delta w} / w_{eq}\ . \qquad (11)$$

The values for the various lead nitrate concentrations are shown in Figs 4 and 5. As the nucleation exponent, these quantities also exhibit pronounced maxima at $Pb(NO_3)_2$ concentrations between 10^{-2} and 10^{-3} %. In view of the fact that in this region the solubility of $PbCl_2$ has been surpassed and thus the mechanism of action of the lead salt on the nucleation of KCl altered, it can be claimed that the results confirm the monotonous shape of the dependence in the region of lower concentrations, as reported by Liu and Botsaris[17], and also the results of study of the system in question[3-9]. In Fig. 6, the ΔT_{max} values observed in this work are compared with data derived from the values by Glasner[8] by means of Eqs (*3*) and (*4*); the agreement at $Pb(NO_3)_2$ concentrations up to 10^{-2}% is very good.

Of interest are the shapes of the dependences of the classical nucleation parameters on the concentration of lead nitrate. Whereas the specific surface energy σ_{12}^* increases monotonically at low lead salt concentrations (Fig. 5), the dependence of the number of particles N^* forming a critical nucleus is more complex. In comparison with nearly pure KCl, the number of particles N^* decreases first markedly, then it increases rapidly

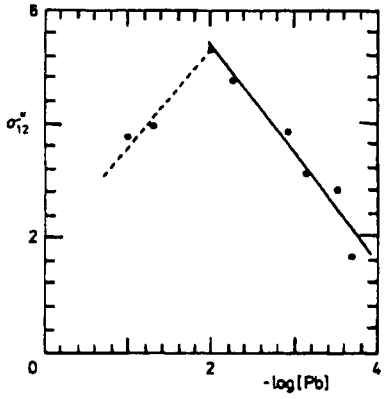

FIG. 5
Dependence of the specific surface energy of the critical nucleus on the lead nitrate concentration

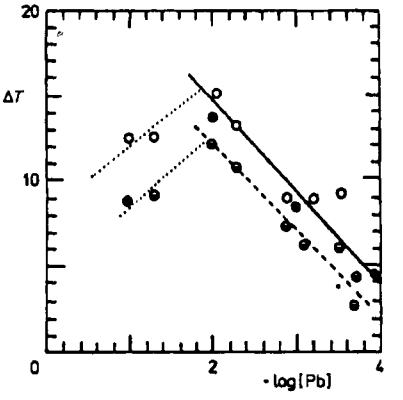

FIG. 6
Maximum undercooling values ΔT_{max} determined in this work (○ for 20 °C / h, ◒ for 5 °C / h) in comparison with the data calculated from Glasner's data[8] (●) by means of Eqs (*3*) and (*4*)

up to a $Pb(NO_3)_2$ concentration about 10^{-3}%, and decreases monotonically if the lead salt concentration is further increased.

The total number of crystal nuclei in a 100 cm^3 sample can be calculated from the weight of the separated crystals and from the critical nucleus size (Eq. (*10*)) as

$$N_c = [(dw_{eq} / dT)\,\Delta T] / (10\,\alpha\,\rho_c\,L^{*3})\,. \qquad (12)$$

TABLE IV
Crystal nuclei size and numbers in 100 cm^3 sample

% $Pb(NO_3)_2$	$-\dot{T}$	$L^* \cdot 10^9$	$N_c \cdot 10^{19}$
0.0002	2	3.47	0.98
	20	2.99	2.40
0.0003	2	2.81	4.03
	20	2.46	8.99
0.0008	2	3.13	3.08
	20	2.84	5.58
0.0012	2	3.64	2.23
	20	3.42	3.25
0.0052	2	3.06	5.45
	20	2.85	8.36
0.01	2	3.04	6.33
	20	2.85	9.34
0.05	2	6.13	6.46
	20	11.23	12.77

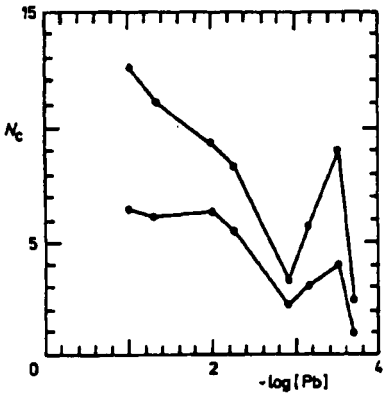

FIG. 7
Dependence of the number of crystals on the lead nitrate concentration. Cooling rate: ● 20 °C / h, ○ 2 °C / h

The result of calculation is given in Table IV and shown in Fig. 7. With increasing concentration of the lead salt the number of KCl crystals increases first rapidly to attain a maximum at an admixture concentration of about $5 \cdot 10^{-4}$%, then it decreases to be lowest at $1 \cdot 10^{-3}$% $Pb(NO_3)_2$ and increases again at higher concentrations. This complex behaviour is consistent with Glasner's concept[8] of the mechanism of nucleation of KCl in the presence of lead(II) ions, according to which the latter constitute nucleation centres for KCl; their number increases with increasing concentration of $Pb(NO_3)_2$, and so does the number of nuclei created, whereas the size of the clusters formed decreases. After surpassing a limit, the subcritical clusters rather participate in the growth of crystals already formed, whereupon the number of crystals decreases. After exceeding a $Pb(NO_3)_2$ concentration of about $5 \cdot 10^{-2}$%, the nature of the $PbCl_2$ clusters changes – stable nuclei are probably formed, so that the number of KCl crystals in the given volume increases slightly with increasing concentration of $Pb(NO_3)_2$.

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SYMBOLS

A, B	constants
$c_{Pb^{++}}$	concentration of lead ions (mol / 1 000 g H_2O)
g	kinetic order of nucleation
k	Boltzmann's constant
k_N	nucleation rate constant ($kg^{-1}\ s^{-1}$)
L^*	critical nucleus size (m)
M	molecular mass (kg $kmol^{-1}$)
m	apparent nucleation order
N_A	Avogadro's constant
N_c	number of crystals in sample
N^*	number of particles forming a critical nucleus
$\dot{N}_N$	nucleation rate ($kg^{-1}\ s^{-1}$)
S	relative supersaturation
T	temperature (°C)
T_{eq}	equilibrium temperature (°C)
T_{cr}	temperature of crystal precipitation (°C)
ΔT_{max}	maximum undercooling (K)
$-\dot{T}$	cooling rate (K h^{-1}, K s^{-1})
w_{eq}	solubility
Δw	supersaturation
α, β	shape factors
δ	mean square deviation
ρ_c	crystal density (kg m^{-3})
σ_{12}^*	specific surface energy (J m^{-2})

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