EFFECT OF THERMAL HISTORY OF AQUEOUS SOLUTIONS OF KCl ON THE METASTABLE ZONE WIDTH

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The metastable zone width of an aqueous solution of KCl was measured as a function of the time and temperature of overheating above the equilibrium solubility temperature. It has been found that when the experiments follow close upon one another, the parameters of the preceding experiment affect the results of the experiment to follow. The results are interpreted in terms of hypotheses advanced in the literature to account for the effect of thermal history of solution. The plausibility and applicability of these hypotheses are assessed for the given case of aqueous solution of a well soluble electrolyte.

In studies on the behaviour of supersaturated solutions, it has been stated many times (*e.g.* in refs[1-14]) that solutions which have been kept for a sufficiently long time at a temperature well above the equilibrium temperature show wider metastable zones, longer induction periods and slower nucleation than solutions whose temperatures have not much exceeded the equilibrium value. A number of hypotheses have been advanced to give a qualitative explanation of the phenomenon, but we are not yet in a position to draw definite conclusions in favour of any of the hypotheses because of insufficient experimental data[15]. The hypotheses are based on the concepts of (*a*) the kinetics of redistribution of the sizes of subcritical clusters of the crystallizing substance, (*b*) the kinetics of dissolution of microscopic or submicroscopic solid particles of the crystallizing substance, (*c*) permanent or temporary deactivation of foreign solid particles, and (*d*) destruction of foreign heterogeneous particles. Each of these hypotheses provides a qualitative explanation for some of the experimentally observed phenomena, even though some of the underlying assumptions are rather forced.

The aim of this work was to measure the metastable zone width for aqueous solution of KCl as a model system of aqueous solutions of well soluble electrolytes, and to use the results as the basis for refuting some of the above hypotheses. A brief account of model concepts involved in the various hypotheses, and of the consequences of the models will first be given to provide an introduction to a later discussion.

a) *Redistribution of the sizes of subcritical clusters of the crystallizing substance.* Clusters of solute particles uncreasingly form and disintegrate in solution according to the scheme

$$A_{i-1} + A \underset{\alpha}{\overset{\beta}{\rightleftarrows}} A_i \, .$$

The steady-state cluster distribution is given by the relation[16]

$$n_i = n_1 \exp\left(-\Delta F_i/kT\right), \tag{1}$$

where n_i is the number of embryos composed of i particles, and n_1 is the number of monomer units. For unsaturated and just saturated solutions, n_i decreases monotonously with increasing i, so that nuclei breeding is impossible. In the case of supersaturated solutions, however, the plot of log n_i *vs* i shows a maximum at $i = N^*$. If supersaturation is produced at a sufficiently slow rate, distribution (*1*) will vary continuously in such a way that at any instant it will correspond to the actual supersaturation. When the supersaturation has reached the metastable zone limit, the number of critical clusters of size N^* will be just that corresponding to observable nucleation. A different situation is found with a rapid or even step change of supersaturation: the initial cluster size distribution must pass over into a new distribution corresponding to the supersaturation created. It takes, however, a certain time for the clusters to grow according to the above scheme. Zeldovich[17] has shown that the distribution change occurs in such a way that the nucleation rate is given by

$$J(t) = J \exp\left(-\tau/t\right), \tag{2}$$

where

$$\tau = (N^* - i_1)^2/4\beta \, . \tag{3a}$$

Other authors have derived similar relations, *e.g.*[18]

$$\tau = (N^*)^2/\beta \, , \tag{3b}$$

which may also be written as[18,19]

$$\tau = (N^*)^2/4\Omega' \, , \tag{3c}$$

where Ω' is the pre-exponential factor in the kinetic equation for nucleation, with a theoretical value of $10^{33 \pm 3}$. Thus, the experimentally found metastable zone width will depend, among other, on the embryo size distribution in the initial state, *i.e.* on the thermal history of the solution[9–11,13,14].

The above hypothesis is compatible with the reversibility of changes observed in the nucleation behaviour of solutions: it accounts for the fact that once the steady state has been reached after overheating a solution, the metastable zone widths and induction period of nucleation are constant within the limits of reproducibility; furthermore, it accounts for the effects of the time of overheating, so long as this is shorter than the time required for the attainment of the steady state. The question remains as to the rate of cluster size redistribution or the time in which the steady state is reached. Whilst experiments usually show fairly long time periods, equations (*3*) indicate extremely short times (minute fractions of a second). Nielsen's analysis of the problem[20] likewise leads to $\tau \approx 10^{-8}$ s, based on the relation

$$\tau \approx 10^{-13}/D \, , \tag{3d}$$

where D is the diffusion coefficient ($cm^2\ s^{-1}$). One may, however, raise the objections that theoretical relations give substantially higher values of τ when applied to viscous solutions and melts, that equations (*3*) hold for very short times[18], and that, for example, the value of the pre-exponential factor Ω' in Eq. (*3c*), when calculated back from experimental data, was found to lie[21] between 10^{18} and 10^{22} or even around 10 only[22,23]; of course, this uncertainty in the value of Ω' gives rise to a very wide range of possible redistribution times. Theoretical description of heterogeneous nucleation[24], on the other hand, leads to redistribution times even shorter than those following from equations (*3*).

b) *The presence of microscopic or submicroscopic crystallites* in the system at temperatures higher than those corresponding to the thermodynamic solubility (*i.e.* the non-equilibrium survival of the crystallites) and their subsequent growth to observable size, or alternatively their functioning as sources of secondary nucleation on repeated supersaturation of the solution, may also furnish an explanation for the effect of overheating on the nucleation behaviour of solution. Depending on the location of a microcrystal in the system, three principal cases may be considered:

1) The microcrystal occurs *in the bulk of the solution.* At temperatures above T_{eq} at which all of the solid phase is just dissolved, such a microcrystal can survive temporarily thanks to small dissolution rate (small compared with the rate at which the solution has been overheated). For this dissolution rate we may write (*e.g.*[25])

$$dr/dt = DV_m(c - c_{eq})/r\,, \tag{4}$$

where r is the radius of spherical crystallite. Integration of this equation (with the assumption of a large mass of solution as compared to the mass of the microcrystals) yields the following expression for the time in which a crystal of initial size $L_0 = 2r_0$ will dissolve completely:

$$t_d = L_0^2/[8DV_m(c_{eq} - c)]\,. \tag{5}$$

Substituting into Eq. (*5*) typical values such as $L_0 = 10^{-5}$ m, $D = 10^{-9}\ m^2\ s^{-1}$, $V_m = 5\,.\,10^{-5}\ m^3\ mol^{-1}$, $(c_{eq} - c) = 500\ mol\ m^{-3}$ for an overheating by 10 K yields $t_d = 0{\cdot}5$ s as the time necessary for complete dissolution of a 10 μm crystal. In this calculation we ignored the increased solubility of small particles as given by the Gibbs–Thomson relation; hence the actual time necessary for a small crystallite to dissolve would be even shorter[26]. A different situation is found with sparingly soluble compounds such as $CaSO_4.10\ H_2O$: neglecting the influence of the particle size on the solubility we find that on overheating a $CaSO_4.10\ H_2O$ solution by 10°C ($c_{eq} - c = 0{\cdot}5\ mol\ m^{-3}$) a 10 μm crystal would dissolve in $t_d = 500$ s, a time comparable with experimental values.

2) The crystal adheres to *flat surface of a heterogeneous substrate* (vessel wall, insoluble impurity). This case was treated by Volmer[27], with the qualitative result that so long as $\sigma_{1s} > > (\sigma_{2s} + \sigma_{12})$ (where σ denotes the interfacial surface energy, and 1, 2 and s designate the solution, crystal and substrate, respectively), a crystal may remain in equilibrium on the substrate even at temperatures T_s above T_{eq}, but the temperature difference is not large. In quantitative terms, we may use model (*b*-1) with the solubility $c_{eq}(T_{eq})$ replaced by $c_s < c_{eq}(T_{eq})$. This, however, does not lead to any significant extension of the time t_d required for an adhering crystal of a well soluble substance to dissolve.

3) The microcrystal rests *in a capillary pore of a heterogeneous substrate* (such as a dust particle or equally well, the vessel wall). This model was qualitatively outlined by Volmer[3] and later developed by Turnbull[5] for the case of a cylindrical capillary, with the result that crystals may survive in a capillary of radius r_c if

$$r = 2\sigma_{12} \cos \Theta \, V_m/\Delta F > r_c\,, \qquad (6)$$

where the free energy change may be written as

$$\Delta F \approx \Delta H_c(T_{eq} - T)/T_{eq}\,. \qquad (7)$$

For every temperature of overheating, T_H, we can find from Eq. (6) a critical capillary radius for which an equilibrium crystal nucleus may just exist in the capillary. On cooling the system below T_{eq} the nucleus retained in the capillary begins to grow towards the capillary mouth. When $r_c \geqq r^*$, the filled capillary mouth starts functioning as a crystal seed. Since the effective r_c decreases with increasing ΔT_H and r^* decreases with increasing ΔT_{max}, the undercooling ΔT_{max} must increase with increasing ΔT_H, which provides a satisfactory explanation of the effect of thermal history on the undercooling ability of solution. It can be shown[5] that

$$\Delta T_{max}/\Delta T_H = \mathrm{tg}\, \Theta\,. \qquad (8)$$

The described theoretical treatment of the model considers equilibrium states only, disregarding both the decreased rate of crystal dissolution in the capillary at the temperature T_H (small surface available, transport of solvent through the capillary limited to diffusion only) and the decreased rate of crystal growth at $T_{eq} - \Delta T_{max}$ (restricted transport of solute to the crystal surface, difficult removal of excess solvent).

A general rule that applies to all the three models under (*b*) is that if the system is overheated for a sufficient time period t_H for the overheating ΔT_H to exceed a certain limiting value, all the crystals catalyzing the nucleation will dissolve and their regeneration will require an energy barrier to nucleation to be surmounted, which for models (*b* - 2) and particularly (*b* - 3) is further increased by the additional term in the equation for ΔF.

c) *Deactivation of solid heteroparticles* present in solution is the assumption underlying a further group of hypotheses. It is beyond doubt that systems on which nucleation from solution is studied always contain foreign solid particles, some of which may catalyze nucleation by lowering the energy barrier to nucleation[3]:

$$\Delta F_{heter} = \Delta F_{hom}(2 + \cos \Theta)(1 - \cos \Theta)^2/4\,. \qquad (9)$$

Even the nucleation studies carried out by using the method of drop solidification cannot be considered unambiguously as involving homogeneous nucleation[19]: assuming the presence of $10^6 - 10^8$ particles of heterogeneous impurities in 1 cm^3 of solution, the droplets would have to be smaller than 10 μm for at least 90 per cent of them not to contain any foreign particles; however, substantially larger droplets were used in most of the studies.

Unfortunately, the proponents of this hypothesis[7,12] have not outlined the mechanism of the deactivation of heterogeneous particles catalyzing the crystallization of the dissolved macrocomponent. One may envisage model (*b* - 2) or (*b* - 3), discussed in the preceding paragraphs, as one of such mechanisms. Another possibility is reversible adsorption and desorption of some micro-admixture blocking the active centres of the heterogeneous particle, subject to the assumption of a strong temperature dependence of such a process. Other mechanisms of deactivation fail to explain the reversibility between the states active particle — deactivated particle.

d) *The hypothesis of heterogeneous particle destruction* assumes that the system contains a sparingly soluble microcomponent in a concentration such that at a temperature T close to T_{eq} there are solid particles of this microcomponent in the system which gradually dissolve or melt in the temperature range between T_{eq} and T_H. The nucleation of the microcomponent must occur at an undercooling ΔT_{max} greater than that for the macrocomponent nucleation. The presence of such a microcomponent has not been proved experimentally in the systems studied, nor is it much probable. Furthermore, the model presupposes little solubility of this compound and at the same time a strong temperature dependence of the solubility, two requirements which are practically incompatible. An argument presented[7] as an indirect proof of this hypothesis is that careful purification of a solution and repeated thermal treatment eliminate a measurable effect of thermal history. However, the results of these experiments may more reasonably be interpreted to mean that very high and frequent temperature cycles cause the thermal history effect to reach its maximum, with further increase in temperature or overheating time no longer producing an observable change.

EXPERIMENTAL

The metastable zone width of an aqueous solution of KCl saturated at *c.* 40°C was measured on an apparatus described previously[28]. The solution was made up by dissolving KCl (Suprapur, Merck) in distilled water. 100 cm^3 of the solution was closed in an Erenmayer flask and stirred with a glass magnetic stirrer (60 rpm). The temperature of the solution was maintained to better than ± 0.02 K by means of a digital temperature-programmed proportional controller activating an infralamp and a fan. The solution saturated at temperature T_0 was heated to $T_H = T_0 + \Delta T_H$, kept there for a time t_H, then cooled at a rate of 100—120 K/h to T_0; immediately on reaching this temperature a constant cooling of 20 K/h was applied until first, just-visible crystals appeared (undercooling ΔT_{max}). The first series of measurements with an overheating of $\Delta T_H = 0.5$ K and $t_H = 10$ min served as a reference base; the measured value of ΔT_{max} did not depend on the time t_H (within a range from 10 to 60 min), nor on whether the experiments followed one another immediately or after an interval (at least 14 h, precipitated crystals, no stirring, uncontrolled temperature between 15 and 25°C). As a check, a part of the measurements in this series were carried out on freshly prepared solution after about half of all measurements described in this paper. The second series of measurements was designed to establish the dependence of ΔT_{max} on t_H at a comparatively high overheating of 20 K. The ΔT_{max} values were measured for $t_H = 60$ min and 300 min; a trial measurement with $t_H = 150$ min was carried out only to check the possibility of interpolating the t_H values. Next, ΔT_{max} was measured for a very long time $t_H = 1\,400$ min. A check on the interpolation of T_H values was provided by several trial measurements at $\Delta T_H = 1$ K and $\Delta T_H = 10$ K. All the measurements in this series were carried out with intervals of at least 14 h between the successive runs, leaving the heterogeneous system unstirred and without temperature control at 15—25°C during the intervals. In the third series of measurements, by contrast, each run was made immediately after the experiment with $t_H = 300$ min and $\Delta T_H = 20$ K or $\Delta T_H = 10$ K. A survey of the total of 100 measurements made is given in Table I, where N denotes the number of runs, δ is the mean square deviation of ΔT_{max}, and $\delta_{rel} = 100\delta/\Delta T_{max}$.

DISCUSSION AND CONCLUSIONS

As can be seen from Table I, both the temperature and time of overheating have an effect on the metastable zone width. A semiempirical equation proposed[10,13] for correlation of these data,

$$\ln\left(c_{u,eff}/c_{0,eff}\right) = B''(t_N/t_{N,0} - 1)\,, \tag{10}$$

relates the ratio of the induction periods of nucleation of overheated solution, t_N, and nonover heated solution, $t_{N,0}$, to the concentration parameters characterizing the time and temperature of solution overheating:

$$c_{u,eff} = c_u - (c_u - c_{0,eff}) \exp(-k_H t_H) . \qquad (11)$$

Here, c_u is the solubility of the crystallizing substance at T_H, and $c_{0,eff}$ is the parameter calculated from Eq. (*12*) for the initial state of the solution,

$$c_{0,eff} = c_0 + (c_{u,eff} - c_0) \exp(-k_0 t_0) , \qquad (12)$$

where c_0 is the solubility of the crystallizing substance at saturation temperature, T_{eq}, and t_0 is the time for which the solution was kept at T_{eq}. The value of the parameter $c_{u,eff}$ was calculated from Eq. (*11*) by using data from the preceding run.

TABLE I

Metastable zone width of aqueous solution of KCl

ΔT_H	t_H	$c_{u,eff}$	ΔT_{max}					N
			exp.	δ	δ_{rel}, %	calc.	Δ	
0·5	10	0·4015	2·36	0·18	7·8	2·36	0	27
1·0	30	0·4030	2·67	0·15	5·7	2·41	−0·26	3
10·0	130	0·4155	3·3			2·80	−0·5	1
10·0	300	0·4240	3·1	0·10	3·2	3·08	−0·02	3
20·0	60	0·4164	2·99	0·20	6·3	2·83	−0·16	19
20·0	150	0·4317	3·30	0·14	4·3	3·35	0·05	2
20·0	300	0·4460	4·06	0·27	6·1	3·88	−0·18	20
20·0	1 400	0·4587	4·2			4·39	0·19	1
1·0	5[a]	0·4463	3·74	0·36	9·8	3·89	0·15	5
10·0	10[b]	0·4243	3·10	0·10	3·2	3·09	−0·01	2
10·0	20[b]	0·4246	3·3			3·10	−0·2	1
10·0	60[b]	0·4257	3·0			3·14	0·14	1
20·0	10[a]	0·4466	3·77	0·25	6·7	3·90	0·13	3
20·0	60[a]	0·4493	3·76	0·26	6·9	4·01	0·25	13

[a] Experiments performed immediately on completing the run with 300 min overheating by 20 K, [b] experiments following the run with an overheating by 10 K.

On the purely formal side, there is a similarity between Eqs (*11*) and (*12*) and the equation describing the time dependence of changes of the distribution function for subcritical clusters[12],

$$f = f_{st} + (f_0 - f_{st}) \exp(-t/\tau_1), \tag{13}$$

where the stationary distribution of embryo sizes is given by[4,10]

$$f_{st} = n_1(w_0/w_H)^i \exp(-\beta\sigma_{12}i^{2/3}/kT_H). \tag{14}$$

Thus, the form of the semiempirical equation (*10*) is compatible, at least formally, with model concepts of hypothesis (*a*).

Suppose that the induction period of nucleation is inversely proportional[25,29] to the nucleation rate or the nucleation rate constant under comparable conditions. Then, $\Delta T_{max} \sim k_N^{-1/n} \sim t_N^{1/n}$ (ref.[28]), and Eq. (*10*) may be rewritten into the approximate form

$$\ln(c_{u,eff}/c_{0,eff}) = B''[(\Delta T_{max}/\Delta T_{max,0})^{1/n} - 1], \tag{15}$$

where $\Delta T_{max,0} = \Delta T_{max}(\Delta T_H = 0)$ is the maximum undercooling of non-overheated solution. The runs listed in the upper part of Table I followed each other after a sufficiently long time period with a low temperature $T \leqq T_{eq}$, so that Eq. (*11*) may be used with the substitution $c_{0,eff} = c_0$. For the solubility data[30] $c_0 = 0.4015$ (40°C) and $c_u = 0.4044$ (41°C), $c_u = 0.4305$ (50°C) and $c_u = 0.4588$ (60°C) kg/kg H_2O, a trial and error procedure has provided the approximate values of the adjustable constants of Eq. (*15*) $B'' = 0.7$ and $k_H = 0.005$, which give a good fit of experimental data. The kinetic exponent, $n = 3.56$, was estimated independently in an earlier work[29].

For experiments listed in the lower part of the table, the value of $c_{0,eff}$ was identified, in accord with the experiments' performance, with the $c_{u,eff}$ value obtained for the preceding run, *i.e.* with 0·4460 for experiments marked (*a*), and with 0·4240 or 0·4155 for experiments marked (*b*). From the data in Table I, where Δ denotes the difference between the experimental value and the value calculated from Eq. (*15*), we can see that Eq. (*15*) or its modified form

$$\Delta T_{max}(\Delta T_H, t_H) = \Delta T_{max}(\Delta T_H = 0) [B''^{-1} \ln(c_{u,eff}/c_{0,eff}) + 1]^n \tag{16}$$

represents the experimental results with an accuracy that is within the limits of their scatter.

An interesting feature to emerge from results of this work is that the thermal history effect will not be erased even after crystallization has occurred in the system:

the result of an experiment is significantly affected by the overheating of the solution in the preceding run.

In terms of hypothesis (*a*) this would imply that the subcritical cluster size distribution has not changed substantially during the first experiment, and consequently plays a significant role in the run that immediately follows. In data correlation this is reflected in that substitution for $c_{0,\mathrm{eff}}$ in Eq. (*16*) or (*15*) of $c_{\mathrm{u},\mathrm{eff}}$ value from the preceding run leads to a satisfactory fit of the experimental data for the metastable zone width. Since, however, nucleation occurs at the end of the first experiment, it necessarily follows that the cluster size distribution has to have changed during the experiment. This contradiction can only be resolved by introducing a new hypothesis, namely that the initial cluster size distribution changes in the bulk solution during an experiment, but remains conserved, or changes far more slowly, in a part of the heterogeneous system, *e.g.* in a surface layer at the vessel wall or within the pores of heterogeneous impurities (an analogy to hypothesis (*b-3*)).

The first two variants of hypothesis (*b*) are unable to account for the experimental observations, and may therefore be rejected. Hypothesis (*b-3*) is compatible, in qualitative terms, with results of experimental studies. Substituting experimental data from Table I into Eq. (*8*), we obtain for $\Delta T_\mathrm{H} = 1$, 10 and 20 K largely differing values of the wetting angle, $\Theta = 69$, 18 and 12°, respectively. Since ΔT_max approaches the value $\Delta T_{\mathrm{max},0}$, and not zero, as ΔT_H is decreased, Eq. (*8*) should rather have the form

$$(\Delta T_\mathrm{max} - \Delta T_{\mathrm{max},0})/\Delta T_\mathrm{H} = \mathrm{tg}\,\Theta \qquad (17)$$

which yields somewhat less scattered values $\Theta = 17$, 5 and 5°.

We cannot make a positive statement about the applicability of hypothesis (*c*) on the basis of the experiments performed until we have a more definite concept of the mechanism of the solid microparticle deactivation. Considering the chemical purity of the substances used, we can rule out the hypothesis of adsorption of a soluble micro-admixture. Analogous results obtained for melts, namely the observation of the nucleation rate and the mean supercooling ability of melts increasing with increasing number of melting-solidification cycles[31,32], have been interpreted[12] as due to performing the experiments under unsteady-state conditions, although one cannot rule out either the effect of heterogeneous nuclei, speculatively formulated by Ziabicki[33].

Hypothesis (*d*) is unable to account for the observed facts; in particular, it fails to explain the continuous dependence of the metastable zone width on the temperature of solution overheating, and the differences in results for experiments performed in close succession and after prolonged time lapses.

The conclusion to be drawn from the above discussion is that two hypotheses may provide plausible explanation of the effect of thermal history of KCl solutions on the metastable zone width: the hypothesis assuming slow redistribution of subcritical cluster sizes of the crystallizing substance (probably in connection with heterogeneous particles present in the system), which has furnished a formal phenomenological description of the observed dependences; and the hypothesis based on the survival of microcrystals in the pores of heterogeneous substrates.

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LIST OF SYMBOLS

B''	constant
c	concentration
c_{eq}, c_0	solubilities at temperature T_{eq} and T_0, respectively
c_u	solubility at temperature T_H
$c_{0,eff}$	quantity defined by Eq. (*11*)
$c_{u,eff}$	quantity defined by Eq. (*12*)
D	diffusion coefficient
f	cluster size distribution function
f_{st}	stationary distribution
ΔF	free energy change
ΔH_c	heat of crystallization
i	number of particles making up a cluster
i_1	number of particles making up a cluster whose population does not yet depend on supersaturation
J	nucleation rate
k_0, k_H	adjustable constants
k_N	nucleation rate constant
L	crystal size
n	nucleation exponent
n_i	number of embryos composed of i particles
N	number of measurements
N^*	number of particles making up a critical nucleus
r	crystal radius
r_c	capillary radius
t	time
t_0, t_H	times of keeping a solution at temperatures T_0 and T_H, respectively
t_d	time required for a crystal to dissolve completely
t_N	induction period of overheated solution
$t_{N,0}$	induction period of non-overheated solution
T	temperature
T_{eq}	saturation temperature
T_H	overheating temperature
ΔT_H	overheating of solution
ΔT_{max}	undercooling
$-\dot{T}$	cooling rate
V_m	molar volume

w_{eq}	solubility
w	concentration
α	rate of detachment of particles from cluster
β	rate of attachment of particles to cluster
δ	mean square deviation
δ_{rel}	relative error, %
Δ	difference between measured and calculated values
σ_{ij}	specific interfacial energy
τ	induction period, cluster redistribution time
Θ	wetting angle
Ω'	pre-exponential factor in nucleation kinetic equation

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