METASTABILITY OF THE SYSTEM POTASSIUM CHLORIDE–
–POTASSIUM BROMIDE–WATER

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The metastable zone width has been determined for pure $KCl-H_2O$, $KBr-H_2O$ and three compositions of the ternary system $KCl-KBr-H_2O$ at temperatures close to 35 and 40°C. In agreement with literature it was confirmed that there are two different regions of solid solutions in the system $KCl-KBr-H_2O$. The data on metastable zone width show a different crystallization behaviour of both of the solutions: the values of critical nucleation parameters calculated from the measurements exhibit a distinct asymmetry which may be connected with different radii of the Cl^- and Br^- ions.

The solid solutions formation is of a great significance in the preparation of pure substances and in several special branches of the industry, e.g. in the preparation of photographic emulsions, where the appearance of mixed crystals can affect greatly their characteristics. The study of solid solutions is a special branch of physical chemistry, but no great attention was paid to this topics in the recent years. This is why a detailed study[1] of the formation of solid solutions has been performed with the aim to get more information on this problem by combination of several experimental and theoretical methods: in particular, nucleation characteristics and several thermodynamic properties of a system with solid solutions formation were investigated.

It is well known that solid solutions are formed in the system $KCl-KBr-H_2O$ so it was chosen as a model for the determination of thermodynamic characteristics in solid solutions. Among other methods, the width of the metastable zone in this system was studied which can give a very important information on the nucleation characteristics as well as on the specific surface energy showing whether there are energetic interactions, which could be correlated with other thermodynamic properties of the system.

The aim of this paper is to present the results of the metastable zone width measurements in the ternary system $KCl-KBr-H_2O$ and to draw conclusions in relation to the formation of solid solutions.

THEORETICAL

The phase equilibrium in the system KCl–KBr–H$_2$O was studied recently by Nikl and Nývlt[2]. Relations were derived correlating the equilibrium data of solid and liquid phases based on thermodynamic condition of phase equilibria:

$$\tfrac{1}{2} \log \left[X_1(X_1 + X_2 m_{20}/m_{10}) \right] - \log y_{1\pm} = \varphi_1 , \qquad (1)$$

where X_i is the relative molality of the i-th component in equilibrium

$$X_i = m_i/m_{i0} , \qquad (2)$$

$y_{1\pm}$ is the mean molecular fraction of component 1 in the solid phase

$$y_{1\pm} = (y_{1+}y_{1-})^{1/2} \qquad (3)$$

and

$$\phi_1 = \varphi_1 + \log y_{1\pm} = Q_1 m_2 + Q_2 m_2^2 + \ldots \qquad (4)$$

Evaluation of experimental results[2] led to the values of interaction constants Q
— for the branch KCl(1)–KBr(2)–H$_2$O at 35°C

$$Q_1 = -0.00826 ; \quad Q_2 = -0.003912$$

— for the branch KBr(1)–KCl(2)–H$_2$O at 35°C

$$Q_1 = -0.0158 ; \quad Q_2 = -0.00896 .$$

It follows from the results that the equilibrium in the whole concentration range cannot be expressed with one set of constants only; this leads to the conclusion that there are two different regions of solid solutions in this system. This fact is also proved by Bryan and Fitch[3]: in their phase diagram there are clearly two regions of solid solutions, namely KBr in KCl and KCl in KBr, separated by a rather narrow region where mixtures of two different solid solutions are in equilibrium with the eutonic aqueous solution. Fantell[4] also studied the phase equilibria in the system KCl–KBr–H$_2$O and found that the two salts do not form a continuous chain of solid solutions at room temperature. That means that there must be a discontinuity in the concentration dependence of measured values. A region in the phase diagram exists where the solid phase in equilibrium with the saturated solution is represented by a mixture of two different solid solutions.

The metastable zone width was measured by the polythermal method[5,6]: the maximal supercooling ΔT_{max} of the solution is determined under different cooling

rates $(-dT/dt)$ and the data are then correlated using equation

$$\log \Delta T_{\text{max}} = (1 - m)/m \cdot \log (dw_{\text{eq}}/dT) - 1/m \cdot \log K +$$
$$+ 1/m \cdot \log (-dT/dt), \tag{5}$$

where m designates the apparent nucleation order and (dw_{eq}/dT) is the temperature coefficient of solubility. It has been shown[7] that the metastable zone width measurements can be used for the calculation of classical nucleation parameters: the size of a critical nucleus is

$$L^* = 11 \cdot 84 \left(N^* M/\alpha \varrho_{\text{c}}\right)^{1/3} \cdot 10^{-10} \tag{6}$$

and the number of particles forming a critical nucleus is

$$N^* = nw_{\text{eq}}/\Delta w \tag{7}$$

with

$$n = 4m - 3g + 4 \tag{8}$$

and the specific surface energy

$$\sigma_{12}^* = 12\ 471 \left[(\alpha \varrho_{\text{c}} T)/(\beta M)\right] L^* \left(\Delta w/w_{\text{eq}}\right), \tag{9}$$

where Δw is the average supersaturation, α and β are shape factors.

EXPERIMENTAL

The metastable zone width was measured by the polythermal method. The investigated solution was placed in a closed 100 cm^3 flask and was stirred by a magnetic stirrer, its speed corresponding to 250 rpm. The temperature of the solution was measured by a platinum resistance thermometer. A temperature programmer controlled the temperature using an infralamp and a fan. The controller was a digital one, which allowed to control the temperature within $\pm 0 \cdot 01$ K and to preset a precise constant cooling rate which has been chosen 2 or 20 K h^{-1}. The investigated solution was cooled down to a temperature at which a sufficient amount of tiny crystals were formed, then it was slowly heated up until the last crystal dissolved. This final temperature was considered to be the saturation temperature, T_{eq}. Before the actual measurement, the solution was kept at the temperature by $0 \cdot 5$ K higher than T_{eq} for 30 minutes in order to dissolve any possibly remaining crystals, then it was cooled at a preselected constant rate of 2 or 20 K h^{-1} and the temperature T at which the first visible crystals appeared was recorded. Corresponding undercooling is then

$$\Delta T_{\text{max}} = T_{\text{eq}} - T. \tag{10}$$

Each measurement was repeated at least ten times.

For the sample preparation the analytical purity potassium chloride and potassium bromide (Lachema, Brno) were used. All solutions were made up in redistilled water. The composition of the solutions given in Table I was chosen from solubility data.

It was found that a difference in saturation temperatures within 5 K has no observable effect on the width of the metastable zone.

The experimental data are summarized in Table II.

RESULTS AND DISCUSSION

The steps for treatment the primary experimental data were as follows:

a) smoothing of experimental data using the method of least squares applied to Eq. (5) in the form

$$\log \Delta T_{max} = A_j + (1/m) \log (-dT/dt) \tag{11}$$

and determination of constants A_j and m for each system separately;

TABLE I

Composition of solutions

Sample	mole % of KCl	wt. % of KCl: wt. % of KBr	T_{eq}, °C
I	100	1·00 : 0·00	40·3
II	62·6	2·67 : 1·00	34·9
III	44·5	1·28 : 1·00	35·4
IV	19·3	1·00 : 2·62	35·2
V	0	0·00 : 1·00	40·2

TABLE II

Directly measured values of the metastable zone width of aqueous solutions in the system KCl--KBr-H_2O

Parameter	System[a]				
	I	II	III	IV	V
Number of experim.	11/19	11/13	15/13	10/11	10/15
ΔT_{max}	1·15/1·87	1·74/2·32	1·91/2·59	1·65/2·34	1·05/2·25
$\pm \delta$	0·02/0·05	0·04/0·02	0·02/0·02	0·02/0·05	0·06/0·09

[a] Numbers in numerators hold for the cooling rate 2 K h^{-1}, in denominators for 20 K h^{-1}

b) determination of the average supersaturation

$$\Delta w = 2^{1/4m} \Delta T_{\max} (dw_{eq}/dT) \tag{12}$$

and of the true nucleation order, Eq. (8), where the growth rate order was found[6] to be 1·0;

c) determination of classical nucleation parameters according to Eqs (7), (6) and (9);

d) calculation of the effective nucleation rate constant k_N:

$$\log k_N = (1 - m) \log (dw_{eq}/dT) - A_j m . \tag{13}$$

The values necessary for calculations were obtained as follows:

— densities of salts:

  — pure salts[8]: 1 989 and 2 750 kg m^{-3}, respectively
  — mixtures: from the equation

$$[x_1 M_1 + (1 - x_1) M_2]/\varrho_c = x_1 M_1/\varrho_{c1} + (1 - x_1) M_2/\varrho_{c2} \tag{14}$$

— temperature coefficients of solubility:

  — pure salts[8]: 0·00293 and 0·00525, respectively
  — mixtures: 0·00228 (II), 0·00246 (III), 0·00329 (IV)
  — shape factors: for cubic crystals $\alpha = 1$, $\beta = 6$.

The results of calculation of kinetic nucleation parameters are summarized in Table III.

For the relative error in determining m holds

$$\delta(m) = 0.868/\log \left[(dT/dt)_1/(dT/dt)_2\right] \left[m\, \delta(\Delta T_{\max}) + \delta(-dT/dt)\right] . \tag{15}$$

The cooling rate could be determined with the accuracy better than 1%, the $\Delta T_{\max}$ for one single measurement with the relative error of about 10% and that of the average of k measurements

$$\delta(k, \Delta T_{\max}) = \delta(1, \Delta T_{\max}) k^{1/2} \tag{16}$$

so that with 10 measurements for each of the two cooling rates, the resulting inaccuracy of the apparent nucleation order m doesn't exceed 10 to 15%. Because of the logarithmic form of the equation employed for the treatment of experimental data, the values of k_N are extremely dependent on the accuracy of determination of

m. If the spread of *m* of 10% is considered, the expected inaccuracy of k_N can be calculated which is given also in Table III.

The results of calculation of classical nucleation parameters are summarized in Table IV.

TABLE III
Kinetic nucleation parameters

Parameter	System				
	I	II	III	IV	V
m	4·70	7·58	6·64	8·21	3·02
n	19·8	31·3	27·6	33·8	13·1
k_N	$6·8 . 10^5$	$1·2 . 10^{11}$	$1·24 . 10^9$	$3·49 . 10^{11}$	$1·94 . 10^4$

TABLE IV
Classical nucleation parameters

Parameter	$-dT/dt$ k h^{-1}	System				
		I	II	III	IV	V
*N**	2	1 459 ±233	1 640 ±214	1 593 ±216	2 075 ±263	714 ±170
	5	1 198 ±191	1 450 ±189	1 383 ±187	1 850 ±235	528 ±126
	20	892 ±142	1 210 ±157	1 123 ±152	1 560 ±199	333 ±80
$L^* . 10^6$	2	45 ± 2	47 ± 2	47 ± 2	52 ± 2	37 ± 3
	5	42 ± 2	45 ± 2	45 ± 2	50 ± 2	34 ± 3
	20	38 ± 2	42 ± 2	42 ± 2	48 ± 2	29 ± 2
σ_{12}^*	2	3·8 ±0·2	6·7 ±0·3	5·6 ±0·2	6·0 ±0·2	2·4 ±0·2
	5	4·3 ±0·5	7·3 ±0·3	6·1 ±0·3	6·5 ±0·3	2·9 ±0·3
	20	5·3 ±0·3	8·3 ±0·4	7·0 ±0·3	7·3 ±0·3	4·0 ±0·3

Considering the relative error of m and taking into account that the supersaturation Δw can be calculated from the maximum undercooling ΔT_{max} with a relative error of about 10%, the total inaccuracy of the critical number of particles N^* thus rises[15] to about 20 to 25% and that one of the critical nucleus size L^* to 8%. The inaccuracy of about 20% can be expected[15] for the specific surface energy σ_{12}^*.

It can be seen from Table III and from Fig. 1 that the critical number of particles N^* and the critical nucleus size L^* have their maximal values for the KBr–rich mixture IV and minimal values for pure KBr. The dependence on the cooling rate employed can be explained so that the increase in cooling rate results in higher supersaturation which makes the nucleation easier – the critical nucleus size decreases but the σ_{12}^* value becomes higher. The values of the specific surface energy can be compared with the values published by various authors (in J m^{-2}, see Table V). The data in refs[10,12–14] were measured in a similar way as in this paper and can be compared with our values with certain except of ref.[12] where the cooling rate was extremely high and the solutions thoroughly filtered in order to avoid heterogeneous nucleation. The values of classical parameters of nucleation calculated from the

TABLE V

Published values of surface energies

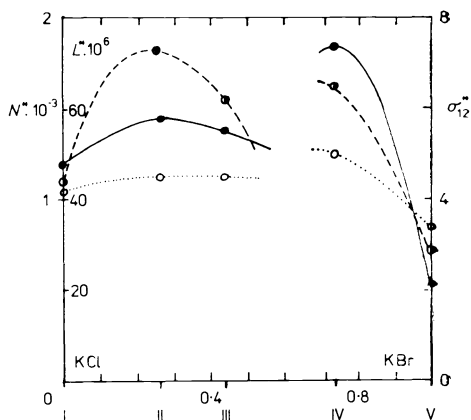| Compound	Ref.[9]	Ref.[10]	Ref.[11]	Ref.[12]	Ref.[13]
KCl	27	2·6	30	17	1·9
KBr	23	1·5	24	7	1·6

FIG. 1

Number of particles forming a critical nucleus N^* (full line), critical size of nuclei L^* (dotted line) and the specific surface energy σ_{12}^* (dashed line) in the system KCl––KBr–H$_2$O calculated from the measurements of the maximum undercooling for the cooling rate 5 K h^{-1}

metastable zone width measurements show a distinct assymetry, which may be connected with different radii of the Cl^- and Br^- ions. The substitution of the smaller Cl^- ion into the crystal lattice of KBr is easier than the substitution of the larger Br^- ions inot the crystal lattice of KCl.

SYMBOLS

A_J	constant
g	growth rate order
K	constant
k	number of experiments
k_N	kinetic constant of nucleation, $kg^{1-n} kg_{H_2O}^{n-1} s^{-1}$
L^*	size of a critical nucleus, m
M	molar mass, $kg\ mole^{-1}$
m	apparent nucleation order
m_i	molality of i-th component, $mole\ kg_{H_2O}^{-1}$
m_{i0}	solubility of i-th component in water, $mole\ kg_{H_2O}^{-1}$
N^*	number of particles forming a critical nucleus
n	true nucleation order
Q_i	interaction constant
T	temperature, °C
T_{eq}	equilibrium temperature, °C
ΔT_{max}	maximal undercooling, K
$(-dT/dt)$	cooling rate, $K\ s^{-1}$, $K\ h^{-1}$
w	concentration, $kg\ kg_{H_2O}^{-1}$
w_{eq}	solubility, $kg\ kg_{H_2O}^{-1}$
Δw	supersaturation, $kg\ kg_{H_2O}^{-1}$
dw_{eq}/dT	temperature coefficient of solubility, $kg\ kg_{H_2O}^{-1}\ K^{-1}$
X_i	relative molality of i-th component
x_i	mole fraction of i-th component in solution
$y_{1\pm}$	mean mole fraction of 1-st component in solid solution
α	volume shape factor
β	surface shape factor
Φ_1	function of activity
φ_1	function of activity
ϱ_c	density of crystals, $kg m^{-3}$
σ_{12}^*	specific surface energy, $J\ m^{-2}$

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