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MEASUREMENT OF CRYSTALLIZATION OF POTASSIUM BROMATE FROM ITS QUIESCENT AQUEOUS SOLUTION BY DIFFERENTIAL SCANNING CALORIMETER

— GROWTH RATE OF CRYSTALLITE —

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Heat evolution rate curves were recorded with KBrO_3 -quiet supersaturated aqueous solution at constant cooling temperature, T , by using a differential scanning calorimeter and were analyzed on the basis of the growth rate of all crystallites pre-formed in the sample solution. Taking microscopic observation into account, the expression of the overall growth rate, R , was derived, on the assumption that the crystallite surface is Kossel's and that its growth rate is determined by two-dimensional nucleation rate, $J' = k_1' S^{m'}$.

$$R = \beta h A J' \doteq k_1'' (C_0 - C)^{2/3} S^{m'} \quad (1)$$

where C , C_0 and S are concentration at $t=t$ and $=0$ and supersaturation ratio, respectively. m' is number of solute in a critical nucleus and is not constant, but depends on S and T .

The values of two-dimensional nucleation parameters (m' , radius, free edge energy σ' and surface energy estimated from σ' and activation energy) were of reasonable order of magnitude. Comparison of these values with those of the three-dimensional parameters obtained previously is discussed. It may be concluded that Eq. (1) and hence the expression for J' proposed in this paper are adequate for the growth rate and two-dimensional nucleation rate, respectively.

Introduction

Figure 1 illustrates the crystallization of potassium bromate from its quiescent supersaturated aqueous solution, obtained by a differential scanning calorimeter, DSC (Perkin-Elmer 1B) with maximum sensitivity of 0.1 [mcal/sec·full-scale]. The curve EJ, recorded at constant temperature (300°K, in Fig. 1),

is conveniently divided into two parts: EFH (region I), where no crystallization takes place at detectable rate, and HIJ (region II), where detectable crystallization is initiated and completed. Previously^{1,2)}, taking the processing time from point E to H as the waiting time for homogeneous nucleation, θ , the measured values of θ were analyzed on the basis of the homogeneous nucleation rate expression proposed previously.

In this work, the data in region II in the DSC chart

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Fig. 1 DSC chart

a) from DSC charts recorded at constant T , KBrO_3

b) from DSC charts recorded at constant cooling rate, KClO_3

Fig. 2 $-dc/dt$ (A) and S (B) vs. t

were analyzed on the assumption that the growth rate of crystallite is responsible for region II, taking into account the separate observations obtained microscopically.

The experimental conditions and the procedures for recording the DSC chart are the same as those described previously^{1,2)}.

1. Results in DSC Measurement and Microscopic Observation

The crystallized amounts of potassium bromate obtained from the area surrounded by the curve, HIJ, and base line, HJ, agreed with those calculated from the initial supersaturation concentration of the sample at crystallization temperature, T , within 5% error. From this, the heat evolution rate is converted into the crystallization rate, Curve A, and the supersaturation ratio, Curve B, as illustrated in Fig. 2(a). Figure 2(b)⁴⁾ shows a pair of similar curves obtained with HIJ curves recorded by the constant cooling rate method, and therefore T instead of the time, t , in Fig. 2(a) is plotted as abscissa.

As shown in Fig. 2(b), the temperature, T_m , at which the maximum crystallization rate appears is lower than the temperature, T'_m , at which the maximum supersaturation ratio, S , appears. This situation was the same regardless of cooling rate. The crystallization rate depends on S and T , and the larger S and/or T , the more rapid the rate may be. Hence T_m should be larger than T'_m , whereas this is not the case. These considerations suggest that the crystallization rate in the above case depends on S and T and further may be accelerated autocatalytically by pre-formed crystallites. Figure 2(a) gives the same suggestion.

Taking into account the above suggestion, together with the sample being in quiescent state, the heat evolution in DSC measurement may be considered to be due not to the formation of crystallites—say, by secondary nucleation—but to the growth of crystallite. To confirm this, a macroscopic observation was carried out under conditions as similar as possible as those in DSC measurement. The sample solution at *ca.* 70°C, with S of *ca.* 2 at room temperature was dropped into a shallow basin of *ca.* 0.18 ml volume built in the middle of a glass plate pre-warmed to *ca.* 70°C. Then the glass was covered as quickly as possible with a cover glass pre-warmed to *ca.* 70°C and microscopic observation was initiated immediately.

Figure 3 shows some of the photographs, where Photo (a) was taken at 72 sec after the microscopic observation and t is the elapsed time after Photo (a) was taken. Photographs (a)–(f) indicates that a crystallite grows rapidly, keeping its initial shape. From the whole view as shown in Photo (g), all the crystallites formed seem to be in the same crystal form. In Fig. 4, the dotted curve shows the change of the representative length of a crystallite, L , observed microscopically with the elapse of time, as shown in Fig. 3, (a)–(f), and the solid curve shows the change of $L^2 dL/dt$ obtained from the dotted curve, which is proportional to the crystallization rate in the sample solution, on

the assumption that all the crystallites grow uniformly, obeying the ΔL law.

The marked resemblance of the shape of the solid curve to that of curve A in Fig. 2(a), suggests that the growth rate of the crystallites is responsible for the data in DSC measurement as shown in Fig. 2.

2. Growth Rate

Since the crystallite size is larger than ten microns, as shown in Fig. 3, there may exist many dislocations in the crystallite. In this experiment, however, the data were obtained under such the high supersaturation ratio ($S=2-3$) that it is predicted that the crystallite grows according to Kossel's theory rather than Frank's. The growth of the Kossel's surface is a consecutive process consisting of surface two-dimensional nucleation, the surface diffusion of solute and the progression of the step. In this work, the data were analyzed, assuming that growth rate is determined by the two-dimensional nucleation rate.

The expression for surface two-dimensional nucleation rate, J' , may be derived in a similar manner to that for three-dimensional (homogeneous) nucleation rate, J , discussed previously³⁾.

Assuming a critical surface nucleus to be a circle of radius, r'_c , consisting of m' units of solute, the free energy change, $\Delta g'_c$, when it is formed from solution is given by⁵⁾

$$\Delta g'_c = m'\mu + 2\pi r'_c \sigma' \quad (1)$$

where σ' is free edge energy [erg/cm] and μ is the chemical potential for one unit of solute with respect to the saturated condition and is expressed by

$$\mu = -kT \ln S \quad (2)$$

From Eqs. (1) and (2),

$$J' = k'_2 \exp \left[-\frac{\Delta g'_c}{kT} \right] \quad (3)$$

$$= k'_1 S^{m'} \quad (4)$$

where

$$k'_1 = k'_2 \exp \left[-\frac{2\pi r'_c \sigma'}{kT} \right] \quad (5)$$

$$m' = \pi (r'_c)^2 / a \quad (6)$$

where S is the supersaturation ratio, k'_2 is the frequency factor having a temperature dependency; E'_d/N_A : the activation energy for the transfer of solutes from solution to the adsorption layer on the crystal surface, and a is the area occupied per unit solute in the surface. The relation between r'_c and S is given by Eq. (7), by determining the condition under which the free energy, $\Delta g'$, for the formation of surface nucleus ($=n'\mu + 2\pi r'\sigma'$: n' is the number of solute in a nucleus of radius, r' .) becomes maximum, i.e. $d\Delta g'/dn' = 0$.

$$r'_c = a\sigma' / kT \ln S \quad (7)$$

Fig. 3 Photographs of crystallites formed under the conditions: $C_0=1.00$, $S_0=2.4$, $T_s=323$, $T=297$

Fig. 4 L (dotted curve) and $L^2 dL/dt$ (solid curve) vs. t

Equation (7) corresponds to the Gibbs-Thomson equation for three-dimensional nucleus, Eq. (7').

$$r_c = 2v\sigma' / kT \ln S \quad (7')$$

From Eqs. (6) and (7) and (1), (2), (6), and (7), respectively,

$$(m')^{-1/2} = (\pi a)^{-1/2} \frac{kT}{\sigma'} \ln S \quad (8)$$

$$\Delta g'_c = \pi r'_c \sigma' = m' kT \ln S \quad (9)$$

Similarly to homogeneous nucleation rate, Eq. (4') was proposed previously²⁾:

$$J = k_2 \exp \left[-\frac{\Delta g_c}{kT} \right] \quad (3')$$

$$= k_1 S^m \quad (4')$$

The expression for two-dimensional nucleation rate,

Table 1 Values of two-dimensional nucleation parameters: m' , $2r'_e$, σ' , σ'/d and $\Delta G'_e$

	T [°K]	S [—]	1.41	1.55	1.66	1.78	1.86	1.95	2.14	2.4
m'	290	—	—	—	—	10.6	9.1	7.1	4.1	3.5
	300	—	—	9.7	7.2	5.5	4.9	3.6	3.2	2.0
	310	—	9.4	5.5	3.5	2.8	2.2	1.9	—	—
$2r'_e$ [Å]	290	—	—	—	—	16.1	14.9	13.2	10.0	9.3
	300	—	—	15.4	13.3	11.6	11.0	9.4	8.9	7.0
	310	—	15.2	11.6	9.3	8.3	7.4	6.3	—	—
$\sigma' \times 10^7$ [erg/cm]	290	8.93	—	—	—	9.56	9.52	9.14	7.89	8.57
	300	7.06	—	7.24	7.17	7.17	7.32	6.73	7.18	6.60
	310	5.28	5.79	5.63	5.17	5.24	5.09	4.74	—	—
σ'/d [erg/cm ²]	290	20.3	—	—	—	—	—	—	—	—
	300	16.1	—	—	—	—	—	—	—	—
	310	12.0	—	—	—	—	—	—	—	—
$\Delta G'_e$ [kcal/g-mol-nuclei]	290	—	—	—	—	3.52	3.25	2.73	1.80	1.71
	300	—	—	2.53	2.18	1.89	1.81	1.43	1.45	1.00
	310	—	1.99	1.48	1.09	0.99	0.84	0.78	—	—

Fig. 5 $\log [(-dc/dt)/(C_0-C)^{2/3}]$ vs. $\log S$

Fig. 6 $(m')^{-1/2}$ vs. $\log S$

Eq. (4) indicates that the rate is proportional to m' power of S , where m' is the number of solute in a surface nucleus. It is not a constant, but depends on S and T , as indicated by Eq. (8). Another expression for surface nucleation rate can be derived from Eqs. (3), (9) and (7), as follows.

$$J' = k'_2 \exp \left[- \frac{\pi a' (\sigma')^2}{(kT)^2 \ln S} \right] \quad (10)$$

This is a well-known equation^{3,5,6)} and is of less easy-to-handle form than is Eq. (4).

Taking into account the consideration mentioned in the preceding section, and that J' is the rate per unit surface area, the overall growth rate, R , of all crystal-

lites in the sample solution is given by

$$R = - \frac{dc}{dt} = \beta h A J' = k'_1 (C_0 - C)^{2/3} S^{m'} \quad (11)$$

where h is the step height and A is the total surface area of all crystallites existing at $t=t$.

3. Results and Discussion

Figure 5 shows the data in Fig. 2(a), rearranged according to Eq. (11). Table 1 shows the values of m' obtained from the slopes of the curves in Fig. 5 and the calculated values of $2r'_e$, σ' and $\Delta G'_e (= N_A \Delta g'_e)$, based on, respectively, Eqs. (6), (7) and (9) and taking a as 19.30 Å². From Table 1, m' (hence $2r'_e$ and $\Delta G'_e$) decreases with increase in S and T , as expected from Eq. (8). The value of σ' is almost constant at constant T and is independent of S . This is confirmed by the straight lines passing through the origin as shown in Fig. 6 where the experimentally obtained m' raised to $-1/2$ power is plotted against $\log S$, on the basis of Eq. (8).

The free edge energy, σ' , may be correlated with the surface energy, σ , by⁶⁾

$$\sigma' = \sigma d \quad (12)$$

Table 1 also shows the values of σ'/d , taking d as $v^{1/3}$ (4.393 Å), where v is the volume of solute in crystal. To compare the parameters for two- (in Table 1) with those for three-dimensional nucleation¹⁾; some of the values at 300°K of m , $2r_e$, σ_3 and ΔG_e are illustrated in Table 2. In Table 2, the surface energy, σ_2 , estimated from σ' , according to Eq. (12) and σ_3 are of the same order of magnitude. The values in parentheses in m' column are the number of solute in an imaginary three-dimensional critical nucleus of radius r'_e . Comparison of this with m (or r'_e with r_e) may indicate that the two-dimensional critical nucleus is smaller than the three-dimensional one. From the theoretical point of view, however, the former is rather large on the basis of the latter, because from

Eqs. (7), (7') and (12) and provided that $\sigma_2 = \sigma_3$,

$$2r'_c = r_c \quad (13)$$

at the same S and T ; e.g., m' and $2r'_c$ based on m and $2r_c$ at $S=2.04$ in Table 2 may be expected to be 2.0 and 7.07 Å, respectively, at $S=1.95$ (corrected for S value). The difference between the values predicted and those in Table 2 may be due to the assumption of $\sigma_2 = \sigma_3$. In any event, more detailed discussion may not be very useful, since these calculations are based on a number of solute of only ten.

Since

$$\Delta G_c = 4\pi r_c^2 \sigma / 3 = mkT \ln S / 2 \quad (9')^{1,2)}$$

then, from Eqs. (9') and (9), and (3') and (3), respectively, at the same S and T ,

$$\Delta G_c / \Delta G'_c = m / 2m' \quad (14)$$

$$(J/k_2) / (J'/k'_2) = (S)^{(2m' - m)/2} \quad (15)$$

From Table 2, $\Delta G_c / \Delta G'_c$ at $S \doteq 2.0$, corrected for S value, is about 2.2 and that at $S \doteq 2.4$ is about 2.3. And this corresponds to the fact that the two-dimensional nucleation rate, J'/k'_2 , is more rapid than the three-dimensional one, J/k_2 , by a factor of about 16 at $S \doteq 2.0$ and 9 at $S \doteq 2.4$. **Figure 7** shows these comparisons and further indicates that, e.g., S at which three-dimensional nucleation has the same rate as two-dimensional nucleation at $S=1.82$ (A in Fig. 7) is 2.72 (B in Fig. 7). These comparisons provide a noteworthy suggestion that the growth of pre-existing crystal (e.g. seed crystal or formed crystallite) and the secondary nucleation rate in a non-quiet system may be more rapid than homogeneous nucleation, when their frequency factors are the same.

Figure 8 illustrates the Arrhenius plots of k_1'' , showing the temperature dependence for overall two-dimensional nucleation, E' , to be 50.8, 45.3 and 30.4 [kcal/g-mol-nuclei] at $S=1.91$, 2.00 and 2.09, respectively. From these values, the activation energies for the transition of solute from solution to the adsorption layer on the crystal surface, E'_d [kcal/g-mol-nuclei] and E'_b [kcal/g-mol-solute] (E'_d/m'), are, e.g., at $S=1.91$ and $T=300^\circ\text{K}$, estimated to be, respectively, about 45.3 and 12.6.

Conclusion

Heat evolution rate curves recorded with DSC at constant T were analyzed by the overall growth rate equation, Eq. (11), which was derived on the assumption that the crystallite surface is Kossel's and that its growth rate is determined by two-dimensional nucleation rate, J' expressed by Eq. (4), where the power value m' is the number of solute in a critical nucleus which depends on S and T .

Applying Eq. (11), reasonable values were obtained as the characteristic properties of two-dimen-

Table 2 Comparison of parameters for three-dimensional nucleation^{a)} with those for two-dimensional nucleation^{b)} at 300°K

S [—]	m [—]	m' [—]	$2r_c$ [Å]	$2r'_c$ [Å]	σ_3 average [erg/cm ²]	$\sigma_2 = \sigma'/d$ [erg/cm ²]	ΔG_c [kcal/gmol-nuclei]	$\Delta G'_c$ [kcal/gmol-nuclei]
1.95	—	3.6(5.1)	—	9.4	12.0	16.1	—	1.43
2.04	14.5	—	13.3	—	—	—	3.09	—
2.14	—	3.2(4.6)	—	8.9	—	—	—	1.45
2.34	—	2.0(2.1)	—	7.0	—	—	—	1.00
2.40	8.9	—	11.3	—	—	—	2.32	—

^{a)} Table 1, in the preceding paper¹⁾

^{b)} Table 1, in this paper

Fig. 7 $m \ln S/2$ or $m' \ln S$ and J/k_2 or J'/k'_2 vs. S , at 300°K

Fig. 8 Arrhenius plot of k_1''

sional nucleus of KBrO_3 . Comparisons of them with three-dimensional ones obtained previously¹⁾ were made. As a result, Eqs. (11) and (4) are considered adequate for the growth rate and two-dimensional nucleation rate, respectively, in this system.

Nomenclature

a	= area occupied by unit solute in surface, $\doteq d^2$	[cm ² , Å ² /solute]
C	= concentration	[g-mol-solute/l]
C_0	= initial concentration	[g-mol-solute/l]
C_s	= solubility concentration	[g-mol-solute/l]
d	= solute diameter, $\doteq v^{1/3}$	[cm, Å/solute]
E'	= overall activation energy for two-dimensional nucleation	[kcal/g-mol-nuclei]
E'_d	= activation energy for transition of solute	

	from solution to adsorption layer on crystal surface	[kcal/g-mol-nuclei]
E'_D	$= E'_d/m'$	[kcal/g-mol-solute]
$\Delta g, \Delta g'$	$=$ free energy change in formation of three- and two-dimensional nucleus	[kcal/nucleus]
$\Delta G_c, \Delta G'_c$	$= N_A \Delta g_c, N_A \Delta g'_c$, respectively	[kcal/g-mol-nuclei]
h	$=$ step height	[cm, Å]
J	$=$ three-dimensional nucleation rate	[number/cm ³ ·sec]
J'	$=$ two-dimensional nucleation rate	[number/cm ² ·sec]
k	$=$ Boltzmann constant	
k_1, k'_1, k''_1	$=$ nucleation rate constant defined in Eqs. (4'), (4) and (11), respectively	
k_2, k'_2	$=$ frequency factor, defined in Eqs. (3') and (3), respectively	
m, m'	$=$ number of solute in three- and two- dimensional critical nucleus, respectively	
N_A	$=$ Avogadro number	
r_c, r'_c	$=$ radius of three- and two-dimensional critical nucleus, respectively	[Å]
S	$=$ supersaturation ratio, $= C/C_s$	
T	$=$ crystallization temperature	[°K]
T_s	$=$ saturation temperature	[°K]
t	$=$ crystallization time	[sec]

V	$=$ volume of sample solution	[cm ³]
v	$=$ volume of crystal $= v_m/N_A$	[cm ³ /solute]
v_m	$=$ molar volume of crystal	[cm ³]
β	$=$ coefficient, defined in Eq. (11)	
μ	$=$ chemical potential of solute with respect to saturated condition	
σ	$=$ surface energy	[erg/cm ²]
σ'	$=$ free edge energy	[erg/cm]
σ_2	$=$ σ estimated from σ' ($= \sigma'/d$)	[erg/cm ²]
σ_3	$=$ σ obtained with homogeneous nucleation rate	[erg/cm ²]

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