Self-Diffusion and Interdiffusion in the AgBr–NaBr System

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The self-diffusion coefficients of silver, sodium and bromine in AgBr–NaBr single crystals have been measured at 400°C over the whole composition range by the tracer technique. It has been found that the self-diffusion coefficient of bromine is two or three orders of magnitude lower than those of silver and sodium, and that the interdiffusion coefficient in the AgBr–NaBr system at 400°C is nearly the same as the self-diffusion coefficient of bromine over the whole composition range. Kirkendall effect observed by means of the movement of natural markers has revealed that the interdiffusion proceeds by the parallel diffusion of silver and bromine ions. For the interpretation of the observed results, a phenomenological equation of interdiffusion has been derived. The interdiffusion coefficient calculated by the equation has been in good agreement with the observed data.

Introduction

The phenomenological theory of the interdiffusion in binary alloys has been developed by Darken (*1*). He treated the interdiffusion from the standpoint that each component has its own diffusivity, and derived an equation

$$\tilde{D} = (N_1 D_2^* + N_2 D_1^*)\left(1 + \frac{d\ln\gamma_2}{d\ln N_2}\right), \quad (1)$$

where N_1 and N_2 are the mole fractions of components 1 and 2, $\tilde{D}$ the interdiffusion coefficient, D_1^* and D_2^* the self-diffusion coefficients, and γ_2 the activity coefficient of component 2.

Cooper and Heasley (*2*) extended Darken's treatment to the binary diffusion in ceramics, particularly in systems with common anions, such as the AX–BX system. They assumed that the diffusion is one-dimensional and the flux J_i of ions of the i-th kind is expressed by

$$J_i = -\frac{C_i D_i^*}{RT}\left(\frac{\partial\mu_i}{\partial x} + Z_i F\frac{\partial\phi}{\partial x}\right) + C_i u, \quad (2)$$

where C_i is the concentration, D_i^* the self-diffusion coefficient, μ_i the chemical potential, Z_i the number

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of charge, ϕ the electrical potential, and u the velocity. For simplification it was also assumed that

(1) The volume of ceramics is primarily determined by that of anion;

(2) Setting of a volume-fixed reference frame gives

$$\bar{V}_A J_A + \bar{V}_B J_B + \bar{V}_X J_X = 0 \quad (3)$$

where $\bar{V}_i$ is the partial volume;

(3) The chemical potential of the anion is independent of the composition ratio of two kinds of cations;

(4) The electroneutrality condition is

$$F(Z_A J_A + Z_B J_B + Z_X J_X) = 0. \quad (4)$$

It was shown that the binary diffusion coefficient can be expressed in terms of self-diffusion coefficients and electrical charges of ionic species A, B, and X, and the activity coefficient of AX as follows:

$$\tilde{D} = \frac{\begin{aligned}Z_B C_{BX} D_A^*(Z_X D_X^* - Z_B D_B^*)\\ + Z_A C_{AX} D_B^*(Z_X D_X^* - Z_A D_A^*)\end{aligned}}{\begin{aligned}Z_A Z_X C_{AX} D_X^* - Z_A^2 C_{AX} D_A^*\\ + Z_B Z_X C_{BX} D_X^* - Z_B^2 C_{BX} D_B^*\end{aligned}}$$
$$\times\left(1 + \frac{d\ln\gamma_{AX}}{d\ln C_{AX}}\right). \quad (5)$$

In order to interpret Blank's (4) experimental result of the interdiffusion in the NiO–MgO system, Schmalzried and Holt (3) expressed the fluxes of Ni^{2+}, Mg^{2+} and h (holes) relative to the fixed oxygen sub-lattice by Eq. (2) with the conditions

$$F(Z_{Ni^{2+}}J_{Ni^{2+}} + Z_{Mg^{2+}}J_{Mg^{2+}}) = 0 \qquad (6)$$

and

$$J_h = 0 \qquad (7)$$

they obtained the following equation

$$\tilde{D} = N_{NiO}D^*_{Mg} + N_{MgO}D^*_{Ni}. \qquad (8)$$

For the interdiffusion of a couple of KCl and RbCl, Müller and Schmalzried (5) assumed that the fluxes of K^+, Rb^+, and Cl^- are expressed in the form of

$$J_i = -\frac{C_i D_i^*}{RT}\left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x}\right). \qquad (9)$$

Employing the electroneutrality condition

$$F(Z_{K^+}J_{K^+} + Z_{Rb^+}J_{Rb^+} + Z_{Cl^-}J_{Cl^-}) = 0 \qquad (10)$$

and the expression

$$\tilde{D} = (C_K D_{Rb} + C_{Rb} D_K)\cdot V, \qquad (11)$$

where D_K and D_{Rb} are the intrinsic diffusion coefficients and V the molal volume, they derived an equation

$$\tilde{D} = N_{RbCl} D_K^* + N_{KCl} D_{Rb}^* \\ - N_{KCl} N_{RbCl}(D_K^* - D_{Rb}^*)^2 \cdot \chi, \qquad (12)$$

where χ represents $F^2(RTV\sigma)^{-1}$ and σ the electrical conductivity.

Lindström (6) discussed the interdiffusion of couples consisting of alkali halides AX and BX from the phenomenological and atomistic viewpoints. Introducing the cross terms into equations of diffusion flux, he derived an equation

$$\tilde{D} = \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln C_A}\right)\left\{C_B D_A^* + C_A D_B^* \\ + 0.28\, C_A C_B \frac{(D_A^* - D_B^*)^2}{C_A D_A^* + C_B D_B^*} \\ - 1.28\, C_A C_B \frac{(D_A^* - D_B^*)^2}{C_A D_A^* + C_B D_B^* + D_X^*}\right\}, \qquad (13)$$

where γ_A is the activity coefficient.

Although several phenomenological equations were derived for the interdiffusion between halides or oxides, the measurements of the interdiffusion coefficient and the self-diffusion coefficients of all ionic species have not been carried out. The present study aims to measure the interdiffusion coefficient in the AgBr–NaBr system and the self-diffusion coefficients of silver, sodium and bromine over the

whole composition range of the system to elucidate experimentally the correlation between the inter-diffusion coefficient and the self-diffusion coefficients in the system of AX–BX type.

In a previous work (7), the authors have measured the emf of solid electrolyte cells of the type Ag/AgBr–NaBr/Br$_2$ and calculated the activity and partial molal quantities of AgBr in the AgBr–NaBr solid solution. Moreover, a miscibility gap was found in the AgBr–NaBr system by the emf measurement. The solubility limit of the system was determined by the emf measurement and the high temperature X-ray diffraction method. Figure 1 shows the phase diagram of the AgBr–NaBr system. It has been found that the system also shows positive deviations from Raoult's law and forms a regular solution defined by Hildebrand (8) above the critical temperature.

Experimental

Samples

High-purity silver bromide and sodium bromide were used in this experiment. Since sodium bromide is hygroscopic, it was dried at 100°C for 24 hr in air. Then the dried sodium bromide was mixed with silver bromide in a desired proportion and the mixture was transferred to a quartz tube of 10 mm in diameter. The quartz tube was evacuated and heated about 200°C for 30 min in order to drive off residual
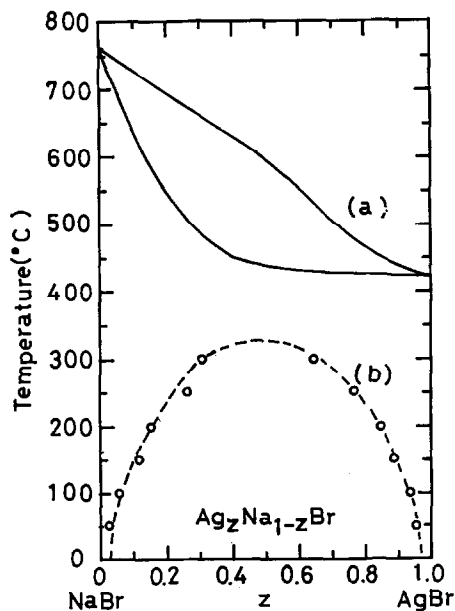

FIG. 1. Phase diagram of the AgBr–NaBr system. (a) Zemczuzny (17); (b) our work (7).

water. Then a bromine atmosphere was introduced into the tube, and the mixture was melted. After the solution became clear, the mixture was cooled, and the tube was sealed in a bromine atmosphere.

The sealed quartz tube was placed in a furnace for zone-melting. The furnace was driven at a rate of 3.7 mm/hr. By this procedure purification of sample and preparation of single crystals of solid solution were achieved. The single crystal thus obtained was annealed at 400°C for about 3 days for homogenization. Although the crystals were transparent at 400°C, they became opaque at room temperature due to the precipitation. Cylindrical samples, about 10 mm in diameter and 5–7 mm in height, were taken from the crystals and annealed at 400°C for about 24 hr in a bromine atmosphere of 0.0864 Torr in order to control the concentration of defects in the samples.

Measurement of Self-Diffusion Coefficients

One end surface of a cylindrical sample was polished by emery paper and attached to the sample holder with synthetic resin Aron-Alpha. The sample holder was mounted to a precision grinding machine which had a similar design as that of Letaw, Slifkin, and Portnoy (9). After polishing by emery paper, the sample was detached from the sample holder and the resin was removed with acetone. Then the tracer was applied to one surface of the sample and dried gently by red lamps. Radioisotopes employed are listed in Table I.

In order to minimize tracer losses, two samples were placed radioactive end to radioactive end and the diffusion couple was placed in a chamber kept at 400°C. During the diffusion run, the temperature

TABLE I

RADIOISOTOPES EMPLOYED FOR THE SELF-DIFFUSION EXPERIMENT

	Silver	Sodium	Bromine
Radioisotope	$^{110m}Ag^a$	$^{22}Na^b$	$^{82}Br^c$
Type of decay	β^-	β^+	β^-
Half-life	253 days	2.6 years	35.9 hr
Form when employed	$^{110m}AgNO_3$ in HNO_3	$^{22}NaCl$ aqueous solution	$Na^{82}Br$ aqueous solution

[a] Activated at New England Nuclear Corp., U.S.A.

[b] Activated at The Radiochemical Centre, England.

[c] Activated at Japan Atomic Energy Research Institute, Japan.

TABLE II

COUPLES USED IN THE INTERDIFFUSION EXPERIMENT

Couple	Time of annealing (hr)
(1) $AgBr/Ag_{0.5}Na_{0.5}Br$	15
(2) $NaBr/Ag_{0.5}Na_{0.5}Br$	15
(3) $Ag_{0.6}Na_{0.4}Br/Ag_{0.4}Na_{0.6}Br$	18
(4) $Ag_{0.4}Na_{0.6}Br/Ag_{0.2}Na_{0.8}Br$	18
(5) $Ag_{0.2}Na_{0.8}Br/NaBr$	18

was kept constant within $\pm 1°C$ by means of an electronic controller.

After a predetermined length of time, the couple was taken out of the furnace and quenched rapidly to room temperature. After the separation, each sample was attached to the sample holder and polished by emery papers to remove successive layers. The weight of the sample together with the sample holder was measured in order to determine the thickness of each layer. The radioactivity of smeared powder on emery papers was measured by means of a Geiger–Müller counter of Toshiba Electric Co., Ltd. Since the half-life of bromine is only 35.9 hr, the time of each measurement was recorded and the correction of natural decay was made. The measurement of radioactivity was made twice a sample. Reproducibility was quite good.

Measurement of Interdiffusion Coefficient

Prior to the diffusion experiment, two samples of different composition were placed end surface to end surface. The combination employed is listed in Table II. Then the diffusion couple was inserted in a Pyrex tube and annealed at 400°C in a bromine atmosphere of 0.0864 Torr. After a predetermined length of time, the diffusion couple was rapidly withdrawn from the electric furnace and allowed to cool in air. Then the couple was sectioned in parallel to the axis of diffusion and the section was polished, washed, dried, and coated with beryllium film. The concentration profile in parallel direction to the diffusion was determined by an electron microprobe analyzer.

Results and Discussions

Self-Diffusion Coefficients

Under the conditions of this experiment an infinitely thin film of tracer is assumed to have been

deposited on a semiinfinite solid. The solution of the diffusion equation for these conditions is given by

$$C(x,t) = \frac{C_0}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4 D^* t}\right), \qquad (14)$$

where C is the tracer concentration, x is the distance below the surface, t is the diffusion time, and D^* is the self-diffusion coefficient. Therefore, the value of D^* was determined from the slope of the plot of $\log C$ vs x^2.

Figure 2 shows the concentration profiles of silver after the annealing of 5400 sec. The agreement between two plots is quite good. In some cases, however, the plot of $\log C$ vs x^2 was not linear, as seen in the case of diffusion in polycrystals. In such cases, the diffusion coefficient was determined from the slope of straight line drawn in the region where the effect of grain boundaries would not appear.

Figure 3 shows the plot of self-diffusion coefficients of silver, sodium, and bromine against the mole fraction of silver bromide. The data by other investigators (10–15) were also given in the same figure. The self-diffusion coefficients of silver and bromine in pure silver bromide obtained in the present work agree well with those by other investigators. However, the self-diffusion coefficients of
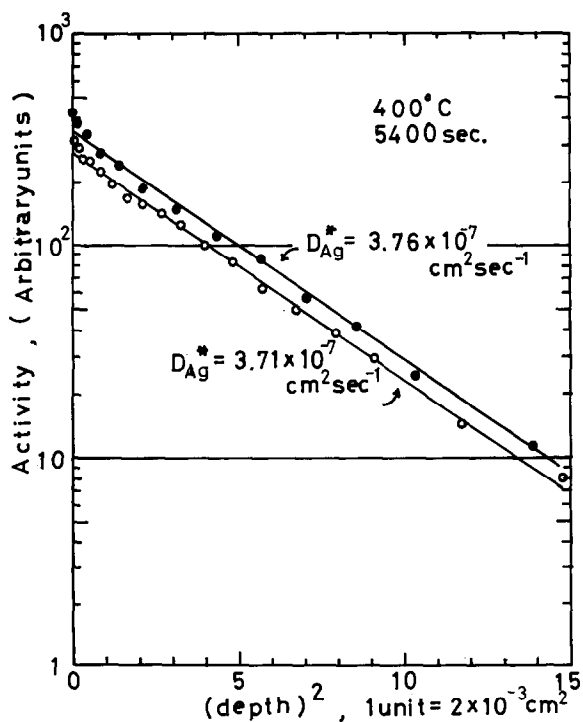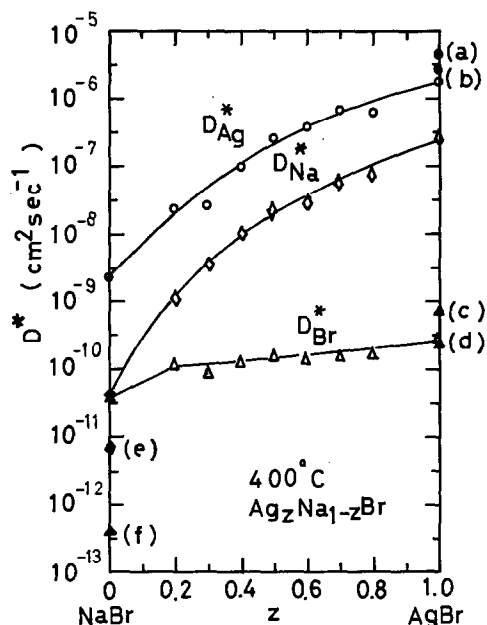

FIG. 3. Self-diffusion coefficients of silver, sodium and bromine as a function of composition. (a) Ref. (10); (b) Ref. (14); (c) Ref. (15); (d) Ref. (11); (e) Ref. (12); (f) Ref. (13).

sodium and bromine in pure sodium bromide are larger than those by other investigators. Such differences are attributed to the difference in defect concentration in sodium bromide employed, because at 400°C sodium bromide is considered to be in the extrinsic range.

It is noted in Figure 3 that the values of self-diffusion coefficient of silver in this system are much higher than those of sodium and bromine, and the self-diffusion coefficient of bromine is nearly independent of the composition of solid solution in a composition range between AgBr and $Ag_{0.2}Na_{0.8}Br$. The independence of D_{Br}^* on the composition suggests that the concentration and mobility of anion vacancies would be nearly constant in this composition range. It has been also found that in the composition range between AgBr and $Ag_{0.2}Na_{0.8}Br$, $\log D_{Ag}^*$ and $\log D_{Na}^*$ increase in parallel as the mole fraction of silver bromide increases, that is, D_{Ag}^*/D_{Na}^* is nearly constant in this composition range.

Interdiffusion Coefficient

Figure 4 shows the concentration profile of sodium bromide for a couple of AgBr and $Ag_{0.5}Na_{0.5}Br$. The interdiffusion coefficient was calculated by Matano solution (16)

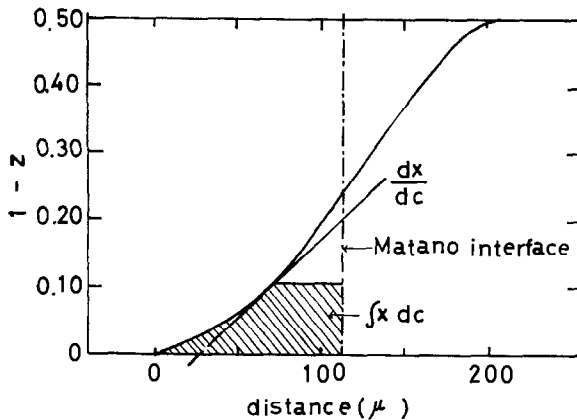$$\tilde{D} = \frac{1}{2t}\frac{dx}{dc}\int x\, dc. \qquad (15)$$

FIG. 2. Typical penetration curves of ^{110m}Ag in $Ag_{0.6}Na_{0.4}Br$.

FIG. 4. Concentration profile of NaBr (Couple (1)).

(a) Couple (5) (NaBr / $Ag_{0.2}Na_{0.8}Br$)

(b) Couple (3) ($Ag_{0.4}Na_{0.6}Br$ / $Ag_{0.6}Na_{0.4}Br$)

FIG. 6. Concentration profiles of NaBr and positions of the Matano and original interfaces.

The values of $\tilde{D}$ are given by circles in Figure 5. Open, solid and semisolid circles represent the values calculated from the data of couples (1), (2) and (3)–(5), respectively. As is seen in the figure, $\tilde{D}$ is nearly constant irrespective of composition and the same as the self-diffusion coefficient of bromine.

Figures 6(a) and (b) show the concentration profiles of sodium bromide and positions of the original and Matano interfaces. From the result of marker experiment, it is concluded that the interdiffusion of this system was caused mainly by the parallel diffusion of silver and bromine ions.
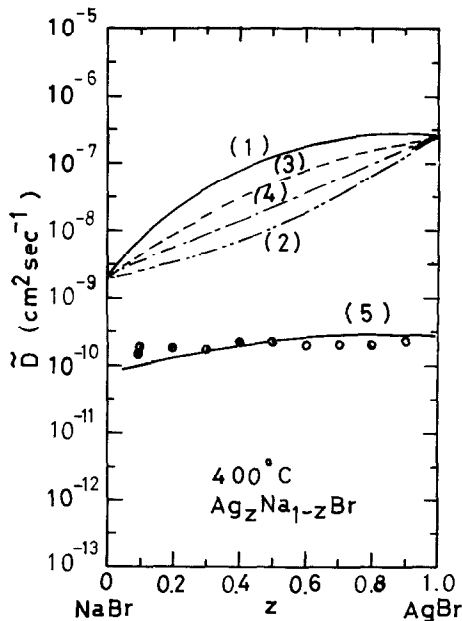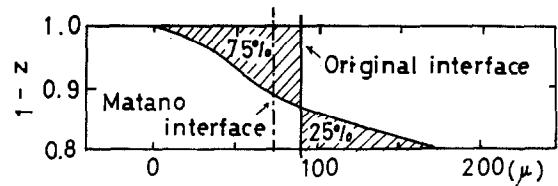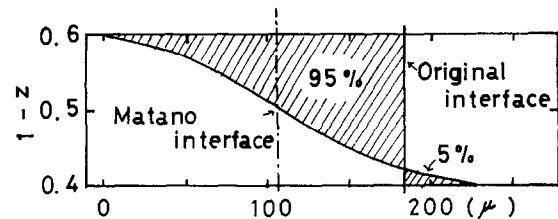

FIG. 5. Interdiffusion coefficients in the AgBr–NaBr system. Curves (1), (2), (3), (4), and (5) represent the values calculated by using Eqs. (5), (8), (12), (13) and (26), respectively.

As mentioned above, several equations have been proposed to correlate the interdiffusion coefficient and the self-diffusion coefficients of constituents in solid solution. In order to check whether or not the proposed equations hold for the present system, the calculation of $\tilde{D}$ was carried out.

Curves (1), (2), (3), and (4) in Figure 5 show the present study with the values calculated by using Eqs. (5), (8), (12), and (13), respectively. Disagreements between the observed and calculated values are remarkable. According to the theories proposed so far, the interdiffusion in the AgBr–NaBr system is expected to be controlled by the counter diffusion of silver and sodium ions, since the measurement of self-diffusion coefficient has revealed $D_{Ag}^* > D_{Na}^* \gg D_{Br}^*$. However, the marker experiment clearly has shown that the interdiffusion is caused mainly by the parallel diffusion of silver and bromine ions. Therefore, a new equation is needed for the interpretation of the observed interdiffusion coefficient.

Let us assume that the diffusion is one dimensional and the flux J_i of ions of i-th kinds are expressed by

$$J_i = -\frac{C_i D_i^*}{RT} \frac{\partial \eta_i}{\partial x}$$
$$= -\frac{C_i D_i^*}{RT} \left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right), \qquad (16)$$

where C_i is the concentration, D_i^* the self-diffusion coefficient, μ_i the chemical potential, Z_i the number

of charge, ϕ the electrical potential, and η_i the electrochemical potential. The electrical current I_i is

$$I_i = Z_i F J_i. \tag{17}$$

As was found in this experiment, the flux of sodium ions is much lower than those of silver and bromine ions. Therefore, as the first approximation the electroneutrality condition is written by

$$I_{Ag^+} + I_{Br^-} = 0 \tag{18}$$

or

$$J_{Ag^+} = J_{Br^-}. \tag{19}$$

From Eqs. (16) and (19) we obtain

$$F\left(\frac{\partial\phi}{\partial x}\right) =$$

$$\frac{-C_{Ag^+} D^*_{Ag^+}(\partial\mu_{Ag^+}/\partial x) + C_{Br^-} D^*_{Br^-}(\partial\mu_{Br^-}/\partial x)}{C_{Ag^+} D^*_{Ag^+} + C_{Br^-} D^*_{Br^-}}. \tag{20}$$

Inserting Eq. (20) into Eq. (16) and equating $\mu_{Ag^+} + \mu_{Br^-}$ to μ_{AgBr}, we obtain

$$J_{Ag^+} = -\frac{1}{RT}\cdot\frac{C_{Ag^+} D^*_{Ag^+} C_{Br^-} D^*_{Br^-}}{C_{Ag^+} D^*_{Ag^+} + C_{Br^-} D^*_{Br^-}}\left(\frac{\partial\mu_{AgBr}}{\partial x}\right). \tag{21}$$

The chemical potential of silver bromide is related to its activity

$$d\mu_{AgBr} = RT d\ln a_{AgBr}$$

$$= RT d(\ln\gamma_{AgBr} + \ln N_{AgBr}), \tag{22}$$

where N_{AgBr} and γ_{AgBr} are the mole fraction and activity coefficient of silver bromide, respectively.

From Eq. (22),

$$\frac{\partial\mu_{AgBr}}{\partial x} = RT\left(1 + \frac{\partial\ln\gamma_{AgBr}}{\partial\ln N_{AgBr}}\right)\cdot\frac{1}{N_{AgBr}}\cdot\frac{\partial N_{AgBr}}{\partial x}. \tag{23}$$

Substituting Eq. (23) in Eq. (21), we obtain

$$J_{Ag^+} = -\frac{C_{Ag^+} D^*_{Ag^+}\cdot C_{Br^-} D^*_{Br^-}}{C_{Ag^+} D^*_{Ag^+} + C_{Br^-} D^*_{Br^-}}\cdot\left(1 + \frac{\partial\ln\gamma_{AgBr}}{\partial\ln N_{AgBr}}\right)$$

$$\times \frac{1}{N_{AgBr}}\cdot\frac{\partial N_{AgBr}}{\partial x}. \tag{24}$$

From Fick's First Law, J_{Ag^+} is also written by

$$J_{Ag^+} = -\tilde{D}\frac{\partial N_{AgBr}}{\partial x}. \tag{25}$$

Comparison of Eq. (24) with Eq. (25) yields

$$\tilde{D} = \frac{C_{Ag^+} D^*_{Ag^+} C_{Br^-} D^*_{Br^-}}{C_{Ag^+} D^*_{Ag^+} + C_{Br^-} D^*_{Br^-}}$$

$$\times \left(1 + \frac{\partial\ln\gamma_{AgBr}}{\partial\ln N_{AgBr}}\right)\cdot\frac{1}{N_{AgBr}}. \tag{26}$$

Therefore, we can calculate $\tilde{D}$ from the self-diffusion coefficients of silver and bromine ions, and the activity coefficient of silver bromide.

Curve (5) in Figure 5 shows the interdiffusion coefficient calculated by using Eq. (26). The self-diffusion coefficients determined in the present study and the activity coefficient in a previous work (7) were used for the calculation. Agreement between the calculated and observed values is good. Therefore, it is concluded that Eq. (26) holds for the interdiffusion in the AgBr–NaBr system. The reason why the parallel diffusion of silver and bromine ions prevails in the interdiffusion in the AgBr–NaBr system in spite of $D^*_{Ag} > D^*_{Na} \gg D^*_{Br}$, is discussed next.

It does not depend on the self-diffusion coefficients, but on the fluxes of constituent ions whether the parallel diffusion of silver and bromine ions prevails or the counter diffusion of silver and sodium ions predominates. Since J_i is the product of the terms $C_i D_i^*/RT$ and $\partial\eta_i/\partial x$,

$$\frac{|J_{Br^-}|}{|J_{Na^+}|} = \frac{C_{Br^-} D^*_{Br^-}|(\partial\eta_{Br^-}/\partial x)|}{C_{Na^+} D^*_{Na^+}|(\partial\eta_{Na^+}/\partial x)|}; \tag{27}$$

therefore, if

$$\left|\left(\frac{\partial\eta_{Br^-}}{\partial x}\right)\right|\bigg/\left|\left(\frac{\partial\eta_{Na^+}}{\partial x}\right)\right|$$

is smaller than $C_{Na^+} D^*_{Na^+}/C_{Br^-} D^*_{Br^-}$, the counter diffusion would be predominant as usually mentioned. However, if

$$\left|\left(\frac{\partial\eta_{Br^-}}{\partial x}\right)\right|\bigg/\left|\left(\frac{\partial\eta_{Na^+}}{\partial x}\right)\right|$$

is larger than $C_{Na^+} D^*_{Na^+}/C_{Br^-} D^*_{Br^-}$, the parallel diffusion would be preferred. In the case of the interdiffusion near the composition of $Ag_{0.5}Na_{0.5}Br$, $|J_{Br^-}|/|J_{Na^+}| = (95-5)/5$, $D^*_{Br^+} = 1.95 \times 10^{-10}$ and $D^*_{Na^+} = 2.24 \times 10^{-8}$. Therefore inserting these data into Eq. (27), we obtain the critical ratio

$$\frac{|(\partial\eta_{Br^-}/\partial x)|}{|(\partial\eta_{Na^+}/\partial x)|} = 1.03 \times 10^3.$$

Similarly in the case of $Ag_{0.1}Na_{0.9}Br$,

$$\frac{|(\partial\eta_{Br^-}/\partial x)|}{|(\partial\eta_{Na^+}/\partial x)|} = 7.25.$$

Conclusion

(1) The self-diffusion coefficients of silver, sodium and bromine in the AgBr–NaBr single crystals have been measured at 400°C over the whole composition range by the tracer technique.

(2) It has been found that (a) $D^*_{Ag} > D^*_{Na} \gg D^*_{Br}$, and

(b) in a composition range between AgBr and $Ag_{0.2}Na_{0.8}Br$, the self-diffusion coefficient of bromine is nearly independent of composition and D^*_{Ag}/D^*_{Na} is nearly constant.

(3) It has been also found that (a) the interdiffusion coefficient is nearly the same as the self-diffusion coefficient of bromine, and (b) the interdiffusion is caused mainly by the parallel diffusion of silver and bromine ions.

(4) With the assumption of the parallel diffusion of silver and bromine ions, an equation for calculating the interdiffusion coefficient $\tilde{D}$ from the self-diffusion coefficients of silver and bromine and the activity coefficients of silver bromide was derived.

(5) The calculated values of the interdiffusion coefficients well agreed with the observed ones.

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