Distribution of Diffusion Coefficient and its Concentration Dependence

by

Shin-ichiro ISHIDA*, Norio SENDA**, Kozo NAKAMURA* and Katsumasa KANEKO*

Synopsis

A new method for determining the distribution of the diffusion coefficient and its concentration dependence by analysis of the diffusion curve of the heterogeneous system is proposed.

This method is computer simulation which is performed by assuming the number of component and the weight fraction of each component and by selecting the diffusion coefficient and the concentration coefficient from pseudorandom numbers.

From the results of the application to theoretically synthetic diffusion curves, it became obvious that this method has high accuracy.

Introduction

When the diffusion coefficient of unfractionated polymer sample in solution has concentration dependence, it is difficult to determine the distribution of the diffusion coefficient, furthermore, the molecular weight distribution from diffusion experiment.

Since the concentration dependence appears as the skewness of the diffusion curve which is relationship of concentration gradient and diffusion distance, we previously proposed an analytical method to eliminate the skewness and to obtain the symmetrical diffusion curve which shows only polymolecularity.[1] Applying the logarithmic analysis[2] and the simultaneous method[3] for this symmetrized diffusion curve, the diffusion coefficient distribution can be obtained theoretically. By these methods, however, the sample is fractionated only into three or four fractions.

In this paper, a new analytical method to obtain the diffusion coefficient distribution is described, in which, the sample is fractionated into ten or twenty fractions and the concentration coefficient for each diffusion coefficient should be obtained theoretically.

Theoretical

Symmetrization of the Diffusion Curve

In dilute solution of homogeneous system, the relationship between the diffusion coefficient D and the concentration c can be represented as follows :

* Dept. of Industrial Chemistry

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$$D = D_0 \ (1 + c_0 k \cdot c/c_0), \tag{1}$$

where D_0 is the diffusion coefficient at infinite dilution, c_0 is the initial concentration of the solution and k is the characteristic parameter of the concentration dependence.

If the average diffusion coefficient D_m obtained from eq. (2) is used, eq. (1) can be transformed into eq. (3), since D_m means weight average value,

$$D_m = m_2 / 2\mathrm{t}, \tag{2}$$

$$D_m = D_0 \ (1 + 0.5 c_0 k). \tag{3}$$

In these equations, m_2 is the second moment of the diffusion curve and t is the diffusion time.

Now, in the system of heterogeneity in molecular weight, if the concentration, the diffusion coefficient and the characteristic parameter of the concentration dependence of each component are designated as c_i, D_i and k_i, respectively, D_m is represented by following equation,

$$D_m = \Sigma c_i D_i \ (1 + 0.5 c_0 k_i) \ / \Sigma c_i. \tag{4}$$

If the standardized concentration gradient and the standardized diffusion distance are represented by Y and X, the weight average diffusion coefficient at any distance can be given as follows:

$$D = \Sigma Y_i D_i / \Sigma Y_i, \quad c_0 k_i = 0. \tag{5}$$

Considering the concentration dependence, we have

$$\frac{D}{D_m} = \frac{\Sigma Y_i D_i \ (1 + c_0 k_i \cdot c/c_0) \ / \Sigma Y_i}{\Sigma c_i D_i \ (1 + 0.5 c_0 k_i) \ / \Sigma c_i}. \tag{6}$$

This is rewritten as follows:

$$\frac{D}{D_m} = \frac{\Sigma Y_i D_i / \Sigma Y_i}{D_m} + \frac{\Sigma Y_i D_i c_0 k_i}{D_m \Sigma Y_i} \ (c/c_0). \tag{7}$$

Using r defined as

$$D_m = r \cdot D_W = r \cdot \frac{\Sigma c_i D_i}{\Sigma c_i}, \tag{8}$$

eq. (7) is transformed into the following formula,

$$\frac{D}{D_m} = \frac{1}{r} \cdot \frac{\Sigma Y_i D_i / \Sigma Y_i}{\Sigma c_i D_i / \Sigma c_i} + \frac{\Sigma Y_i D_i c_0 k_i}{D_m \cdot \Sigma Y_i} \ (c/c_0), \tag{9}$$

$$c/c_0 = \int_{-\infty}^{X} Y dX. \tag{10}$$

The first term of the right-hand in eq. (9) is D/D_m which is independent of the concentration and then gives a diffusion curve symmetry about $c/c_0=0.5$. Considering a pair of concentration $(c/c_0)_1$and $(c/c_0)_2$ which satisfy the condition $(c/c_0)_1+(c/c_0)_2=1$ and a pair of diffusion coefficient $(D/D_m)_1$ and $(D/D_m)_2$ which correspond to each concentration, the following equation is given,

$$\frac{\Sigma Y_i D_i c_0 k_i}{D_m \cdot \Sigma Y_i}=\frac{(D/D_m)_2-(D/D_m)_1}{(c/c_0)_2-(c/c_0)_1} \cdot \tag{11}$$

Substituting this equation into eq. (9), the value of the first term of the right-hand is determined corresponding to each concentration.

This treatment gives the curve of $(D/D_m)\ /r$ vs. c/c_0 in which the conentration dependence is eliminated.

Now the following equation can be written,

$$\int_0^1 (D/D_m)\ d\ (c/c_0)\ =1\ . \tag{12}$$

Then r is given as follows :

$$\frac{1}{r}=\int_0^1\frac{(c/c_0)_2\ (D/D_m)_1-(c/c_0)_1\ (D/D_m)_2}{(c/c_0)_2-(c/c_0)_1}d\ (c/c_0). \tag{13}$$

From the relationship between $\dfrac{\Sigma Y_i D_i/\Sigma Y_i}{\Sigma c_i D_i/\Sigma c_i}$ and c/c_0, the diffusion curve which has not the concentration dependence can be obtained by iterative method using eqs. (14) and (10),

$$Y=\frac{(D_0/D)\ \exp\left\{-\int_0^X (D_m/D)\ X\ dX\right\}}{\int_{-\infty}^{\infty}(D_0/D)\ \exp\left\{-\int_0^X (D_m/D) X\ dX\right\}dX}. \tag{14}$$

As the diffusion curve without concentration dependence has the additive properties, we get the following equations from eq. (9),

$$Y=\frac{d(c/c_0)}{dX}=\Sigma Y_i$$

$$=\frac{(\Sigma c_i D_i)^{1/2}}{(2\pi)^{1/2}\ (\Sigma c_i)^{3/2}}\ (\Sigma c_i D_i^{-1/2})\exp\left(-\frac{X^2}{2\ D_i}\cdot\frac{\Sigma c_i D_i}{\Sigma c_i}\right), \tag{15}$$

$$\frac{D}{D_m}=\frac{\Sigma c_i\ \Sigma c_i D_i^{1/2}\ \ (1+c_0 k_i \cdot c/c_0)\ \exp\left(-\frac{X^2}{2\ D_i}\cdot\frac{\Sigma c_i D_i}{\Sigma c_i}\right)}{\Sigma c_i D_i\ \ (1+0.5\ c_0 k_i)\ \ \Sigma c_i D_i^{-1/2}\exp\left(-\frac{X^2}{2\ D_i}\cdot\frac{\Sigma c_i D_i}{\Sigma c_i}\right)}\ . \tag{16}$$

The diffusion coefficient at any diffusion distance is given as the weight average and so next equation is obtained,

$$\left(\frac{D}{D_m}\right)_{c_0k=0}=\frac{\Sigma Y_iD_i/\Sigma Y_i}{\Sigma c_iD_i/\Sigma c_i}. \tag{17}$$

The weight average diffusion coefficient D_W is expressed as

$$D_W=(D_m)_{c_0k=0}=\Sigma c_iD_i/\Sigma c_i. \tag{18}$$

The concentration average coefficient D_k is represented by the following formula,

$$D_k=\left(\frac{\Sigma Y_iD_i}{\Sigma Y_i}\right)_{X=0}=\frac{\Sigma c_iD_i^{1/2}}{\Sigma c_iD_i^{-1/2}}, \tag{19}$$

and the average diffusion coefficient obtained from area of the diffusion curve is shown as follows :

$$D_A=\left(\frac{\Sigma c_i}{\Sigma c_iD_i^{-1/2}}\right)^2. \tag{20}$$

The values of D_W, D_k and D_A can be determined by the following relationships from the analysis of the symmetrized diffusion curve and c/c_0 vs. D/D_m curve.

$$D_W=D_m/r, \tag{21}$$

$$D_k=D_W/(D/D_m)_{c/c_0=0.5}, \tag{22}$$

$$D_A=D_W/2\pi(Y_{max})^2. \tag{23}$$

The characteristic parameter of the concentration dependence is related to r by the next equation,

$$k_r=2(r-1)/c_0. \tag{24}$$

In heterogeneous system, k_r is the average defined by the following equation,

$$k_r=\Sigma c_iD_ik_i/\Sigma c_iD_i. \tag{25}$$

Determination of the Distribution of the Diffusion Coefficient

Several methods have been proposed for determining the distribution of the diffusion coefficient from analysis of the diffusion curve, but in these methods, it muts be need to assume a function. On the contrary, the logarithmic analysis and the simultaneous method need no such assumption and can directly estimate the distribution from the diffusion curve. By these methods, the sample is hypothetically fractionated in only 3 or 4 fractions, but 10 to 20 fractions are obtained by our new theoretical method described below.

Assuming the number of component n (e. g. 10 or 20), weight fraction of each component c_i (e. g. $c_1 = c_2 = \cdots\cdots = c_{10} = 0.1$ or $c_1 = c_2 = \cdots\cdots = c_{20} = 0.05$) and D_i/D_W by using pseudorandom numbers, the theoretically synthetic diffusion curves were obtained by the following equation,

$$Y' = \Sigma \frac{c_i}{\sqrt{2\pi D_i/D_W}} \exp\left(-\frac{X^2}{2D_i/D_W}\right). \tag{26}$$

An average error is defined as follows :

$$\xi = \sqrt{(Y-Y')^2_{X=0} + (Y-Y')^2_{X=0.2} + (Y-Y')^2_{X=0.4} + \cdots\cdots + (Y-Y')^2_{X=3.0}}. \tag{27}$$

The group of D_i/D_W which makes ξ the smallest is the nearest to the true composition of the sample. Repeating the modification, a group of D_i/D_W whose synthetic diffusion curve is very similar to the experimental one is obtained.

Similarly assuming n, c_i, D_i/D_W and c_0k_i from pseudorandom numbers, the $c/c_0 - D/D_m$ curves corresponding to those groups are obtained by the following equation,

$$\left(\frac{D}{D_m}\right)' = \frac{\Sigma c_i \Sigma c_i (D_i/D_W)^{1/2} (1 + c_0k_i \cdot c/c_0) \exp\left(-\frac{X^2}{2D_i/D_W}\right)}{\Sigma c_i (D_i/D_W)\ (1 + 0.5\, c_0k_i)\ \Sigma c_i\ (D_i/D_W)^{-1/2} \exp\left(-\frac{X^2}{2D_i/D_W}\right)}. \tag{28}$$

An average error is defined as follows :

$$\xi' = \sqrt{\left[\left(\frac{D}{D_m}\right) - \left(\frac{D}{D_m}\right)'\right]^2_{X=-3.0} + \left[\left(\frac{D}{D_m}\right) - \left(\frac{D}{D_m}\right)'\right]^2_{X=-2.8} + \cdots\cdots + \left[\left(\frac{D}{D_m}\right) - \left(\frac{D}{D_m}\right)'\right]^2_{X=3.0}} \tag{29}$$

Similarly selecting c_0k_i from pseudorandom number for each D_i/D_W and choosing the group of c_0k_i which has the smallest value of ξ', this group is the nearest to the true c_0k_i of the sample. Repeating the modification, a group of c_0k_i whose synthetic $c/c_0 - D/D_m$ curve is very similar to that of the sample is obtained.

In such way, the sample is fractionated theoretically in n fractions, each of which has arbitrary weight fraction c_i and concentration coefficient c_0k_i.

Theoretical Example

The accuracy of the new analytical method is checked by three theoretical examples. Computer FACOM 230-25/35 in KANAZAWA University is used for calculation.

Each example is composed of 10 fractions as shown in Tables 1, 2 and 3. The distribution function of example 1 is resembled to Gralén's. Integral distribution of example 2 is linear.

Example 3 has the distribution as same as that of PVAc–acetone system.

Table 1 Components of theoretical example 1

D_i	0.06	0.10	0.13	0.16	0.20	0.25	0.31	0.42	0.60	1.0
c_i	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
c_0k_i	4.07	2.55	1.91	1.36	1.02	0.83	0.61	0.39	0.20	0.07

Table 2 Components of theoretical example 2

D_i	1	2	3	4	5	6	7	8	9	10
c_i	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
c_0k_i	10	9	8	7	6	5	4	3	2	1

Table 3 Components of theoretical example 3

D_i	1.73	2.13	2.44	2.84	3.27	3.72	4.44	5.85	8.96	13.97
c_i	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
c_0k_i	4.07	2.55	1.91	1.36	1.02	0.83	0.61	0.39	0.20	0.07

Figs. 1, 2 and 3 show the synthetic diffusion curves obtained from above tables and the symmetrized one.

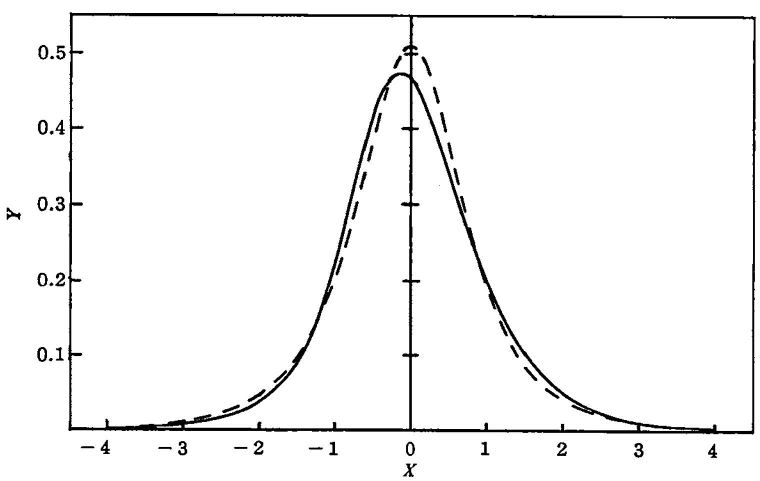

Fig. 1 Original and symmetrized diffusion curve of example 1

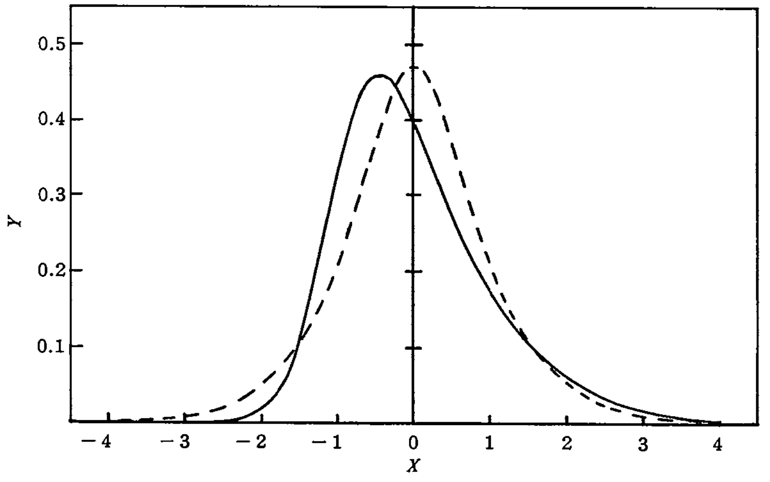

Fig. 2 Original and symmetrized diffusion curve of example 2

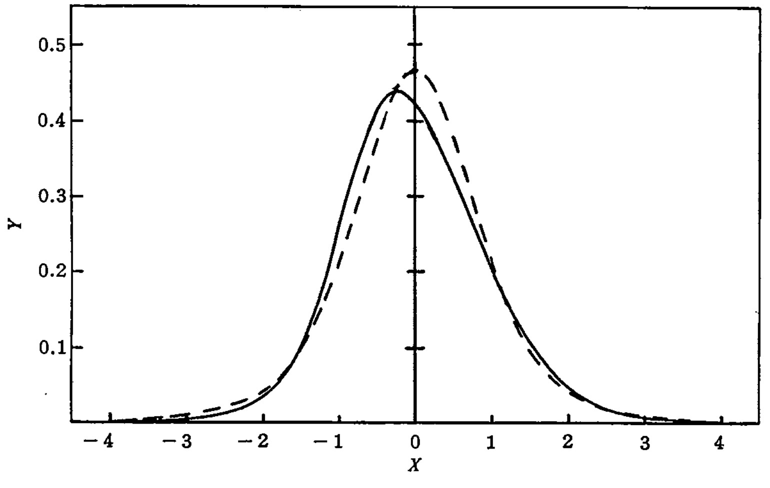

Fig. 3 Oiginal and symmetrized diffusion curve of example 3

The relationship between c/c_0 and D/D_m of these diffusion curves are shown in Fig. 4, 5 and 6, respectively.

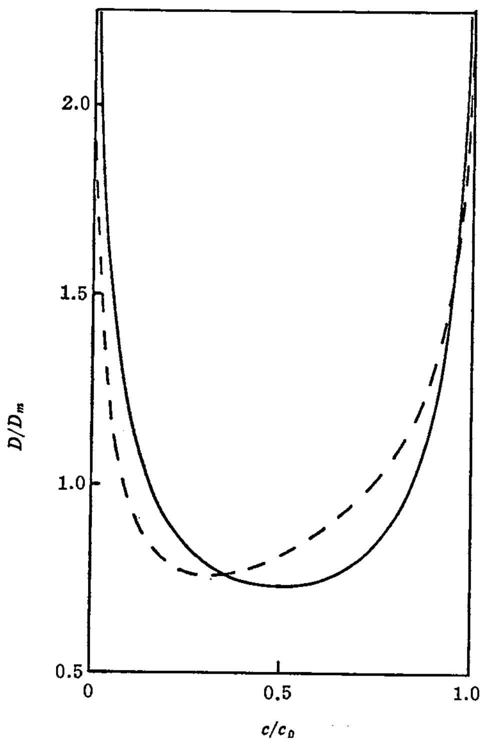

Fig. 4 c/c_0 vs. D/D_m Curve for example 1

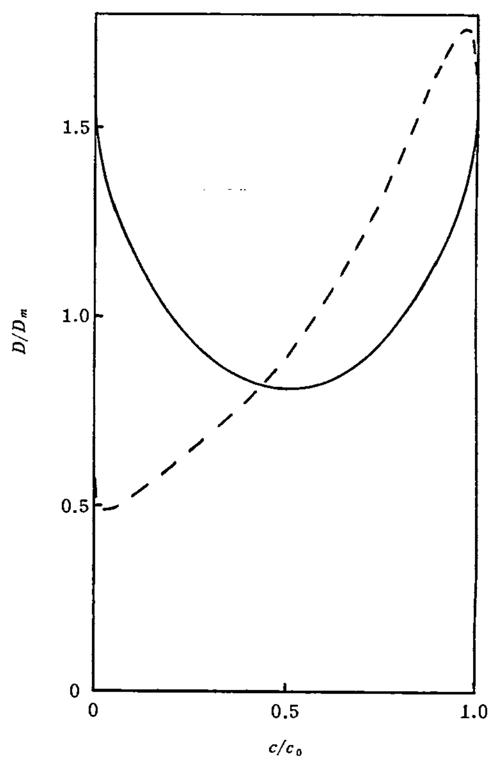

Fig. 5 c/c_0 vs. D/D_m Curve for example 2

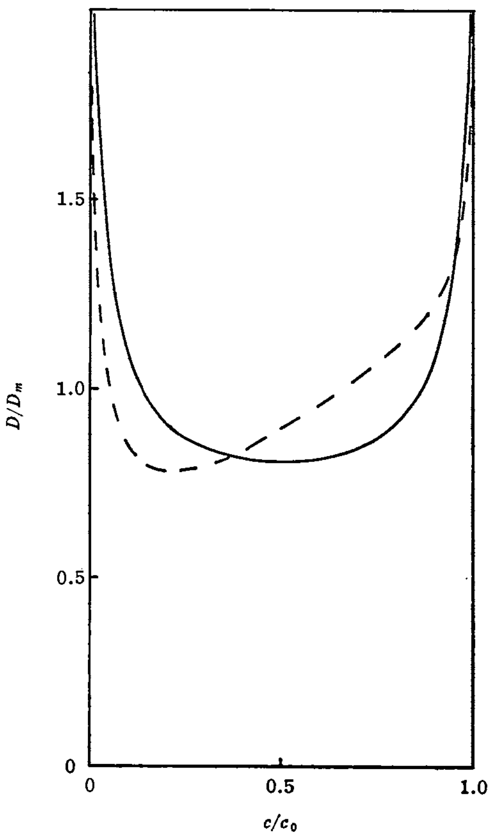

Fig. 6 c/c_0 vs. D/D_m Curve for example 3

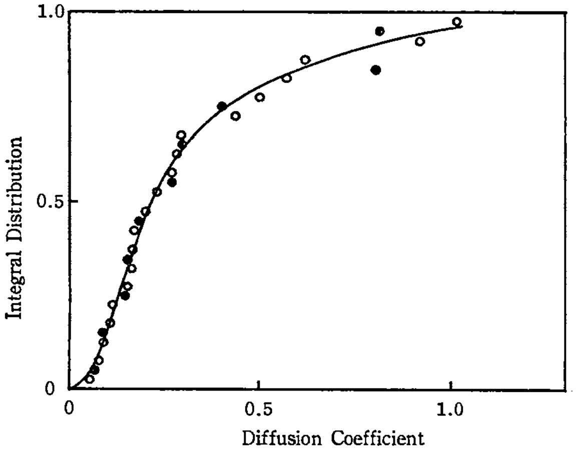

Fig. 7 Distribution of diffusion coefficient of example 1
(circle : analyzed by the new method, solid line : theoretical)

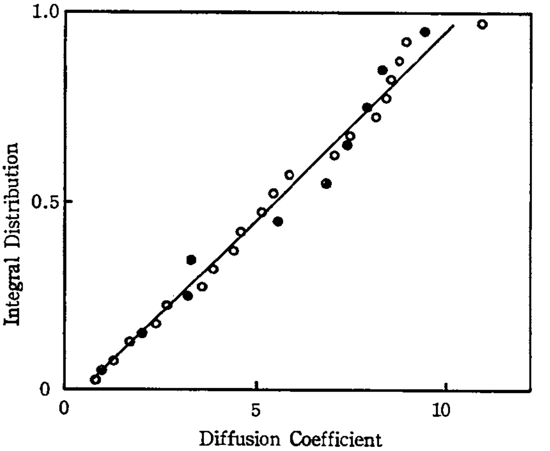

Fig. 8 Distribution of diffusion cofficient of example 2
(circle : analyzed by the new method, solid line : theoretical)

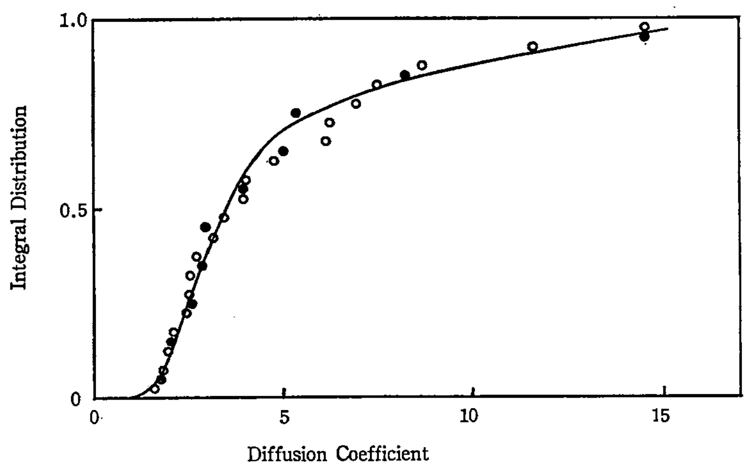

Fig. 9 Distribution of diffusion coefficient of example 3
(circle : analyzed by the new method, solid line : theoretical)

It is obvious from Figs. 7, 8 and 9 that the distributions of the diffusion coefficient calculated by our new method are good agreement with the given distributions.

The concentration coefficient versus the diffusion coefficient are plotted in Fig. 10, 11 and 12.

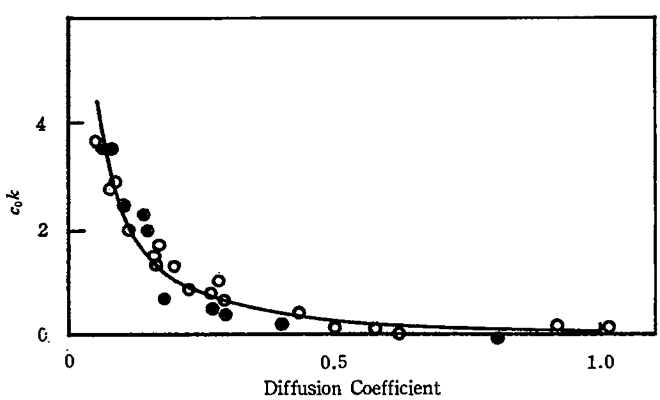

Fig. 10 A plot of concentration coefficient vs. diffusion coefficient for example 1
(circle : analyzed by the new method, solid line : theoretical)

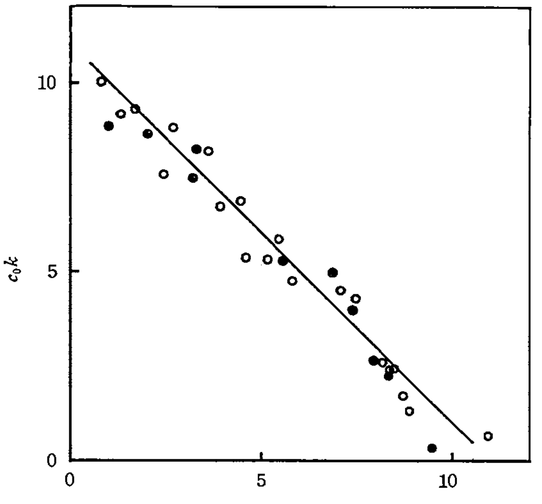

Fig. 11 A plot of concentration coefficient vs. Diffusion coefficient for example 2
(circle : analyzed by the new method, solid line : theoretical)

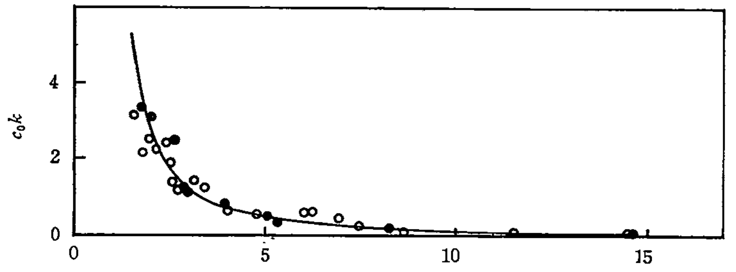

Fig. 12 A plot of concentration coefficient vs. diffusion coefficient for example 3
(circle : analyzed by the new method, solid line : theoretical)

From these results, it is shown that the new method has the high accuracy.

Acknowledgement

The authors are very grateful to the staff of the Computer Center of Kanazawa University.

Reference

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(Recieved Sept. 20, 1972)