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SELF-DIFFUSION OF HYDROCHLORIC ACID IN POLYAMIDE

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Self-diffusion of hydrochloric acid in polyamide was measured by means of radio tracer method. The self-diffusion coefficients depend on the concentration of hydrochloric acid in the polymer substrate. The results can be interpreted by the concentration dependence of the jump distance of the tracer chloride ion.

We have already reported the behaviour of self-diffusion of sulfuric acid anion in nylon-6 [1,2]. The self-diffusion coefficients D* depend on the concentration of the penetrant ion. The results were interpreted by the presence of both bisulfate and sulfate ions as the diffusing entities [3,4]. Marshall [4] reported the constant self-diffusion coefficient of bromide ion in nylon 66. Hayashi [5] measured the D* of chloride ion in nylon at 33° C and found the values of 0.120 X 10^{-9} and 0.176 X 10^{-9} $cm^2 \cdot sec^{-1}$ from the hydrochloric acid solution of 10^{-2} and 10^{-3} mol. l^{-1}, respectively.

In this work hydrochloric acid was used as a penetrant to elucidate the mechanism of self-diffusion more clearly. D* was determined by the same method reported earlier[2]. The polyamide (nylon-6) film was prepared by Tokyo Kakō Sangyo Co. and had the following properties: thickness, 30μ; crystalinity, 41.2% ; amino end-group content, 4.03×10^{-2} $meq.g^{-1}$; $\bar{M}v$, 2.40×10^4. The film roll was dipped into and aqueous hydrochloric acid solution containing an appropriate amounts of tracer Cl^-(Cl-36, $\tau = 2 \times 10^5$ y., β^- 0.714 Mev), and kept constant temperature (± 0.1° C) for diffusion. Before dipping, the film was kept to equilibrium in a solution of the same composition as the following diffusion experiment except the tracer ion. After finishing the diffusion experiment, the radio activity of each layers of the unrolled film was determined by Geiger Muller counter. An example of the concentration profile in the self-diffusion was shown in Fig.1. C/Co in the figure is the relative

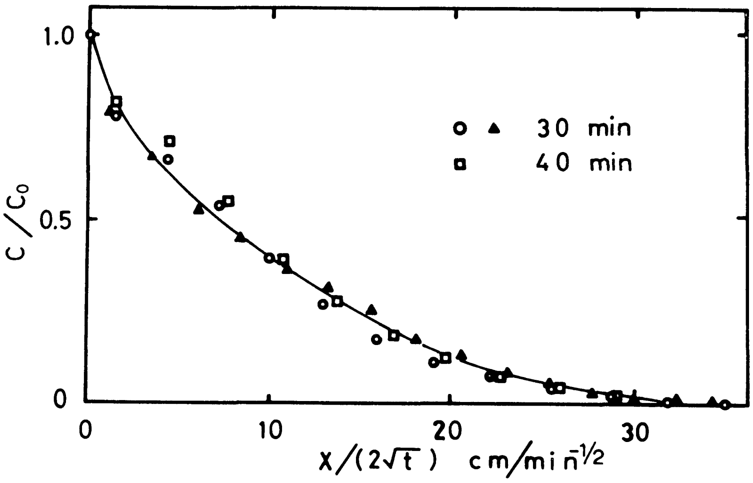

Figure 1. Concentration profile of Cl-36 (70° C, pH 3.00)

concentration to the surface concentration of Cl^-.

D* was calculated from the concentration profile by the method described earlier 6) as a constant irrespective of the distance, x , from the surface of the polymer. Degree of saturation of chloride anion to the total cationic site in polyamide was determined by the adsorption isotherm 7). The dependence of the D* on the degree of saturation was clearly observed in Table 1. The same pattern was also found in the case of ethanesulfonic acid as a penetrant 8).

Table 1. Concentration dependence of self-diffusion coefficient of chloride ion (70° C)

pH	4.00	3.60	3.00	2.77
Degree of saturation	0.189	0.402	0.750	0.820
$D^* \times 10^6 (cm^2 min^{-1})$	2.40	2.69	2.92	3.13

It is suggested that as the concentraion of the penetrant increases the distance between sites which must travel will decrease. The decrease of the distance will cause the greater probability to jump from one site to the adjacent site, resulting the increase of diffusion coefficient. Quantitative discussion will be published later.

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