Diffusion and Adsorption of a Model Cationic Dye, *m*-Nitrobenzylamine, in Polyacrylonitrile

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A model cationic dye, *m*-nitrobenzylamine (NBA), was synthesized, and the diffusion and adsorption behavior in polyacrylonitrile was investigated by the cylindrical film roll method. pK_a of NBA was determined spectroscopically to be 9.2 at 25 °C. The diffusion was concentration dependent and was described by the chemical potential gradient model. The temperature dependence of the diffusion coefficients above T_g, which was found to be 65 °C from the inflection point of Arrhenius plot, could be described by WLF equation, where C_1^g and C_2^g are 1.64 and 17.09 (deg.) at pH 4.2, and 2.41 and 33.11 (deg.) at pH 6.8, respectively. Adsorption isotherm of NBA was obtained at 95 °C and pH 1.5, 4.2 and 6.8. The adsorption of NBA, bis(*m*-nitrobenzyl)amine and Malachite Green at pH 4.2 and those of NBA and bis(*m*-nitrobenzyl)amine at pH 6.8 were more or less the same. It is concluded that the adsorption of cationic compounds on polyacrylonitrile is virtually dependent upon the ion exchange mechanism. But the presence of sodium chloride in the dye bath did not change the adsorption of NBA at pH 4.2 and 95 °C. The surface concentration of NBA was gradually increased with rise of temperature at pH 1.5, 4.2 and 6.8.

In previous papers, the diffusions of Malachite Green, a model cationic dye, *i.e.*, bis(*m*-nitrobenzyl)-amine and some model disperse dyes in polyacrylonitrile were investigated in detail.[1–4] The model cationic penetrant was synthesized to give a general view of dyeing of polyacrylonitrile. A comparison was made between the diffusion behavior of Malachite Green and bis(*m*-nitrobenzyl)amine. In both the cases the profiles as cationic penetrants were shown to be non-Fickian. It should be noted that the experimental concentration profiles of Malachite Green at pH 4.2 was described by chemical potential gradient model without any modification. But in the case of bis(*m*-nitrobenzyl)amine, the Fickian and non-Fickian diffusions were observed because it behaved simultaneously as both ionic and non-ionic penetrants. In this connection, a cationic compound having higher pK_a value than that of bis(*m*-nitrobenzyl)amine may be much better model penetrant.

Temperature dependence of diffusion and surface concentration was investigated with Malachite Green but no experiment with the variation of pH except at pH 4.2 was possible. On the other hand, diffusion and surface concentration experiments with variation of pH were carried out with bis(*m*-nitrobenzyl)amine only at 95 °C. The results obtained in both the cases of Malachite Green and bis(*m*-nitrobenzyl)amine differed in some aspects from those of the former workers in this field.[5–9] Besides different opinion and experimental data, new aspects of kinetics and equilibria in polyacrylonitrile were also revealed which need further verification and confirmation by experiments and discussion. Thermal properties, *i.e.*, glass transition temperature and the value of constants in the WLF equation were found to vary widely from the value of original WLF equation and that of Rosenbaum.[7] Again surface concentration, instead of decreasing, increased with rise of temperature. Different assumptions were made to explain the data. It is therefore desirable that in order to establish the generality of the conclusions, confirmatory experiments should be done with a better model compound, which may provide a comprehensive description of dyeing of polyacrylonitrile. With this purpose the present paper is aimed at synthesizing a suitable compound, *m*-nitrobenzylamine, to carry out the experiments of diffusion and equilibrium adsorption. Wide range of temperature and pH are taken to study the diffusion and thermal properties of polymer.

Experimental

Polymer: The polymer was the same polyacrylonitrile film that was prepared in the previous papers.[3] *Penetrant:* The penetrant, *m*-nitrobenzylamine hydrochloride, was synthesized by Gabriel method[10] with some modifications. The *m*-nitrobenzylamine produced was extracted by ether, dry potassium hydroxide was added to the extracted solution and kept overnight to absorb water in solution. It was then filtered. The ether was removed by distillation and finally completely by vacuum. Yellowish *m*-nitrobenzylamine was obtained in liquid state which was dissolved in benzene and then dry HCl gas was passed through, white precipitate of *m*-nitrobenzylamine hydrochloride was obtained instantaneously, which on crystallization from water gave the product (mp 228.5—229.0 °C). Found: N, 15.0; Cl, 18.8%. Calcd for $C_7H_9N_2O_2Cl$: N, 14.9; Cl, 18.8%. pK_a was determined spectroscopically and found to be 9.2 in water at 25 °C. pH of the solution was adjusted by HCl and CH_3COONa keeping ionic strength constant (I=0.1). *Diffusion and Adsorption:* The diffusion experiments were carried out with the concentration of 0.05 g/50 ml bath at pH 1.5, 4.2 and 6.8 with HCl–CH_3COONa buffer (I=0.1) over the temperature range between 55 and 95 °C. The equilibrium adsorption experiments were carried out at 95 °C and pH 1.5, 4.2 and 6.8 in 50 ml diffusion bath. Three different concentrations of 0.05 g/50 ml, 0.1 g/50 ml and 0.2 g/50 ml were taken. The values of equilibrium adsorption C_s were obtained from the surface concentration of respective diffusion experiment. The absorption spectra of solution and dyed film were measured by a Shimadzu SV-50A recording spectrophotometer.

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Results and Discussion

Diffusion. At pH 1.5 due to the low surface concentration the suitable concentration/distance curve for calculation of diffusion coefficient was not obtained. The distribution profiles C/C_s *vs.* $x/2\sqrt{t}$ of *m*-nitrobenzylamine in polyacrylonitrile at 95 °C and pH 4.2 is shown in Fig. 1, where C is the concentration, C_s, the surface concentration, x, the distance, and t, the diffusion time. Diffusion coefficients in respective cases were calculated by Matano's method. D *vs.* C/C_s $(=\theta)$ plots were shown in Fig. 2. The concentration dependence of diffusion coefficients in both the cases was well described by the chemical potential gradient model as in the case of Malachite Green.[1)]

The diffusion coefficients and surface concentrations for different temperatures from 55 to 95 °C were shown in Arrhenius plots of log D_0 *vs.* $1/T$ (Fig. 3). The results shown the inflection points in both pH 4.2 and 6.8 at 65 °C which may be assigned as the glass transition temperature of polyacrylonitrile during diffusion with *m*-nitrobenzylamine just as in the case of Malachite Green and model disperse dye penetrants.[1–4)] The transition point during diffusion with Malachite Green in the same polymer was 80 °C. The difference may be explained by the larger size of the penetrant, which requires much energy than that required for a small size molecule like *m*-nitrobenzylamine. The occurence of the transition point at the same temperature for pH 4.2 and 6.8 was shown in Fig. 3. The ionic character of the penetrant is not changed at pH 4.2 and 6.8 due to high pK_a $(=9.2)$ but the ionic character of the polymer is changed. At pH 4.2 sulfonate end group completely and weak acidic groups, carboxyl end group, partly are ionized in polyacrylonitrile, while at pH 6.8 the weak acidic groups including strong sulfonate end groups are all completely ionized. It was already shown in previous paper with bis(*m*-nitrobenzyl)amine, from the dependence of the surface concentrations on the pH of the dye bath.[4)] Thus pH of dye bath was found to be meant for the availability of the acidic groups in polymer to cationic penetrant. The appearence of the transition point in both the cases of pH 4.2 and 6.8 at the same temperature may be explained in the

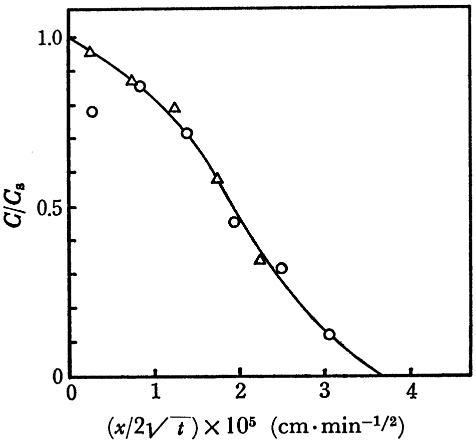

Fig. 1. Diffusion profile of *m*-nitrobenzylamine. 95 °C; pH 4.2; concentration 1.0 g/l; ○: 39 hr, △: 48 hr

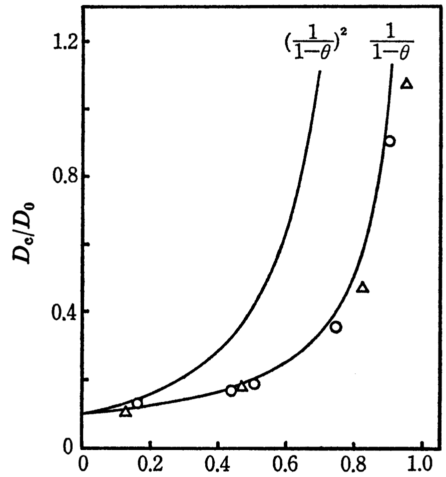

Fig. 2. Relative diffusion coefficients of *m*-nitrobenzylamine at 95 °C.
○: pH 6.8, △: pH 4.2

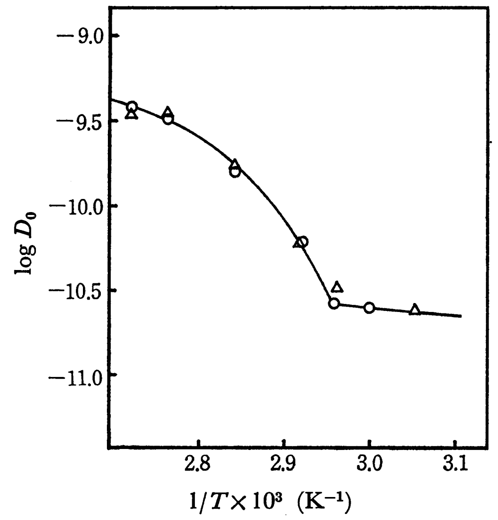

Fig. 3. Arrhenius plot of diffusion coefficients D_0 of *m*-nitrobenzylamine into polyacrylonitrile at pH 4.2 and 6.8.
○: pH 6.8, △: pH 4.2

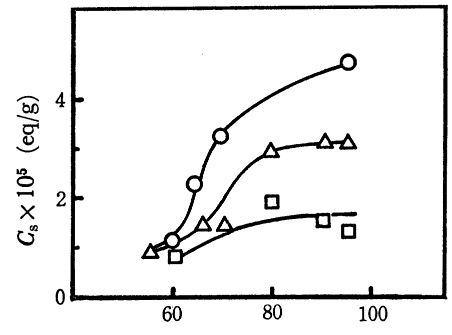

Fig. 4. Surface concentration of *m*-nitrobenzylamine at various temperatures.
○: pH 6.8, △: pH 4.2, □: pH 1.5

way that below T_g in both pH 4.2 and 6.8 only sulfonate end groups of polymer are concerned in diffusion. In Fig. 4 the variation of surface concentration with temperature is found to be of same pattern as in the case of Malachite Green above T_g.[1)] A little difference is observed in the pattern below T_g where in the case of Malachite Green, the surface concentrations are almost constant, but in the case of *m*-nitrobenzylamine gradual increase with rise of temperature which is similar in shape as in the case of *m*-nitroaniline.[3)]

As in the case of Malachite Green the diffusion behavior above T_g was applied to the general form of WLF equation. The constants C_1^g and C_2^g were calculated by least square method and found to be 1.64, 17.09 (deg.) for pH 4.2 and 2.41, 33.11 (deg) for pH 6.8, respectively.

The good fit of WLF equation with diffusion behavior above T_g in both pH 4.2 and 6.8, confirms the fact that the diffusion in polyacrylonitrile is governed by the segmental motion of the polymer, which sets in at T_g. The result is in agreement with those of Rosenbaum[7–9)] and in previous papers.[1–4)] The physical significance of the constants C_1^g and C_2^g of WLF equation from diffusion experiments with those of Malachite Green and *m*-nitrobenzylamine is not yet clear. As mentioned in the previous papers that the constant C_1^g is directly related with fractional free volume f_g at T_g, and C_2^g with f_g as well as $\Delta\alpha$, the difference of thermal expansion coefficient above and below T_g.[3)] The different values of C_1^g and C_2^g for different penetrants in the same polymer may be reasonable, but the proper explanation and theoretical treatment has not yet been made.

Equilibrium. Surface concentration from the diffusion experiments carried out at 95 °C and pH 1.5, 4.2 and 6.8, were used for adsorption isotherm plot. The plot of C_s *vs.* dye bath concentration was shown in Fig. 5. The reciprocal plots, by Eq. (1), which were all straight lines were in Fig. 6.

$$\frac{[D]_\phi}{[D]_\sigma} = K_L([S]_\phi - [D]_\phi) \qquad (1)$$

In Eq. (1), $[D]_\phi$ and $[D]_\sigma$ denote the dye concentration on fiber and that in the dyebath, K_L, Langmuir constant, and $[S]_\phi$, the site content in the fiber.

It was found that same results were obtained for different cationic penetrants. So it may be concluded that the adsorption of cationic penetrants is adequately described by Langmuir isotherm, which may be superimposed by constant partition isotherm or Freundlich isotherm dependent upon penetrant as in the case of bis(*m*-nitrobenzyl)amine. It is found from the results of Malachite Green, bis(*m*-nitrobenzyl)amine and *m*-nitrobenzylamine at pH 4.2 and 6.8 that the uptake of these three compounds at pH 4.2 and those of bis(*m*-nitrobenzyl)amine and *m*-nitrobenzylamine at pH 6.8 are more or less the same.[1–4)] As regards to the dyeing of polyacrylonitrile especially with cationic dye, important aspect is the ion exchange phenomenon. Rosenbaum showed the increase of equilibrium uptake which shows virtually no ion exhange mechanism in polyacrylonitrile dyeing.[11)]

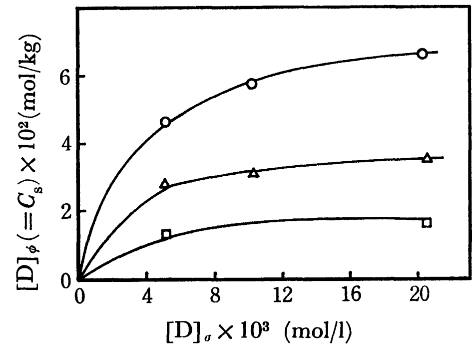

Fig. 5. Adsorption isotherms of *m*-nitrobenzylamine at 95 °C.
○: pH 6.8, △: pH 4.2, □: pH 1.5

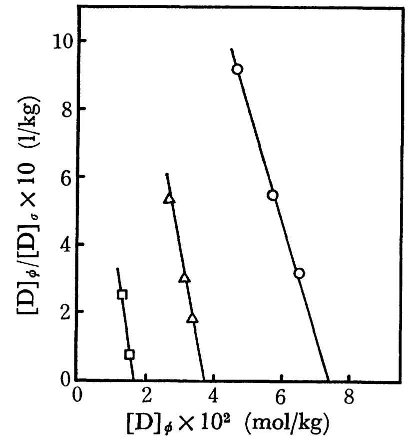

Fig. 6. Reciprocal plots of Fig. 5 by Eq. (1).
○: pH 6.8, △: pH 4.2, □: pH 1.5

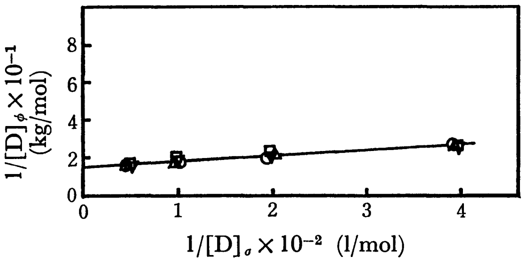

Fig. 7. Adsorption isotherm of *m*-nitrobenzylamine at 95 °C and pH 4.2 in the presence of NaCl.
○: 0 g, △: 0.4 g/l, ▽: 2.5 g/l, □: 4.0 g/l

In the series of these experiments, however, it is concluded that the adsorption of cationic compounds on polyacrylonitrile is nearly equal to the anionic site in the polymer available at that pH. No adsorption more than the anionic site in the polymer could be observed except the case such as bis(*m*-nitrobenzyl)amine where the non-ionic species coexisted in the dyebath and were also adsorbed by the substrate.

On the other hand Sand, Glenz *et al.*, and Harwood *et al.* showed the decrease of the uptake by the addition of salt in the dye bath.[5,12,13)] In this paper, an attempt was made to study the problem by the addition of sodium chloride in the bath. As is shown in Fig. 7, no change of equilibrium was detected. The adsorption of cationic compounds will be due to the salt formation or ion exchange and non-ionic interaction of ionic species also due to the non-ionic adsorption of non-ionic species. The addition of salt will influence the salt formation and increase the non-ionic interaction and the formation of non-ionic species in the dyebath. In the series of these experiments, the salt addition was considered to bring about no influence on the salt formation and no change of the non-ionic species.

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