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ACTIVATION VOLUME FOR THE DIFFUSION OF DYE MOLECULE IN POLY(ETHYLENE TEREPHTHALATE)*

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Synopsis

Pressure effect on the diffusion coefficient D of nine disperse dyes in poly(ethylene terephthalate) (PET) sheet was investigated at 130°C under pressures up to 1 kbar by the multiple membrane method. The values of $\ln D$ showed linear decrease with increasing pressure, giving the activation volume $\Delta V^\ddagger$ for diffusion, 64–123 cm³/mol for p-nitroaniline (pNA) and C.I. Disperse Blue 1 (DB1), respectively. The molecular volumes of the penetrants in crystalline state were evaluated from the density measurements, x-ray data and the van der Waals contact models of the molecules. For example, the molecular volumes of pNA and DB1 were 99 and 182 cm³/mol, respectively. The results of $\Delta V^\ddagger$ were now compared with the molecular volumes of the penetrants. It was found that $\Delta V^\ddagger$ increased almost linearly with increasing molecular volume. It was further demonstrated that the anthraquinone derivatives needed larger $\Delta V^\ddagger$ than the azo derivatives compared at the same molecular volume. These as well as the differences between the observed $\Delta V^\ddagger$ and the molecular volumes of the penetrants were discussed from the viewpoint of the free volume theory.

INTRODUCTION

The activation volume $\Delta V^\ddagger$ for the diffusion of dye in a polymeric solid can be obtained^{1–3}) by measuring the effect of hydrostatic pressure (P) on the diffusion coefficient (D) of the dye molecule (penetrant molecule) according to

$$\Delta V^\ddagger = -RT (\partial \ln D / \partial P)_T, \quad (1)$$

where R and T are the gas constant and absolute temperature, respectively. In application of eq. (1) to a system composed from a dye dissolved in water (solvent) plus a polymeric solid material, $\Delta V^\ddagger$ may be written as

$$\Delta V^\ddagger = \Delta V_{EH}^\ddagger + \Delta V_D^\ddagger + \Delta V_P^\ddagger + \Delta V_S^\ddagger, \quad (2)$$

where $\Delta V_{EH}^\ddagger$ is the positive local volume change⁴⁾ allowing accommodation of the diffusing penetrant which results from fluctuation of the Eyring's hole (EH), $\Delta V_D^\ddagger$, $\Delta V_P^\ddagger$ and $\Delta V_S^\ddagger$ are the associated changes of the partial volumes occupied by, respectively, the penetrant, the polymer and the

solvent in the swollen polymer matrix. Such local volume changes are referred only to those that are involved in the diffusion of the penetrant, based on one mole of the penetrant. Since the primary step in the dye diffusion in a solid or in a quasi-crystalline liquid can be imagined^{2,5–6)} to proceed through the displacement of a penetrant from a normal adsorbed site into a high energy hole, the rate of the process will be governed by the ease with which the EH's can be formed. If the EH formation is assumed to be the rate-determining process, then $\Delta V^\ddagger$ in eq. (2) is approximated by

$$\Delta V^\ddagger = \Delta V_{EH}^\ddagger. \quad (3)$$

From eq. (3), it is expected that larger dye molecule needs larger $\Delta V^\ddagger$ and suffers larger pressure effect, because larger penetrant requires larger EH for accommodation. The purpose of the present paper is to refer $\Delta V^\ddagger$ obtained by eq. (1) to the molar volume of the penetrant (V) and to clarify the relationship between them.

For the purpose of introducing eq. (1) into the present study, the followings are desirable to be taken into account. First, the $\Delta V^\ddagger$ obtained from

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eq. (1) is dependent on the free volume initially present in the polymer matrix^{1,3,7}). This is because the activation volume gives the excess free volume of the transition state over the free volume present in the initial state, considered within the range of the local volume⁸⁻⁹). It is evident that both the $\Delta V^\ddagger$ and the initial free volume contribute without distinction to the formation of the EH for accommodating the diffusing penetrant, whether or not the free volume was initially present or formed at the activated state. In order to minimize the swelling by water and thus the contribution by the initial free volume which will leave more or less ambiguous room in correlating $\Delta V^\ddagger$ with V of the penetrant, it is necessary to use a hydrophobic polymer material such as polyethylene, PET, etc. Secondly, the penetrant substance should also be hydrophobic which makes special bonds such as electrostatic-, hydrogen- and coordination-bonds, etc. with the polymer molecule as least as possible. This is for minimizing the contributions from the terms $\Delta V_D^\ddagger$, $\Delta V_P^\ddagger$ and $\Delta V_S^\ddagger$ which have been neglected in obtaining eq. (3). The above situation led us to study the diffusion of various disperse dyes in PET at 130°C under high hydrostatic pressure.

EXPERIMENTAL

A PET sheet supplied by courtesy of Toray Industries, Inc. (grade #6) was used. This is the same sample as was used in a previous paper¹). The sheet was heat-treated in water at 160°C for an hour in the same way as previously described. The density of the heat-treated and dried sample was 1.408 g/cm³ at 30°C and the thickness in the wet state was 6.3 μ m. For the penetrants, p-nitroaniline (pNA), p-aminoazobenzene (pAAB), 4'-nitro-4-dimethylaminoazobenzene (4'-N-4DMAAB), C.I. Disperse Orange 1 (DO1), C.I. Disperse Red 7 (DR7), 1-aminoanthraquinone (1AA), C.I. Disperse Red 15 (DR15), C.I. Disperse Violet 1 (DV1) and C.I. Disperse Blue 1 (DB1) were used. Among these, pNA, pAAB, 4'-N-4DMAAB, 1AA, DR15 and DV1 were commercial grade chemical reagents, while DO1, DR7 and DB1 were kindly supplied in the form of color cake by Mitsubishi Kasei Kogyo Co. These penetrant samples were purified by repeated recrystallizations to give single crystals in size which enabled density measurement by

floating method. Melting points were determined on a Yanagimoto Model MP-S3 micromelting apparatus. Table I includes these characterizations. Aqueous solutions of the penetrants were prepared according to the last column of Table I. For pNA and pAAB, the crystals were completely dissolved in water to give solutions at room temperature. For the other crystals, the listed recipe was above the saturation and the undissolved crystals remained during the experiment. The measurement of D of the penetrant in the PET sheet was carried out at 130°C under high pressures up to 1 kbar by the use of the multiple membrane method. The apparatus, the experimental procedure and the analysis by Matano's formula have been described in detail in the previous paper^{1,7}). The accurate determination of the diffusion time was successful by the method described in Figure 1 of ref. (7) where the polypropylene tube was not used in the present study.

by the use of Matano's multiple membrane method. The apparatus and the experimental procedure have been described in detail in the previous paper¹).

THE VOLUME OF THE PENETRANT MOLECULE

In order to evaluate V of the penetrant, the molar volume in the crystalline state was used¹). According to whether the crystalline density was supplied by dilatometry or from the x-ray unit cell dimension, V_ρ or V_x can be calculated for V by, respectively,

$$V_\rho (\text{cm}^3/\text{mol}) = M/\rho \quad (4)$$

$$V_x (\text{cm}^3/\text{mol}) = 0.6022 v/Z, \quad (5)$$

where M is the molecular weight, ρ the CGS dilatometric density, v the volume of the unit cell expressed in $\text{\AA}^3$, Z the number of the molecules contained in the unit cell. The crystal structures determined by x-ray analysis, by themselves, have been so determined that the data of v and Z were compatible with the dilatometric density.

It is the real situation, however, that one has often to use a dye having known chemical constitution for which neither V_x nor V_ρ is available. In this case, some conventional method was necessary to evaluate V . This was settled by the

Table I Characterization of disperse dyes

Disperse dyes (Abbreviation)	Chemical constitution	m.p. (°C)	Density at 30°C (g/cm ³)	Preparation of the aq. solution (mg/l)
p-Nitroaniline (pNA)		145	1.395	800
p-Aminoazobenzene (pAAB)		127	1.196	20
4'-Nitro-4-dimethyl- aminoazobenzene (4'-N-4DMAAB)		235	—	(50)
C.I. Disperse Orange 1 (DO1)		162	1.325	(50)
C.I. Disperse Red 7 (DR7)		192	1.461	(50)
1-Aminoanthraquinone (1AA)		250	1.434	(50)
C.I. Disperse Red 15 (DR15)		219	1.487	(50)
C.I. Disperse Violet 1 (DV1)		267	—	(50)
C.I. Disperse Blue 1 (DB1)		> 300	—	(50)

V_w as described in the following. It is well known that the dye molecule is very often a flat molecule because of the network of the conjugated chain within it. Neglecting the effect of the thicker knobs due to sulfonic anions ($-\text{SO}_3^-$) in some cases, the volume of a dye molecule may approximately be given by the area of the silhouette (A_w) of the flat molecule multiplied by the thickness. because of the network of the conjugated double bonds chain within it. Neglecting the effect of the thicker knobs due to sulfonic anions ($-\text{SO}_3^-$) in some cases, the volume of a dye molecule may approximately be given by the area of the silhouette (A_w) of the flat molecule multiplied by the thickness. This volume, converted to the value per mole of the molecule, was defined as V_w . The silhouette This volume, converted to the value per mole of the molecule, was defined as V_w . The silhouette can be drawn by making the van der Waals (vdW) contact model of the molecule according to the description by Kitaigorodskii¹⁰, while the thickness, in the case of dye molecule, may be roughly put equal to the thickness of the benzene ring¹¹, i.e. 3.70 Å. The silhouettes of some twenty

aromatic compounds selected from the textbook by Kitaigorodskii¹⁰ which are essentially similar in the structure to the dye molecule were drawn as shown in Figure 1 in which examples for trans-azobenzene and anthraquinone were given. A_w for the silhouette was calculated by dividing it into several simple geometrical figures. In Table II were listed V_x and V_w for those aromatic compounds for which the x-ray data, including bond-lengths and bond-angles, were all available¹⁰. Here the V_w was obtained from eq. (6),

$$V_w (\text{cm}^3/\text{mol}) = N_A (3.49 \times A_w), \quad (6)$$

where N_A is the Avogadro number and the volume term in the right hand side, $3.49 \times A_w$, was expressed in cm^3 . In eq. (6), a value of 3.49 Å instead of 3.70 Å was used for the thickness, because the latter value was found to be a little too much overestimated to obtain V_w which agrees with V_x . The relationship between V_w and V_x for the above aromatic compounds was given in Figure 2 where the points of V_w are seen to come on the 45° line of $V_w = V_x$. From Figure 2, it is justifiable that the volume of a dye molecule

Fig. 1 Drawing of the silhouettes of the van der Waals contact model for trans-azobenzene (a) and anthraquinone (b). All the data for the bond-lengths, bond-angles and the van der Waals radii were referred to Kitaigorodskii¹⁰).

Fig. 2 Plots of V_W vs. V_x . The solid line indicates 45° line.

Table II Twenty aromatic compounds selected from Kitaigorodskii¹⁰) having similar structures to the disperse dye for the purpose of examining relationship between V_W and V_x . A_W denotes the area of the silhouette of the flat van der Waals contact model of the molecule.

No.	Compound	M.W.	V_x (cm ³ /mol)	A_W (Å ²)	V_W (cm ³ /mol)
1	p-Benzoquinone	108.10	81.4	37.1	78
2	p-Dimethoxybenzene	138.17	114.4	50.6	106
3	p-Toluidine	107.16	94.9	45.2	95
4	p-Dinitrobenzene	168.11	101.8	49.6	104
5	m-Dinitrobenzene	168.11	108.6	49.6	104
6	Diphenyl	154.21	124.9	62.4	131
7	p-Diphenylbenzene	230.31	185.0	89.8	188
8	p,p'-bis-(Phenyl)-diphenyl	306.41	238.4	117.1	246
9	Stilbene	180.25	154.1	72.9	153
10	trans-Azobenzene	182.23	148.6	70.0	147
11	cis-Azobenzene	182.23	149.2	70.0	147
12	Naphthalene	128.17	108.2	50.9	107
13	α-Naphthol	144.17	112.0	53.6	112
14	β-Naphthol	144.17	111.7	53.6	112
15	1,5-Dinitronaphthalene	218.17	133.6	62.5	131
16	Anthracene	178.23	142.8	67.8	142
17	Anthraquinone	208.22	146.8	69.7	146
18	1,2,5,6-Dibenzanthracene	278.35	213.4	99.1	208
19	p-Nitroaniline	138.12	96.5	47.2	99
20	p-Aminoazobenzene	197.23	162.1	75.4	158

for which both V_ρ and V_x are unknown can safely be estimated from their V_W 's, so long that the molecule is decorated with not many side groups and flexible bridges. In Figure 3 were drawn the silhouettes of the vdW model for the penetrants used in the present work, where, for DR7, the two $-\text{CH}_2-\text{CH}_2-\text{OH}$ side groups were not drawn and, instead, the volume increments¹⁰⁾ due from four CH_2 groups ($16.6 \text{ \AA}^3$ per CH_2) and two OH groups ($10.7 \text{ \AA}^3$ per OH) were added to obtain V_W . In Table III, the V_W 's obtained from Figure 3 were compared with V_ρ 's for those penetrants whose densities were successfully known from the density measurements of the single crystals. A good agreement within 3% was found between V_W and V_ρ . The reason for the discrepancy (9%) found for DR7 is not very clear, but it is likely that the two tails of the $-\text{CH}_2-\text{CH}_2-\text{OH}$ groups reduce the packing efficiency in the crystal structure of DR7 which causes larger V_ρ . In the present paper, V_W will be used in preference to both V_x and V_ρ from the viewpoint to give consistency throughout the discussion.

It is worthwhile giving a comment here that the net volume of the vdW contact model of a molecule is related with V_x , V_ρ or V_W through the packing density k defined by the relationship,

$$k = (\text{the total volume of the vdW contact models of the } Z \text{ molecules})/v. \quad (7)$$

Since the values of k for most organic molecular crystals range¹⁰⁾ between 0.7 and 0.8, V_x , V_ρ or the above estimated V_W is larger by 20–30% than the net vdW contact model of the molecule. The excess volume is the dead space which arises when the molecules are packed in the crystalline state.

RESULTS AND DISCUSSION

The diffusion profile for DB1 in PET sheet obtained at 130°C and 800 bar was shown as an example in Figure 4. The D -value was calculated¹²⁾ by Matano's method as a function of the relative concentration $C = c/c_0$, where c and c_0 are the concentrations of the adsorbed dye at the surface and at the depth x from the surface, respectively. Except for the steep increase of D seen at high C region, D remains almost constant with the variation of C . The reason for the increase of D at $C > 0.8 \sim 0.9$ was ascribed in the previous

Fig. 3 The silhouettes of the van der Waals contact model for the nine penetrants used in the present study. The data for constructing the model were the following¹⁰⁾. Van der Waals radii (r): $r_C = 1.8 \text{ \AA}$, $r_H = 1.17 \text{ \AA}$, $r_O = 1.36 \text{ \AA}$, $r_N = 1.57 \text{ \AA}$, $r_{Cl} = 1.78 \text{ \AA}$. Bond lengths: C–C (aromatic ring) = $1.4 \text{ \AA}$, C–N (aromatic) = $1.43 \text{ \AA}$, C–N in the amino group bonded directly to the aromatic ring = $1.37 \text{ \AA}$, N–H = $1.02 \text{ \AA}$, N=O (nitro) = $1.24 \text{ \AA}$, C–Cl = $1.7 \text{ \AA}$, N=N = $1.25 \text{ \AA}$, C=O (quinone) = $1.15 \text{ \AA}$. An ideal angle of 120° was used for all the bond angles. The two $-\text{CH}_2-\text{CH}_2-\text{OH}$ groups were removed from DR7 (see text).

paper¹²⁾ to an artifact due to the inherent character of the exponential function used to fit to the observed points of the profile and seems not essential. As shown in Figure 4, the D value defined at C dividing the area under the diffusion profile into two equal areas by the horizontal line parallel to the distance axis was represented with $\bar{D}$ (given in Figure 4 by the square mark) and will be used in the following discussion. The $\bar{D}$ values in PET sheet at 130°C under various high hydrostatic pressures were listed in Table IV for the

Table III Data for $\Delta V^\ddagger$, atmospheric pressure diffusion coefficient $\bar{D}_0$, A_w , V_w and V_ρ for various disperse dyes

Disperse Dyes	M.W.	$\bar{D}_0$ (10^{-8} cm ² /min)	A_w (Å ²)	V_w (cm ³ /mol)	V_ρ (cm ³ /mol)	$\Delta V^\ddagger$ (cm ³ /mol)
p-Nitroaniline	138.12	32.2	47.2	99.3	99.0	64
p-Aminoazobenzene	197.23	16.8	75.5	158.6	164.9	83
4'-Nitro-4-dimethyl- aminoazobenzene	270.32	3.12	92.8	194.9	—	106
C.I. Disperse Orange 1	318.36	3.20	108.6	228.3	240.3	116
C.I. Disperse Red 7	364.79	1.46	83.5	228.3*	249.7	103
1-Aminoanthraquinone	223.23	6.84	73.6	154.6	155.7	87
C.I. Disperse Red 15	239.23	5.77	76.0	159.8	160.9	110
C.I. Disperse Violet 1	238.25	5.17	77.9	163.7	—	109
C.I. Disperse Blue 1	268.28	2.58	86.6	181.9	—	123

* Volume increments from two $-\text{CH}_2-\text{CH}_2-\text{OH}$ groups were added.Table IV $\bar{D}$ data at 130°C under various pressures

		(a) $\bar{D}$ (10^{-7} cm ² /min)										
		Pressure (bar)										
Penetrant		1.0	98.1	196.1	245.2	294.2	392.3	490.3	735.5	980.7	1225.8	1471.0
pNA		3.22	3.09	2.31	---	1.61	1.56	1.21	0.59	0.41	0.28	0.25
pAAB		1.68	1.36	---	0.93	---	0.60	0.53	---	---	---	---

		(b) $\bar{D}$ (10^{-8} cm ² /min)								
		Pressure (bar)								
Penetrant		1.0	100.0	200.0	300.0	400.0	500.0	600.0	800.0	1000.0
4'N-4DMAAB		3.12	2.01	1.56	1.04	0.91	0.62	---	---	---
DO1		3.20	1.97	1.68	1.10	0.77	0.58	---	---	---
DR7		1.46	1.09	0.97	0.66	0.47	0.38	0.27	0.13	---
1AA		6.84	5.21	3.57	3.44	2.27	1.86	1.49	0.79	0.55
DR15		5.77	---	---	2.34	1.59	1.16	1.01	0.46	0.23
DV1		5.17	4.12	3.43	1.65	1.31	1.05	0.77	0.47	0.21
DB1		2.58	1.51	1.00	---	0.47	---	0.32	0.12	---

nine penetrants. Evidently, the pressure effect on the diffusion of the penetrant in PET was large. It was found that a pressure of 500 bar reduced $\bar{D}$ down to 38% for pNA and 18% for DO1 of the values at the ambient pressure. Such pressure effects are essentially in accordance with the criterion by eq. (1) operating by a positive $\Delta V^\ddagger$. The diffusivity of the penetrant was the most large for pNA whose molecular volume is the smallest among the nine penetrants. As shown in Table III, it is interesting to note that the

value of $\bar{D}$ obtained at atmospheric pressure, denoted with $\bar{D}_0$, decreases with an increase of the molecular volume of the penetrant; particularly, the order of decrease is consistent with the increase of V when the comparison is limited within either of the groups of the azo or the anthraquinone dyes. However, such consistency does not hold when the comparison is made among all the nine penetrants.

In order to evaluate $\Delta V^\ddagger$, $\ln \bar{D}$ for each penetrant was plotted against pressure in Figure 5. In

Fig. 4 Profile of the diffusion of DB1 in PET from aqueous solution at 130°C and 800 bar. The inserted diagram gives dependence of the diffusion coefficient $\bar{D}$ on the relative concentration C where the symbol Δ indicates $C=0.5$. For the symbol $\square$, refer to the text.

spite of the scatter of the points which could not be removed, the results were approximated by linear relationships drawn in Figure 5. Because the free volume in the PET sheet should decrease with increasing pressure, some nonlinear relationship between $\ln \bar{D}$ and P may be expected. If so, the application of eq. (1) which originates from the thermodynamic considerations^{4,9)} should be valid only at $P \rightarrow 0$. However, reviewing all the data in our study which included not only PET but Nylon 6⁹⁾ and regenerated cellulose (cellophane)⁷⁾, no indication for a nonlinear relationship has been found within the experimental error. This is also the case in the study by Assink³⁾ who measured the pressure effect (2000 bar) on the diffusion of dichlorodifluoromethane in poly(dimethyl siloxane) by means of NMR pulsed-field-gradient method. A small, non-negligible curvature might have been masked and missed by the experimental error in our and Assink's studies.

Apart from the above points, $\Delta V^{\ddagger}$'s for diffusion could be obtained from the slopes of the linear lines in Figure 5 by the least squares method and were listed in Table III. In order to see the correlation between $\Delta V^{\ddagger}$ and the volume of the penetrant molecule, $\Delta V^{\ddagger}$ was plotted against V_w

Fig. 5 Plots of $\ln \bar{D}$ vs. pressure for various disperse dyes.

Fig. 6 Relationship between $\Delta V^{\ddagger}$ for diffusion and the molecular volume (V_w) of the penetrant.

in Figure 6. In Figure 6, there may be noted two points; first, $\Delta V^{\ddagger}$ increases with increase in V_w with an apparently linear relationship, and second, the points for the anthraquinone derivatives fell on a line separating from that for the azo derivatives, the slope against increase in V_w in the former being larger than for the latter. These will be discussed in the following.

The fact that $\Delta V^{\ddagger}$ increases with increasing V_w may be self-evident from a simple consideration

that the larger penetrant needs the larger EH. However, the fact that such a simple consideration could be applicable should nevertheless be pointed out here, since it means that the contributions of ΔV_P^* , ΔV_D^* and ΔV_S^* in eq. (2) are not effective, as was assumed in obtaining eq. (3). On the other hand, it is not simple to explain the linear relationships. At first, in Figure 6, one can note the difference along the direction of the ordinate axis from the two solid experimental lines to the dotted line representing $\Delta V^* = V_w$. On the basis of the consideration in one of the preceding sections, these differences should be ascribed to the initial free volume inherently distributed in the solid PET material held in water at 130°C.

Now, let assume, as schematically illustrated in Figure 7, four PET chains, each of which consisted from 1.75 chemical repeating units (19 Å long) along the chain, are associated with the diffusion of one pNA — they are the “neighbors” accommodating one pNA molecule and give the range of the local volume to be used to define ΔV^* . The size of a pNA molecule was evaluated to be 9.5 Å (length) $\times$ 6.5 Å (width) $\times$ 3.7 Å (thickness) from Figure 3 (a), while the PET chains, if aggregated in the crystalline state, have spacing¹³ between their chain-axes ranging from 4.6 to 6.0 Å and length of 19 Å (see above). The spacing between chains will expand to some degree in the noncrystalline region. The illustration of Figure 7 was drawn to scale. The hole drawn with dotted line and viewed along the chain-axis may be justifiable to be of a size that can accommodate one pNA molecule.

Fig. 7 The pNA molecule accommodated in an EH which in turn is surrounded by PET chains, the “effective” neighbors determining local volume expansion during activation for diffusion.

From the above consideration, 1345.1 g of PET, corresponding to 7 moles of the repeating chemical unit, should supply at 130°C the free volume of $V_w - \Delta V^* = 36 \text{ cm}^3$ per mole of pNA as evaluated from Figure 6. It is well known that the WLF relationship predicts 2.5% by volume of free volume at the glass-temperature (T_g) under the atmospheric pressure. Calculated from this prediction, the above weight of PET is estimated to contain about 25 cm³ of free volume at T_g , assuming the density of the noncrystalline PET material to be 1.34 g/cm³¹⁴). According to the recent ¹³C high-resolution NMR studies by Kitamaru and co-workers¹⁵), it was clearly demonstrated that the thermal motion, having the correlation time of 10⁻⁵–10⁻⁶ sec, initiates at 125°C in the phenyl carbon atoms of the noncrystalline PET chain. If this temperature was taken as T_g of PET on one hand, and if its water-induced shift was evaluated to be 20°C from the diffusion study by Dumbleton et al.¹⁶) on the other, and if, further, the difference between the expansion coefficients for the rubbery and the glassy PET's at T_g is assumed⁶) to be 4.8 $\times 10^{-4}$ degree⁻¹, the above weight of PET held in water at 130°C, 25°C above T_g , is calculated to contain about 37 cm³ of the free volume in good agreement with the expected value of 36 cm³. Since, however, T_g depends quite significantly on the method of measurement and, moreover, the model employed in Figure 7 is a crude one and not quantitative, our conclusion obtained above should be regarded as giving an essential support to our scheme of consideration. The linear increase of the ΔV^* with increasing V_w may consequently be understandable if the difference between ΔV^* and the dotted $\Delta V^* = V_w$ line increases linearly with increasing V_w . The latter correlation may be expected because the increase of the longitudinal length of the penetrant molecule requires longer EH for accommodation which has longitudinal length proportional to that of the penetrant molecule. Here the cross-sectional area of the penetrant was assumed to remain constant with increasing molecular length.

It is worth noting that ΔV^* for diffusion as compared at the same molecular volume of the penetrant differs significantly for the azo and the anthraquinone derivatives. This means that not only V , the total volume, but some shape factor

of the penetrant molecules works effective in determining $\Delta V^\ddagger$, provided, of course, any physico-chemical interactions between the penetrant and the macromolecule are tentatively not considered. The molecules of the anthraquinone derivatives listed in Table I are all rigid molecules, having no flexible parts in the structure; the ratios of the length to the width for them are about 3:2. On the other hand, the molecules of the azo derivatives have the azo bridges which are supposed to have flexibility to some extent because the conjugation energy between the azo group and the phenyl rings will not be sufficient to hold the completely flat conformation between the azo group and the phenyl rings¹⁰⁾. The ratio between length and width is more or less larger for the azo derivatives than for the anthraquinone derivatives. The difference between these shape characteristics of the penetrants of the azo and the anthraquinone derivatives suggest that a rigid and "far" penetrant needs larger $\Delta V^\ddagger$ than a flexible and "slim" penetrant compared at the same molecular volume. Probably, such correlation must have regards with the long chain molecules consisting the polymer matrix in which the penetrant molecule diffuses. Since the $\Delta V^\ddagger$, in itself, arises from the effects of pressure and volume, it should not contain any "shape" effect. However, the dead space produced from the packing of the penetrant molecule and the surrounding polymer chains suffers such shape effect. It is likely that the dead space produced from the packing of the penetrant and the long polymer segment will be smaller for the azo derivatives, which are as slim as the PET segment, than for the anthraquinone derivatives which are fat and will make more dead space when packed with the polymer chains.

Finally, it is interesting to note that Sakai, Miyasaka and Ishikawa reported similar results¹⁷⁾ on the diffusion of disperse dyes in PET sheet under zero pressure by the sublimation method. These authors concluded that the anthraquinone derivatives needed larger critical free volumes for diffusion than the azo derivatives compared at the same molecular weight. It seems significant that the studies by means of different experimental methods led to essentially the same conclusion on the EH space for the diffusion of the azo and the anthraquinone derivatives.

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ポリエチレンテレフタレートに対する 染料分子の拡散の活性化体積

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ポリエチレンテレフタレート皮膜に対する9種の精製分散染料の130°Cでの水溶液からの拡散係数(D)を、1 kbarまでの高圧下において多層膜法と俣野の解析法を用いて測定した。 D は圧力の増加により鋭敏に減少し、 $\ln D$ vs. P プロットの直線の勾配より拡散の活性化体積($\Delta V^\ddagger$)を得ることができた。たとえばp-nitroanilineおよびC.I. Disperse Blue 1に対し、 $\Delta V^\ddagger$ の値はそれぞれ64および123各 cm^3/mol であった。一方、用いた染料分子のファン・デル・ワールス接触模型の平面シル

エット図を作図し、その面積に厚さ3.49 Åを乗じて各染料分子の容積(V_w)を計算した。 $\Delta V^\ddagger$ と V_w との関係を作図すると、 $\Delta V^\ddagger$ は V_w の増加とともにほぼ直線的に増加することが認められた。しかしアゾ系染料とアントラキノン系染料とで異なる直線関係が得られ、後者に対し直線はより大きな勾配を与える。以上の結果を、まず得られた $\Delta V^\ddagger$ の数値そのものについて拡散の活性化状態の観点より吟味し、その知見に基づき、上述の $\Delta V^\ddagger$ と V_w との関係について考察を試みた。