

# Permselectivities of Some Aromatic Compounds in Organic Medium Through Cellulose Acetate Membranes by Reverse Osmosis

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## Synopsis

Reverse osmosis of some aromatic compounds in 1-propanol solution using porous cellulose acetate membranes and some factors which influence the organic solute permeability were investigated. Reverse osmosis data for a number of benzene derivatives showed that only phenol was rejected and the others were enriched. For the compounds with various substituent groups, the solute permeabilities have the following order;  $\text{OH} < \text{CH}_3 < \text{H} < \text{Cl} < \text{NH}_2 < \text{NO}_2$ . In the series of benzene, naphthalene, and anthracene, the permeability is related to the molar volume of solutes and varied as follows: benzene > naphthalene > anthracene. Generally speaking, there are two factors—a partition coefficient and a diffusion coefficient—for governing the permeation behavior through the membrane. Under the condition that no steric effect is exerted, the partition coefficient exclusively is a dominant factor. A good correlation between the partition coefficient of a particle and that of the membrane was found. The partition coefficients are closely related to the dipole moment of solutes.

## INTRODUCTION

In recent years, a prodigious development has marked investigations on reverse osmosis process and some examinations have been made also for organic system. For example, various aspects of the pervaporization process for separation of organic compounds have been examined,<sup>1,2</sup> and a series of parameter analyses has been extensively conducted by Matsuura et al.<sup>3</sup> In the present paper, the permselectivities of some aromatic compounds in organic media were investigated. In order to examine the factors governing permeabilities of organic solutes through cellulose acetate membranes on the reverse osmosis, two kinds of experiments were carried out; one is the measurement of the diffusion coefficient in the dialysis, and the other is the measurement of the partition coefficient  $Kd'$  between the membrane and the solution phases. For the partition coefficients, the value obtained by the usual immersion method was compared with that derived from the column method.

## EXPERIMENTAL

### Reverse Osmosis

The apparatus used is shown in Figures 1 and 2. The membranes used are Loeb-Sourirajan-type porous cellulose acetate membranes. The membranes were prepared by casting at room temperature from solutions of the following composition (wt-%): acetone, 45.0; cellulose acetate (degree of acetylation 39.8%),

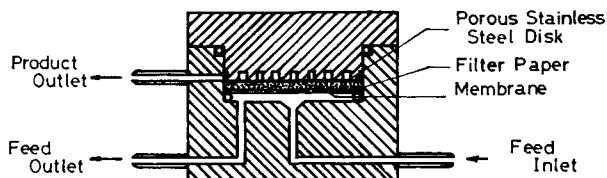


Fig. 1. Permeation cell for reverse osmosis studies.

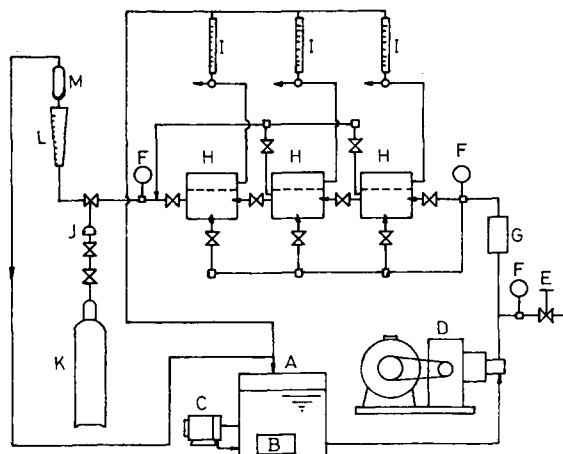


Fig. 2. Flow sheet of test apparatus for reverse osmosis studies: (a) feed reservoir; (b) heater and cooler; (c) agitator pump; (d) volumetric pump; (e) safety valve; (f) pressure indicator; (g) filter; (h) permeation cell; (i) graduated pipette; (j) pressure regulator; (k) N<sub>2</sub> gas cylinder; (l) flowmeter; (m) thermometer.

25.0; formamide, 30.0. The membranes were annealed at 90°C in hot water for 5 min. The characteristics of some membranes thus prepared are shown in Table I. Reverse osmosis experiments were carried out at 25°C. If not otherwise stated, the concentrations of organic solutes in the feed solutions were 0.05 mole/l., and the operating pressure was 100 kg/cm<sup>2</sup>. 1-Propanol was used as a solvent. The concentrations of organic solutes were determined by high-speed liquid chromatography.

The fractional solute permeability  $P_S$  is calculated from following equation:

$$P_S = \frac{\text{solute concentration in product}}{\text{solute concentration in feed}} \quad (1)$$

TABLE I  
Characteristics of Some Cellulose Acetate Membranes in Aqueous Solution at 25°C

Film no.	$L_p$ , <sup>a</sup> (m <sup>3</sup> /kg-day) × 10 <sup>-7</sup>	Product rate, <sup>b</sup> (m <sup>3</sup> /m <sup>2</sup> -day) × 10 <sup>-2</sup>	Salt rejection, <sup>b</sup> %
CA-6	1.36	6.09	79.9
CA-7	1.02	3.64	97.5
CA-8	1.06	4.19	99.5

<sup>a</sup>  $L_p$  = Pure water permeability constant.

<sup>b</sup> Feed: 5000 ppm NaCl-H<sub>2</sub>O; operating pressure: 40 kg/cm<sup>2</sup>.

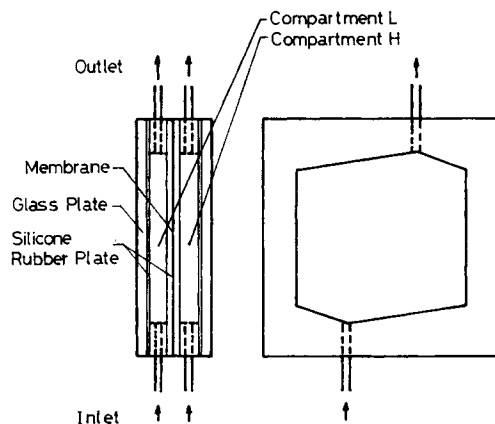


Fig. 3. Diffusion cell for dialysis studies.

In this study, benzene was selected as reference solute, and the permselectivity coefficient  $T_B^S$  is defined as

$$T_B^S = \frac{\text{fraction solute permeability of a given solute } S}{\text{fraction solute permeability of benzene (reference)}} = \frac{P_S}{P_B} \quad (2)$$

The circulating velocity of the feed solution was 24 l./hr. Under this condition, the concentration polarization near the membrane surface could be ignored because the circulating velocity is much larger than the total product rate (15 ml/hr or less).

### Dialysis Studies

The dialysis cell and the apparatus are shown in Figures 3 and 4, respectively. In order to reduce the concentration polarization near the membrane surface, the feed solution was circulated at a flow rate of 1.4 ml/min. The membrane was 0.0103 cm thick and 22.5 cm<sup>2</sup> in effective area. All experiments were carried out at 25°C. The concentrations of organic solutes were determined by high-speed liquid chromatography. The membranes used in this experiment were porous cellulose acetate membranes which were prepared without the evaporation step,

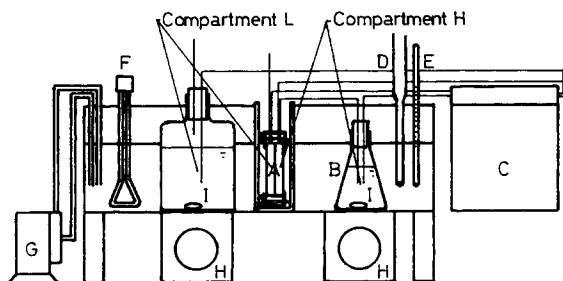


Fig. 4. Test apparatus for dialysis studies: (a) diffusion cell; (b) Erlenmeyer flask; (c) microtube pump (2-ways); (d) thermoregulator; (e) thermometer; (f) heater; (g) agitator pump; (h) magnetic stirrer; (i) rotor.

and unannealed. In the transport across these membranes, the steric effect is almost completely eliminated.

Fick's law is applied for the transport of solute across a membrane and expressed as<sup>4</sup>

$$J = PA(C_h - C_l)/\delta \quad (3)$$

where  $A$  is the membrane area;  $C_h$  and  $C_l$  are the concentrations of the solute in the compartments H and L, respectively; and  $\delta$  is the membrane thickness. Under the condition that  $C_l = 0$  and the volume  $v$  of the solution in compartment H is constant, the following relation holds for the decrease in  $C_h$  at time  $t$ :

$$\ln C_h = \frac{PA}{\delta v} t + \text{const.} \quad (4)$$

In these equations,  $P$  is an apparent diffusion coefficient and called permeation coefficient. Under the assumption that the partition equilibrium of solute attains between the membrane and the solution phase,  $P$ , can be expressed as

$$P = Kd \cdot D \quad (5)$$

where  $Kd$  is a partition coefficient and  $D$  is a diffusion coefficient in the membrane phase.

### Partition Equilibria

Two methods were adapted for measurements of partition coefficients between the solution and the membrane phase. One is the usual method used for determining partition equilibria of membranes.<sup>5</sup> The cellulose acetate membranes were immersed in the solutions and allowed to attain equilibrium for 24 hr at 25°C. The equilibrated membranes were removed from the solution, blotted, rinsed in pure solution, and blotted again. Then the membranes were immersed in a known volume of pure solution for 24 hr, and the concentration of the desorbed solute was determined by high-speed liquid chromatography. For this measurement the same membrane as the one used for measurements of diffusion coefficients were employed. The apparent membrane partition coefficient  $Kd_M$  is defined as

$$Kd_M = \frac{\text{concentration of solute in a unit volume of membrane}}{\text{concentration of solute in a unit volume of solution}} \quad (6)$$

The other is a method using liquid chromatography with the column packed with cellulose acetate particles which are prepared from the membrane material. The apparatus used is shown in Figure 5. The column was packed by a dry method and conditioned with 1-propanol. The packed column was 500 mm in height and 9.8 ml in volume. After conditioning, a 5- $\mu$ l portion of each sample solution of 0.05 mole/l. in 1-propanol was added to the column and developed with 1-propanol at an elution rate of 0.21 ml/min. The calculation of partition coefficients is based on the theory of liquid chromatography, and the value of the volume of mobile phase in the column was approximated to equal the retention volume of 2-propanol.

The particle partition coefficient  $Kd_P$  and the apparent partition coefficient  $Kd'_P$  are defined as

$$Kd_P = \frac{\text{concentration of solute in a unit weight of dried particles}}{\text{concentration of solute in a unit volume of mobile phase}} \quad (7)$$

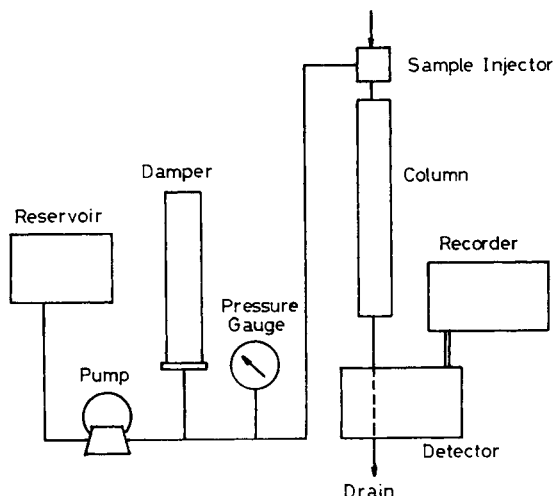


Fig. 5. Detailed arrangements of liquid chromatography apparatus.

$$Kd'_p = \frac{\text{concentration of solute in a unit volume of column}}{\text{concentration of solute in a unit volume of mobile phase}} \quad (8)$$

According to the theory of liquid chromatography, an apparent partition coefficient  $Kd'_p$  is determined by using the following equation:

$$V = V_c \cdot Kd'_p + I \quad (9)$$

where  $V$  is the retention volume of the sample solute,  $I$  is the volume of the mobile phase in the column, and  $V_c$  is the volume of the column. Usually in this paper,  $Kd_M$  and  $Kd'_p$  were used.

## RESULTS AND DISCUSSION

### Permselectivity of Some Aromatic Compounds

The product rate of 1-propanol and the permeability of benzene are listed in Table II for the membranes prepared as described in the experimental section. It is to be noted that the permeability of benzene is nearly of the same value in spite of a large variation in the product rate of 1-propanol.

TABLE II  
Product Rate of 1-Propanol and Permeability of Benzene of Cellulose Acetate Membranes at 25°C

Film no.	Product rate of 1-propanol, <sup>a</sup> (m <sup>3</sup> /m <sup>2</sup> -day) × 10 <sup>-2</sup>	Permeability of benzene <sup>a</sup>
CA-1	4.13	1.16
CA-2	3.70	1.17
CA-3	7.55	1.15
CA-4	0.62	1.14
CA-6	0.70	1.14
CA-8	3.13	1.17
CA-10	4.12	1.15

<sup>a</sup> Feed: 0.05 mole/l. C<sub>6</sub>H<sub>6</sub>-1-propanol; operating pressure: 100 kg/cm<sup>2</sup>.

TABLE III  
Permselectivity of Some Aromatic Compounds in 1-Propanol Solution

Solutes (S-B)	$PR,^a$ ( $\text{m}^3/\text{m}^2\text{-day}$ ) $\times$ $10^{-2}$	$P_S^b$	$P_B^b$	$T_B^S{}^c$
Phenol-Benzene	3.94	0.97	1.18	0.83
Toluene-Benzene	3.73	1.14	1.17	0.97
Aniline-Benzene	3.76	1.36	1.21	1.12
Chlorobenzene-Benzene	4.90	1.23	1.22	1.01
Nitrobenzene-Benzene	6.79	1.39	1.22	1.14

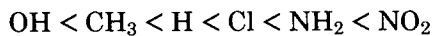
<sup>a</sup>  $PR$  = Product rate.

<sup>b</sup>  $P_S, P_B$  = Permeability of solute and benzene.

<sup>c</sup>  $T_B^S$ : Permselectivity coefficient.

<sup>d</sup> Membrane: CA-2; operating pressure: 100 kg/cm<sup>2</sup>.

Table III summarizes the values of product rate, fractional solute permeability, and permselectivity coefficient of some aromatic compounds obtained from the reverse osmosis experiments. Among benzene and its derivatives tested, only phenol was rejected, and the others were enriched in 1-propanol. By comparing the values of permselectivity coefficients  $T_B^S$ , the solute permeability varies according to the effect of substituent groups as follows:



In the series benzene, naphthalene, and anthracene, the permeation rate is primarily influenced by the bulkiness of molecules, which is measured in terms of the molar volume. Figure 6 shows a linear relation between the permselectivity coefficient and the molar volume, where the molar volume is estimated by adding the atomic volumes and the correction value<sup>6</sup>; the following values are employed: benzene, 96.0; naphthalene, 147.6; anthracene, 196.7 cm<sup>3</sup>/mole.

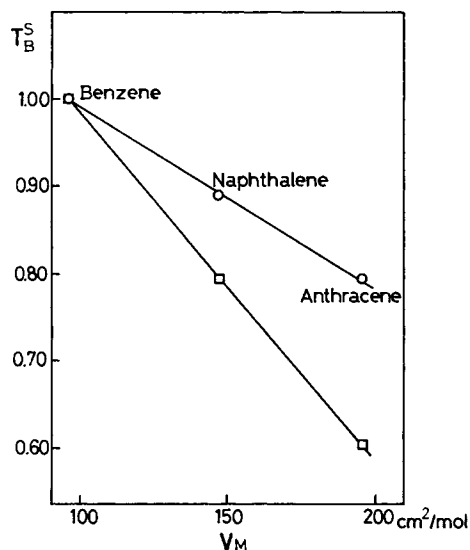


Fig. 6. Variation of permselectivity coefficient  $T_B^S$  with molar volume  $V_M$  of solute: (O) film CA-8; (□) film CA-10. Operating pressure, 100 kg/cm<sup>2</sup>.

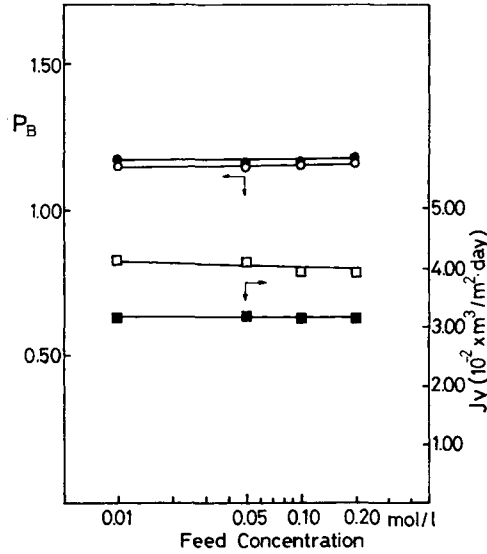


Fig. 7. Effect of feed concentration on solute permeability  $P_B$  and product rate  $J_v$ : (●) (■) film CA-8 (○) (□) CA-10. Operating pressure, 100 kg/cm<sup>2</sup>. Sample solute, benzene.

**Effects of Operating Conditions on Solute Permeabilities**

By using benzene as a reference solute, the changes of the product rate and the solute permeability with the concentration of the feed solution and the operating pressure were examined. The effect of the concentration is not remarkable, as shown in Figure 7. The effect of the pressure is shown in Figure 8. The permeability increases very slightly, but the product rate increases steeply with increasing operating pressure. This is characteristic for the organic solvent system, in contrast with the aqueous systems, where the product rate increases linearly with the pressure.<sup>7</sup>

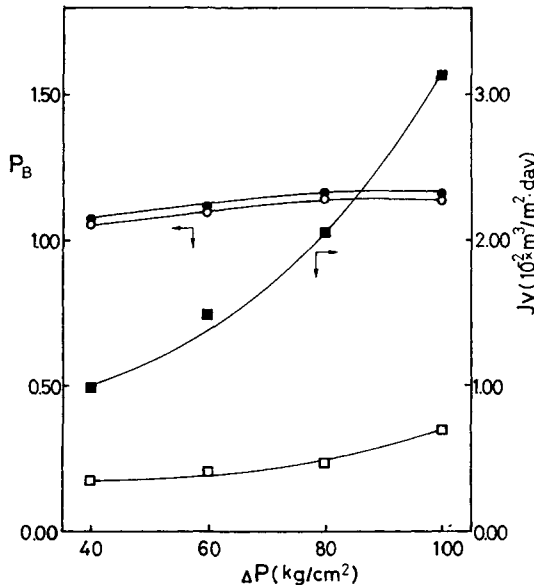


Fig. 8. Effect of operating pressure on solute permeability  $P_s$  and product rate  $J_v$ : (○) (□) film CA-6; (●) (■) CA-8. Sample solute, benzene.

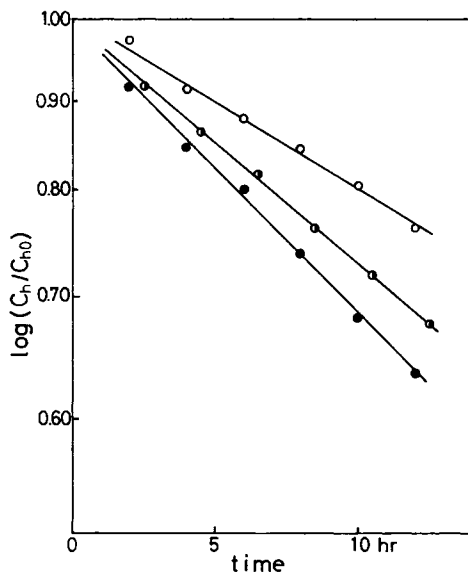


Fig. 9. Transport amounts of some aromatic solutes against time. Sample solute: phenol (—○—), aniline (—●—), benzene (—●—).

### Dialysis Studies

Figure 9 shows that the amount transported by diffusion in the progress of time obeys Fick's diffusion equation. The permeability coefficient  $P$  defined by eq. (3) is obtained directly from the slope of the curves in Figure 9 by using eq. (4). The results are given in Table IV. The values of  $P$  of benzene and aniline, which were measured in a mixed solute system, agree with those obtained for single solute systems.

### Measurements of Partition Coefficients

The apparent partition coefficient  $Kd_M$  of the membranes was obtained by the immersion method, and the results are given in the third column of Table IV. On the other hand, Figure 10 traces the elution curves in the chromatography of some aromatic compounds. From these curves, the apparent partition

TABLE IV  
Permeability Constants, Apparent Solute Partition Coefficient, and Diffusion Coefficients for Some Aromatic Compounds

Solute	$Kd'_M$ <sup>a</sup>	$P$ , (cm <sup>2</sup> /sec) × 10 <sup>7</sup>	$D$ , (cm <sup>2</sup> /sec) × 10 <sup>6</sup>
Single-Solute Systems			
Benzene	0.228	4.53	2.21
Phenol	0.456	2.81	0.69
Toluene	0.212	4.53	2.38
Aniline	0.823	3.80	0.51
Chlorobenzene	0.324	4.03	1.38
Nitrobenzene	0.487	4.53	1.03
Mixed-Solute System			
Benzene	—	4.60	—
Aniline	—	3.70	—

<sup>a</sup> In units of moles/cm<sup>3</sup> of membrane divided by moles/cm<sup>3</sup> of solutions.



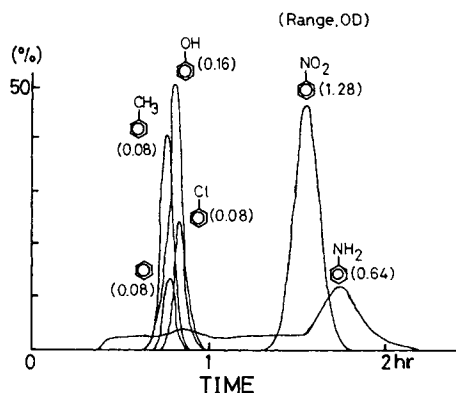


Fig. 10. Elution curves at some aromatic compounds. Sample size: 5  $\mu$ l; sample conc.; 0.05 mole/l, detector: 254 nm; column: CA (E-398-3); length: 50 cm; diam.: 5.0 mm; eluent: *n*-propanol; flow rate: 0.21 ml/min.

coefficient  $Kd'_p$  of particles was calculated according to eq. (9). The comparison of  $Kd_M$  with  $Kd'_p$  is shown in Figure 11. There is a good correlation, but the values do not numerically coincided with one another. The numerical disagreement should be ascribed to a difference in characteristics of the methods: one is dynamic, and the other is static in character.

From the values of permeability coefficient  $P$  by the dialysis method and those of partition coefficient  $Kd_M$  by the immersion method, the values of diffusion coefficient  $D$  in the membrane phase were calculated under the assumption of eq. (5), and the results are shown in the fourth column of Table IV.

### Relation Between Permselectivity Coefficients and Apparent Solute Partition Coefficients or Diffusion Coefficients

From a comparison of the fractional solute permeability  $P_S$  in Table III and the diffusion coefficient  $D$  in Table IV, no close relationships were found between

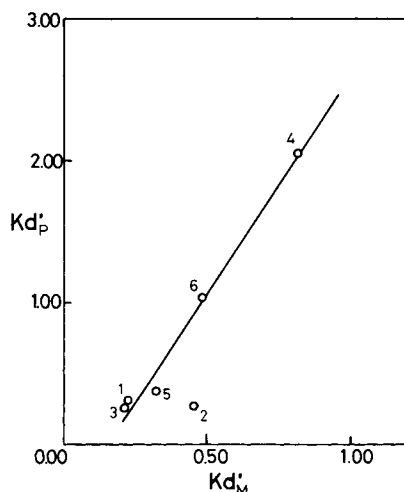


Fig. 11. Apparent solute partition coefficients  $Kd_M$  of membrane, vs those of particle,  $Kd_p$ . Solute: 1, benzene; 2, phenol; 3, toluene; 4, aniline; 5, chlorobenzene; 6, nitrobenzene.

these values. This suggests that the solute permeation on reverse osmosis is not governed by the diffusion process in the membrane phase but is characterized by the plug flow in the cavity of the membrane created by the pressure difference. On the basis of the permeation mechanism, the solute permeability would be mainly controlled by the partition behavior of the solute near and in the surface layer of the membrane. Then, one could expect a relation between the permselectivity coefficient  $T_B^S$  and the ratio of apparent solute partition coefficients of solute,  $Kd'(S)$ , to that of the benzene,  $Kd'(B)$ . As shown in Figure 12, there exists a close correlation between  $T_B^S$  and  $\log [Kd'_p(S)/Kd'_p(B)]$  for most the compounds tested. This result confirms the permeation mechanism above stated; that is, the partition coefficient  $Kd$  is a dominant factor determining the reverse osmosis permeation for the solutes with nearly the same molar volume. These conclusions support the validity of the preferential sorption-capillary flow mechanism developed by Sourirajan and his group.<sup>7,8</sup>

The exceptional points for phenol and aniline in Figure 12 could not be ex-

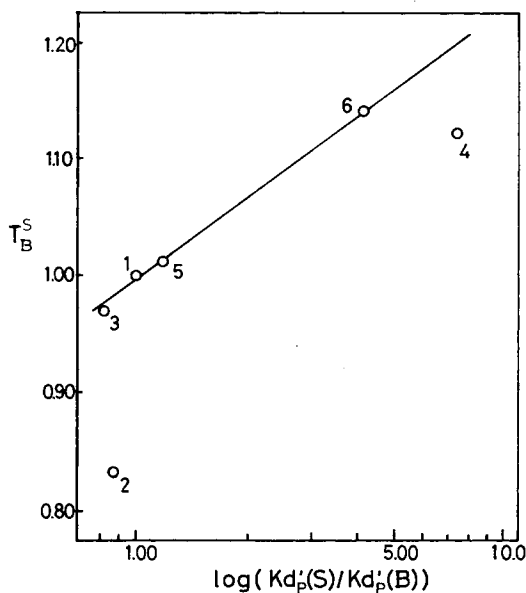


Fig. 12. Interrelation between permselectivity coefficients  $T_B^S$  and ratios of apparent solute partition coefficients. Sample solute: 1, benzene; 2, phenol; 3, toluene; 4, aniline; 5, chlorobenzene; 6, nitrobenzene.

plained adequately, although the acidic or basic property is considered to be partly responsible for the behavior.

### Interaction Between Solute and Membrane

The partition coefficient  $Kd'$  is affected by the interaction between solute molecules and the membrane matrix. For the present system, a dipole-dipole interaction should be considered between the solute and the membrane; the extent of the interaction could be measured by the dipole moment of solute  $\mu_S$ . Thermodynamic consideration on the partition equilibria leads the following relation,

$$-\Delta G = RT \log Kd' \propto \mu_S/r^6$$

where  $r$  is the nearest distance from a solute molecule to the membrane. The

TABLE V  
 Dipole Moments of Some Aromatic Compounds<sup>9</sup>

No.	Electron acceptor		No.	Electron donor	
	Substituent group	$\mu$ , Debye		Substituent group	$\mu$ , Debye
1	Ph—CN	4.02	9	Ph—NH <sub>2</sub>	1.52
2	—NO <sub>2</sub>	3.93	10	—OH	1.52
3	—COCH <sub>3</sub>	2.97	11	—OCH <sub>3</sub>	1.16
4	—CHO	2.75	12	—CH <sub>3</sub>	0.39
5	—COOC <sub>2</sub> H <sub>5</sub>	1.92			
6	—Cl	1.56			
7	—Br	1.53			
8	—F	1.46			

apparent partition coefficients  $Kd'_p$  of 12 kinds of substituted benzenes which are listed in Table V were measured, and the values are plotted against the dipole moment  $\mu_S$  in Figure 13. Two straight lines were obtained. One is for the benzene derivatives with electron-attracting substituents, and the other is for the derivatives with electron-releasing substituents. The ratio of the slopes of the two lines was about 2.5; and, if the dipole moments of the derivatives with electron-attracting substituents are divided by 2.5, a straight line is obtained between  $\log Kd'_p$  and the dipole moment or the corrected dipole moment.

This result shows that the interaction with the membrane matrix is larger for the derivatives with electron-releasing substituents than for those of electron-attracting substituents. The cellulose acetate membrane has a portion of negative charge and, therefore, interacts with the positive site of the molecule; that is, the aromatic compounds with electron-releasing substituents interact at the substituent group, and those with electron-attracting substituents interact at the benzene ring, with the membrane matrix. The above result is probable, since the charge disperses in the benzene ring<sup>10-14</sup> and the interaction between the

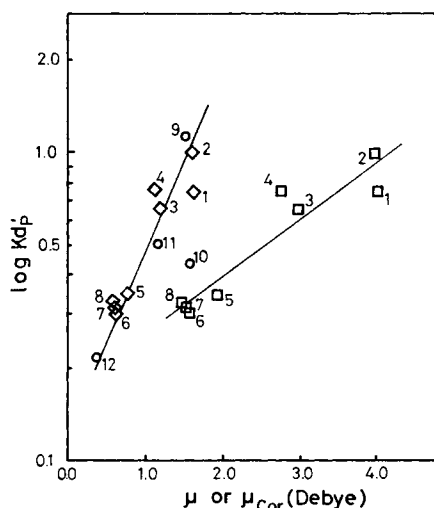


Fig. 13. Apparent solute partition coefficient  $Kd'_p$  vs dipole moment  $\mu$ . Substituent group: electron acceptor ( $\square$ ), electron acceptor (corrected) ( $\diamond$ ), electron donor ( $\circ$ ). Solute numbers are the same as in Table V.

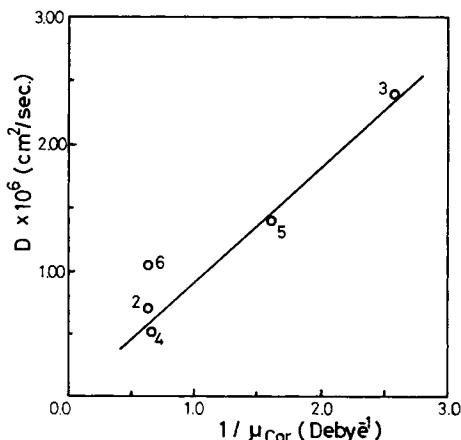


Fig. 14. Interrelation between corrected dipole moment  $\mu_{\text{cor}}$  and diffusion coefficient,  $D$ . Solute: 2, phenol; 3, toluene; 4, aniline; 5, chlorobenzene; 6, nitrobenzene.

positive ring and the negative membrane is weak in comparison with the interaction with the positive substituent.

Since the diffusion coefficient  $D$  is related to the inverse of the dipole moments as shown in Figure 14, the dipole-dipole interaction would not influence the solute permeability  $P$  in the dialysis process forced by the concentration difference.

The results obtained in the present investigation could provide a method of prediction for the reverse osmosis separation of organic compounds on the basis of liquid chromatographic analysis. The close correlation between the partition coefficients and the dipole moments of homologous compounds is useful for this prediction.

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