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Permeation characteristics of 4-substituted phenols and anilines in aqueous solution during removal by a silicone rubber membrane

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ABSTRACT

The objective of this study is to determine the correlation of permeability of phenols and anilines through the silicone rubber membrane (SRM) with hydrophobicity and acid–base properties and to gain insight into the permeation characteristics of phenols and anilines through the SRM. The permeation characteristics of 4-substituted phenols and anilines for a SRM in the permeation and chemical desorption (PCD) method were investigated. The phenols or anilines in aqueous solution were successfully recovered to aqueous NaOH or HCl solutions, respectively. Although permeation rates increased with alkyl chain length for both phenols and anilines, a marked difference was found in permeation characteristics based on molar volume. An increase in permeability of anilines through the SRM with increasing molar volume was significantly greater than that of the phenols. This was due to a greater membrane distribution coefficient (m_c) and a smaller reduction of diffusivity (D) in the SRM with increasing molar volume of the anilines, as compared with the phenols. During permeation of the phenols and anilines through the SRM, their distribution process through the membrane had a significant influence. Hydrophobicity ($\log P_{OW}$: 1-octanol/water partition coefficient) and acid dissociation constant (pK_a) values of the compounds played an important role in the distribution process. A regression equation was derived that related $\log m_c$ of the compounds through the SRM, including $\log P_{OW}$ and pK_a values. The strong correlation indicates that the permeation rate of a target compound through the SRM using the PCD method may be predicted from known physical properties, such as P_{OW} and pK_a .

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1. Introduction

Separation using nonporous membranes is applied to processes such as separation of oxygen from air (to achieve oxygen enrichment) and separation of volatile organic compounds (such as alcohols), which are separated industrially under vacuum using a pervaporation (PV) method [1,2]. An organic polymer membrane, such as a silicone rubber membrane (SRM), is often used as the nonporous membrane. However, few industrial applications of the PV method for low-volatile organics exist because of the compounds' low vapor pressure.

A compound permeating a polymeric membrane can be separated and recovered by adjusting the properties of the compound to reduce the affinity toward the membrane by neutralization or oxidation and reduction [3]. Iodine recovery was accomplished by reducing the iodine that passed through a nonporous membrane in alkaline solution; this method has been proposed as a permeation and chemical desorption (PCD) method [4,5]. Han et al. [6]

and Ferreira et al. [7] presented a membrane aromatic recovery system (MARS) for recovering anilines and phenols using an SRM. The MARS process has low energy requirements because it exploits the acid–base functionality of aromatic acids and bases to drive the process chemically. Recently, the successful scale-up and operation of the MARS process through pilot trials has been reported [8,9].

In a previous study [10], the separation and recovery of 4-substituted phenols and anilines from aqueous solutions was explored by the PCD method using an SRM. Phenols or anilines in aqueous solution were successfully recovered into aqueous NaOH or HCl solutions, respectively. A comparison between the PCD and PV methods also was investigated using a tube-type apparatus. Removal rate of phenols by the PCD method was much greater than that by the PV method, indicating effective separation and recovery of low-volatile compounds using the PCD method. The overall mass transfer coefficient (K_{OL}) for phenols and anilines closely correlated with their 1-octanol/water partition coefficient (P_{OW}), respectively. For permeation through a polymeric membrane such as an SRM, the distribution in the membrane was more important than the size-sieving ability of the diffusion process [11]. The objective of this study is to determine the correlation of permeability of phenols and anilines through the SRM with hydrophobicity and acid–base properties and to gain insight into the permeation characteristics

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Table 1
Model substances.

Substances	Purity (%)	pK _a	log P _{OW} ^h	log m _c	D × 10 ^{−10} (m ² s ^{−1})
Phenol ^a	99	9.82 ^c	1.5	−0.30	1.46
4-Cresol ^b	99	10.26 ^c	1.9	0.36	1.07
4-Ethylphenol ^b	97	10.38 ^d	2.5	0.76	0.59
4-Propylphenol ^b	96	NA	3.2	1.33	0.45
4-Butylphenol ^b	96	9.9 ^c	3.8	2.02	0.12
Aniline ^b	99	4.65 ^g	0.9	0.56	0.39
4-Toluidine ^b	98	5.1 ^g	1.5	1.08	0.83
4-Ethylaniline ^b	98	5.03 ^e	1.9	1.40	0.38
4-Propylaniline ^b	96	NA	2.4	1.97	1.01
4-Butylaniline ^b	98	4.95 ^f	2.8	2.28	0.29

NA: not available.

^a From Wako Pure Chemicals (Osaka, Japan).

^b From Kanto Chemicals (Tokyo, Japan).

^c Value obtained from ref. [2].

^d Value obtained from ref. [24].

^e Value obtained from ref. [25].

^f Value obtained from ref. [26].

^g Value obtained from ref. [27].

^h Value obtained in the previous study [10].

of phenols and anilines through the SRM. 4-substituted phenols and anilines were used as model compounds to examine their distribution coefficients and permeation rate in the SRM. A regression equation was derived that related log m_c of the compounds through the SRM, including log P_{OW} and pK_a values.

2. Experimental

2.1. Model compounds

The 4-substituted phenols and anilines used as model compounds for the experiments are listed in Table 1. The model compounds were used without additional purification and were prepared in distilled water solutions. The purity values in Table 1 were obtained from the suppliers. For the anilines, the solution pH was adjusted to 11.0 with NaOH.

2.2. PCD method

Fig. 1 illustrates the flat membrane apparatus of our own making for the PCD method. The SRM (A.S. One Co., Ltd., Osaka, Japan) was inserted between two cells made of polystyrene (capacity: 400 ml) and was fixed by a flange. The thickness of the SRM varied from 0.05 to 0.3 mm, and it had an effective area of 3.2 × 10^{−3} m². A solution of

the 4-substituted phenol or aniline (0.1 mmol/l, 400 ml) was poured into the feed side cell. For phenols, 20 mmol/l NaOH (400 ml) was added to the recovery side cell; for anilines, 20 mmol/l HCl (400 ml) was added. In a previous study [10], the value of K_{OL} became constant for phenols and anilines at a recovery solution concentration of 50 times or more the feed solution. The absorbent (NaOH or HCl) is present in large excess compared to the target compounds. The solutions on both sides were agitated using a magnetic stirrer. The experiment was conducted in a thermostatic chamber at 25 °C and at normal pressure.

A high performance liquid chromatograph (HPLC) with a UV detector was used to measure the phenol and aniline concentrations. Samples (1 ml) were withdrawn from both cells at regular intervals, and phenol and aniline concentrations were determined under the conditions shown in Table 2.

The relative standard deviation of the overall mass transfer coefficient (K_{OL}) was less than 5% (n = 5), confirming that the experiments provided sufficient accuracy.

2.3. Measurement of membrane distribution coefficient – m_c

A 3 cm × 7 cm SRM of 0.05-mm thickness was immersed for 24 h in a weighing bottle containing 10 ml of a 0.1 mmol/l phenol or aniline solution. The equilibrium concentration of the model com-

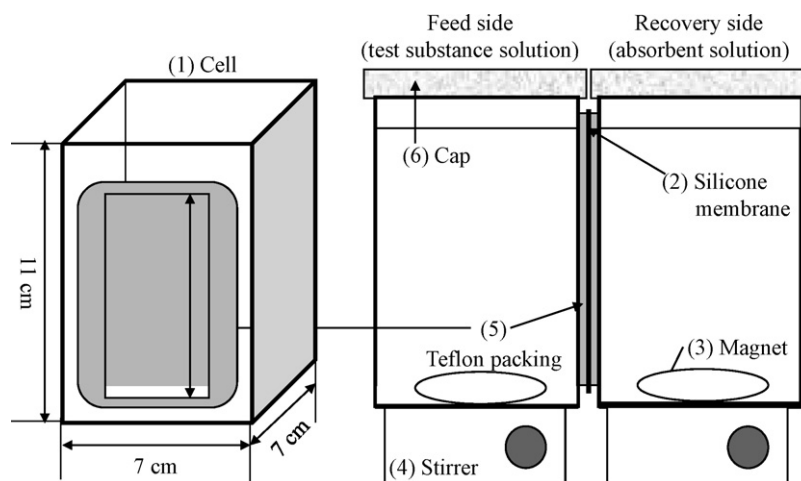


Fig. 1. The apparatus for the PCD method. The experiment was conducted in a thermostatic chamber at 25 °C and at normal pressure.

Table 2
HPLC measurement conditions.

Model	L-7000 (Hitachi Inst.Serv. Co., Ltd., Tokyo, Japan)
Detector	UV spectrophotometric detector L-7400 (Hitachi Inst.Serv. Co., Ltd)
Column	220 nm for phenols, 234 nm for anilines
Column temperature	Inertsil ODS-3 (GL Sciences Inc., Tokyo, Japan)
Mobile phase	40 °C
Flow rate	Phenol: methanol/distilled water = 50/50
Injection volume	4-Cresol: methanol/distilled water = 60/40
	4-Ethylphenol methanol/distilled water = 60/40
	4-Propylpheno methanol/distilled water = 80/20
	4-Butylphenol methanol/distilled water = 80/20
	Aniline: methanol/distilled water = 60/40
	4-Toluidine: methanol/distilled water = 60/40
	4-Ethylaniline methanol/distilled water = 70/30
	4-Propylanilin methanol/distilled water = 80/20
	4-Butylaniline methanol/distilled water = 80/20
	0.5 ml/min
	5 µl

pound (C_1 : mol/m³) was determined by HPLC under the conditions shown in Table 2. The SRM was removed from the solution, drained well, and immersed for 24 h in 20 mmol/l NaOH or HCl for phenols or anilines, respectively, after which the concentration of the model compound released from the SRM in the NaOH or HCl solution (C_2) was determined by HPLC. The concentration of the model compound in the SRM (C_3 : mol/m³) was estimated by:

$$C_3 = C_2 \times \frac{V_1}{V_2} \quad (1)$$

where V_1 and V_2 are the volume of NaOH (or HCl) solution and the SRM, respectively. The membrane distribution coefficient, m_c , was obtained by dividing C_3/C_1 . The experiments were performed at 25 °C.

2.4. Measurement of molar volume – V_M

The density of the phenols and anilines at 25 °C was measured using a 5-ml Gay-Lussac specific gravity bottle. The bottle was weighed, filled with pure water, and weighed again. The density was estimated from the difference in weights divided by the volume of the bottle. The molar volume was calculated by multiplying molecular weight by the reciprocal of the density.

3. Theoretical background

SRM is hydrophobic, and does not allow adsorption the compounds having an electric charge easily. A solution of the 4-substituted phenol or aniline was poured into the feed side cell. For phenols, 20 mmol/l NaOH was added to the recovery side cell; for anilines, 20 mmol/l HCl was added. Phenols (R–OH) or anilines (R–NH₂) penetrating the membrane from the feed side through to the recovery side change from their unionized to ionized form, R–O[−] or R–NH₃⁺, respectively. The electrolytic dissociation constants, K_a , can be expressed as follows:

$$\text{for phenols: } K_a = \frac{[R-O^-][H^+]}{[R-OH]} \quad (2)$$

$$\text{for anilines: } K_a = \frac{[R-NH_2][H_3O^+]}{[R-NH_3^+]} \quad (3)$$

From Eqs. (2) and (3), the molar ratios of unionized forms to the total of unionized and ionized forms for phenols (R_p^U) and anilines (R_A^U) can be obtained.

$$\text{for phenols: } R_p^U = \frac{1}{1 + K_a/10^{-pH}} \quad (4)$$

$$\text{for anilines: } R_A^U = \frac{1}{1 + 10^{-pH}/K_a} \quad (5)$$

The pH of phenol or aniline solutions in distilled water was approximately 5.5–6.5. The pK_a values of the 4-substituted phenols were approximately 10 (Table 1), indicating that they exist completely in an unionized form on the feed side ($R_p^U = 1.0$) and in the ionized form on the recovery side ($R_p^U = 0$). In contrast, the pK_a values of the 4-substituted anilines are approximately 5 (Table 1), indicating that about 10% of the total aniline exists in an ionized form in the solution prepared with only distilled water (pH 5–6). Thus, the pH of the aniline solution was adjusted to 11.0, at which R_A^U is equal to 1.0 on the feed side. The anilines that completely penetrate the membrane exist in an ionized form on the recovery side (20 mmol/l HCl solution). The permeation experiments were conducted using these conditions.

Assuming that the amount of absorbent (NaOH or HCl) is in large excess compared to the target compounds and that the concentration of target compounds on the recovery side is always zero initially ($C_{L2} = 0$), the concentration on the feed side can be represented by [3,12]:

$$V dC_{L1} = K_{OL} A C_{L1} dt \quad (6)$$

where A and V are the effective membrane area and liquid volume in the feed cell, respectively. Integrating equation (6) under the initial conditions, $t = 0$, $C_{L1} = C_0$, gives

$$\ln \frac{C_{L1}}{C_0} = -\frac{A}{V} K_{OL} t \quad (7)$$

The K_{OL} values were obtained using Eq. (7) for phenols and anilines.

The resistance-in-series model has been used to describe the transport of molecules through a membrane with liquid films on both sides. The $1/K_{OL}$ value represents overall mass transfer resistance and can be written as [13]:

$$\frac{1}{K_{OL}} = \frac{1}{k_{L1}} + \frac{1}{m_c k_m} + \frac{1}{k_{L2}} \quad (8)$$

where k_{L1} and k_{L2} are the liquid boundary film mass transfer coefficients of the feed and recovery sides, respectively, and k_m and m_c are the mass transfer coefficient in the membrane and a membrane/aqueous distribution coefficient, respectively. Here, k_m is connected by diffusivity, D , and film membrane thickness, d , as shown by Eq. (9).

$$k_m = \frac{D}{d} \quad (9)$$

Thus, Eq. (8) can be written as:

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{d}{m_c D} \quad (10)$$

where, $1/k_L = 1/k_{L1} + 1/k_{L2}$. Eq. (10) describes a linear relation between d and $1/K_{OL}$. The permeability ($P = m_c D$) can be obtained from the slope of the line and D values can be estimated from the m_c values obtained in Section 2.3.

4. Results and discussion

4.1. Membrane permeability of phenols and anilines

The reductions in 4-substituted phenol concentrations in the feed cell are shown in Fig. 2. The SRM thickness was 0.05 mm. The phenols were recovered using a NaOH solution in the recovery cell, and the permeation rate increased with alkyl chain length. When $\ln(C_{L1}/C_0)$ and time were employed as the ordinate and abscissa, respectively, $\ln(C_{L1}/C_0)$ decreased linearly, indicating that

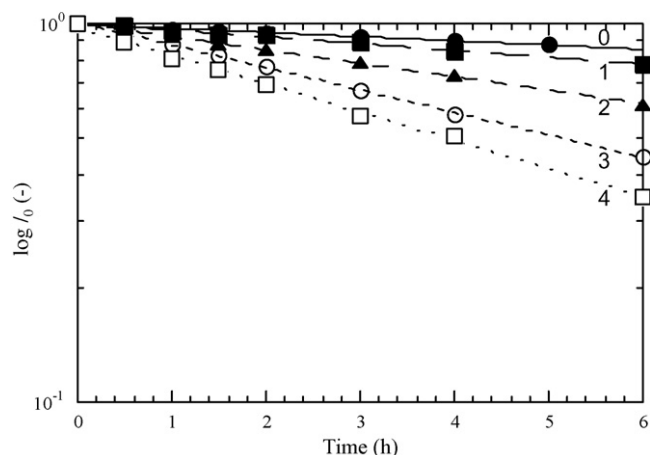


Fig. 2. Concentration profiles of 4-substituted phenol derivatives (on the side 1 cell) with time for the PCD method: (●) phenol; (■) 4-cresol; (▲) 4-ethylphenol; (○) 4-propylphenol; (□) 4-butylphenol. The numbers 0–4 refer to the number of carbons in the alkyl chain.

a decrease in phenol concentration in the feed cell follows first-order kinetics (Eq. (7)). The value of K_{OL} could be obtained from the slope of the line. A similar tendency was observed for anilines.

Figs. 3 and 4 show the variation in K_{OL} for 4-substituted phenols and anilines, respectively, with varying SRM thickness (d). For both phenols and anilines, the transfer resistance decreased (i.e., K_{OL} increased) with increasing alkyl chain length, and increased (i.e., K_{OL} decreased) with increasing SRM thickness. Anilines with the same alkyl chain length penetrated more easily than did the phenols. As shown in Figs. 3 and 4, a linear correlation between $1/K_{OL}$ and d was obtained for both phenols and anilines.

Fig. 5 shows the effect of molar volume, V_M , on P ($=m_c D$), obtained for phenols and anilines from the slopes in Figs. 3 and 4, respectively. For both phenols and anilines, the value of P increased with the value of V_M . The observed increase in P with increasing V_M indicates that larger molecules penetrate through the SRM more quickly than smaller molecules. The increase in P with increasing V_M for anilines was greater than that for phenols. Other studies have reported the permeability of various gases and vapors through polymeric membranes [14–16]. Permeation through glassy polymeric membranes is influenced by molecular size-sieving during the diffusion process, which is stronger than the distribution or sol-

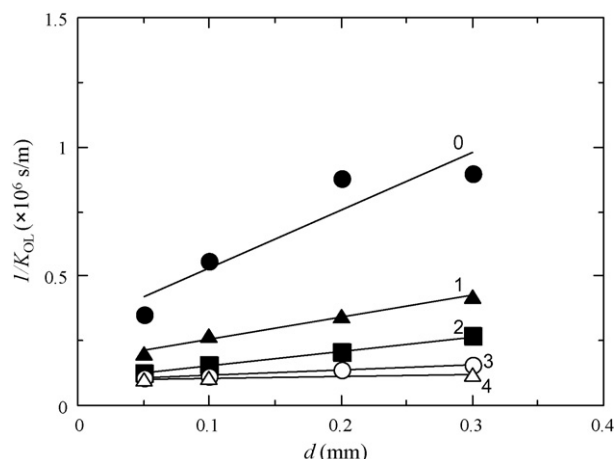


Fig. 4. Effect of thickness (d) of silicone rubber membrane on overall mass transfer coefficient (K_{OL}) for 4-substituted aniline derivatives: (●) aniline; (▲) 4-toluidine; (■) 4-ethylaniline; (○) 4-propylaniline; (△) 4-butylaniline. The numbers 0–4 refer to the number of carbons in the alkyl chain.

ubility selectivity, and the permeability of gases via the membranes decreases with increasing molecular size [14–16]. Thus, smaller molecules penetrate glassy polymeric membranes more quickly. In contrast, for rubbery polymeric membranes such as SRMs, solubility selectivity is more influential than size-sieving ability and thus gas permeability increases with molecular size [11]. As shown in Fig. 5, the P values for phenols and anilines in water to water displayed a tendency consistent with the rubber polymeric membrane in gas to gas, indicating that the solubility selectively dominates size-sieving ability in this system.

4.2. Diffusivity in silicone rubber membranes (D)

The m_c and D values of phenols and anilines in the SRM were investigated separately, because the P of the membrane is the product of m_c and D . The D values obtained for the 4-substituted phenols and anilines in the SRM are summarized in Table 1. The D value of phenol obtained was 1.5×10^{-10} m²/s. Han et al. [6] reported that the D values of phenol and 4-cresol in a silicone membrane at 50 °C were 5.36 and 2.25×10^{-10} m²/s, respectively. Also, the D value of phenol determined using ATR-FTIR by Plessis et al. [17] was

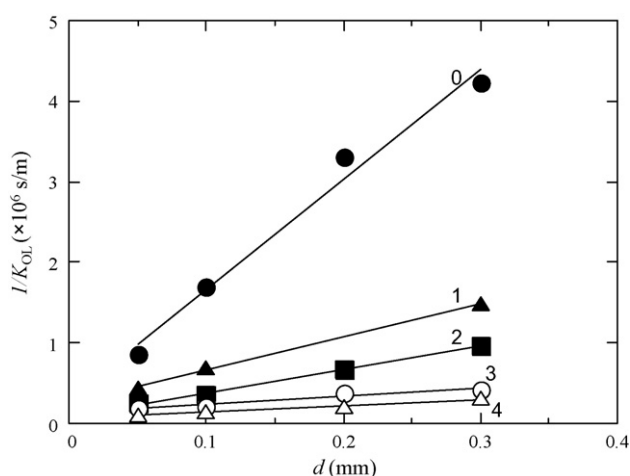


Fig. 3. Effect of thickness of silicone rubber membrane on overall mass transfer coefficient (K_{OL}) for 4-substituted phenol derivatives: (●) phenol; (▲) 4-cresol; (■) 4-ethylphenol; (○) 4-propylphenol; (△) 4-butylphenol. The numbers 0–4 refer to the number of carbons in the alkyl chain.

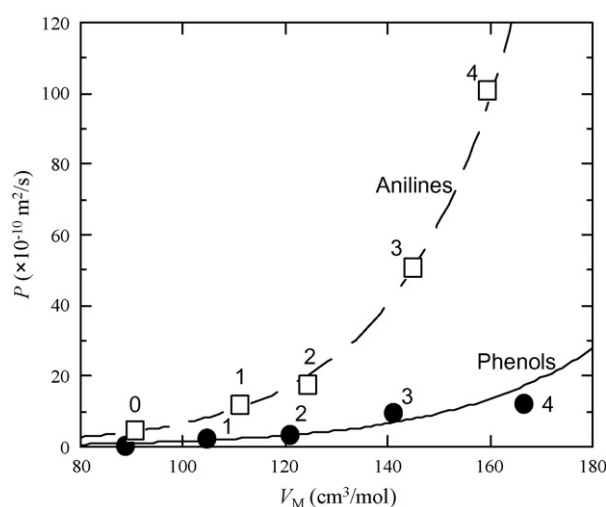


Fig. 5. Relation of membrane permeability (P) and molar volumes (V_M) for 4-substituted phenol and aniline derivatives: (●) phenols; (□) anilines. The numbers 0–4 refer to the number of carbons in the alkyl chain.

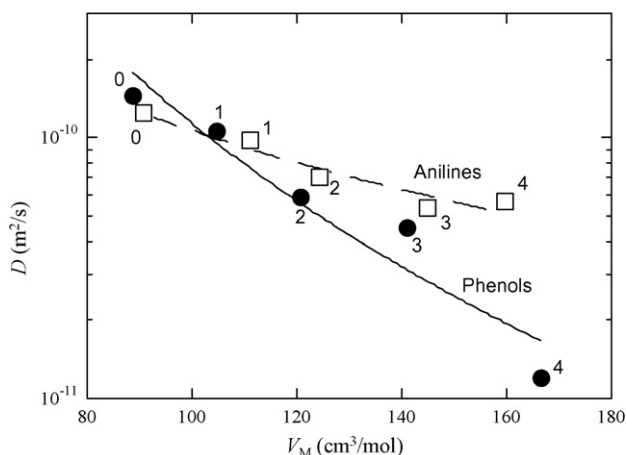


Fig. 6. Effect of molar volume (V_M) of 4-substituted phenol and aniline derivatives on diffusivity (D) in a silicone rubber membrane: (●) phenols; (□) anilines. The numbers 0–4 refer to the number of carbons in the alkyl chain.

approximately 1×10^{-10} m²/s at 25 °C. The small difference in these D values was dependent on the preparation process of SRMs, their composition, and the measurement technique.

Fig. 6 shows the relation of D to V_M for phenols and anilines in a silicone membrane. The D values decreased with increasing V_M , consistent with the results obtained by Harogoppad and Aminabhavi [18]. The decrease in D for the phenols was greater than that for the anilines. The higher P values of the anilines compared with the phenols (as shown in Fig. 5) were considered to originate from a higher m_c and a slight reduction in the D value with V_M . For a dilute solution, the empirical equation of $D \propto 1/V_M^{0.6}$ proposed by Wilke and Chang [19] has been established. Although the diffusion process in SRM is more strongly influenced by molecular size than that in dilute solution, the D values for phenols and anilines were proportional to $1/V_M$ to the powers of 3.7 and 1.4, respectively, indicating that phenols are more significantly influenced by molecule size than are anilines.

Blair et al. [20] examined the diffusivity of various polar and nonpolar compounds, such as alcohols and hydrocarbons, in silicone and discovered that the D values of the hydrocarbons were larger than those of the alcohols at the same molar volume. Plessis et al. [17] studied the diffusion of a series of phenols across silicone

rubber membranes impregnated with either octanol or toluene. Phenols (phenol, catechol, resorcinol, hydroquinone, pyrogallol, benzenetriol, and phloroglucinol) were chosen because simple substitutions introduced significant variation in hydrogen (H-) bonding properties. They showed that H-bonding effects on permeability occur when the membrane is capable of interacting with the target compound. The diffusion behavior of phenols through SRMs differed greatly than that of anilines, and the differences observed in this study also originated from H-bonding of the phenols.

4.3. Distribution coefficient in silicone rubber membranes (m_c)

In a previous study [10], the correlation between P_{OW} and K_{OL} was examined for 4-substituted phenols and anilines. Although high linearity between P_{OW} and K_{OL} was observed, the correlation equations were expressed separately. The dominant physicochemical properties that control transport across a nonporous polymeric membrane were distribution and diffusion. As described above, solubility selectivity governs permeability for rubber polymeric membranes such as SRMs. The m_c values of phenols and anilines on the SRM were obtained experimentally (Table 1). The m_c of phenol in this study was 0.5 ($\log m_c = -0.30$) and agreed with that estimated by Doig et al. [13]. The m_c values of both the phenols and anilines increased with alkyl chain length. These results indicate that distribution of the target compound on the SRM is the main factor governing the permeation rate.

Brookes and Livingston [21] identified m_c as an important parameter for determining the magnitude of membrane mass transfer resistance and estimated m_c from a knowledge of the compound's solubility parameter and molecular volume. In the study described here, the value of m_c was estimated using more easily obtained parameters. The P_{OW} value is used as a standard parameter of hydrophobicity, and many values are available in the literature. The hydrophobicity of a compound can indicate toxicity toward animal and aquatic life and environmental fate [22]. Fig. 7(A) shows the relation between $\log m_c$ and $\log P_{OW}$ for phenols and anilines. Although a linear relation was observed, the $\log m_c/\log P_{OW}$ relation for phenols and anilines could be expressed by two different correlation formulae. However, the slopes of the two derived lines were nearly equal. Of note, the m_c values of anilines with higher acid dissociation constants ($pK_a \sim 10$) were larger than those of the phenols ($pK_a \sim 5$). Dmitrienko et al. [23] investigated the sorption of phenols by several polyurethane foams (PUF) and derived a regres-

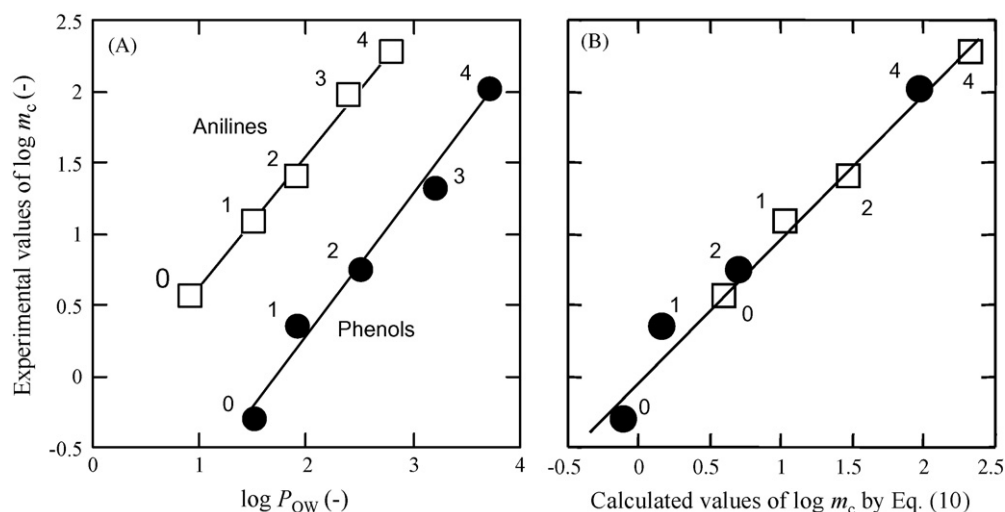


Fig. 7. Dependence of membrane distribution coefficient (m_c) of phenols (●) and anilines (□) on 1-octanol/water partition coefficients (P_{OW}) and constants of acid dissociation (pK_a). (A) Experimental values of $\log m_c$ vs. $\log P_{OW}$; (B) Experimental values of $\log m_c$ vs. calculated values of $\log m_c$ by Eq. (11). The numbers 0–4 refer to the number of carbons in the alkyl chain.

sion equation connecting the distribution coefficient by PUF with the hydrophobicity parameter ($\log P_{OW}$) and pK_a . When the same regression analysis as used by Dmitrienko et al. [23] was performed for the SRMs, the m_c values of phenols and anilines for the SRM correlated with $\log P_{OW}$ and pK_a , as follows:

$$\log m_c = 0.906 + 0.95 \log P_{OW} - 0.249pK_a \quad (11)$$

The $\log m_c$ values calculated from Eq. (11) and the experimentally obtained values for both phenols and anilines are given in Fig. 7(B). Since the values of pK_a for 4-propylphenol and 4-propylaniline were unavailable, no plots for them are shown. The experimental values were proportional to the calculated values of the phenols and anilines with a correlation factor of $r^2 = 0.98$. The strong correlation indicates that the permeation rate of a target compound through the SRM using the PCD method may be predicted from known physical properties, such as P_{OW} and pK_a .

5. Conclusions

This study investigated the permeation characteristics of 4-substituted phenols and anilines through SRMs using the PCD method. The distribution process of the model compounds through the SRM dominated among the permeation processes of the membrane. The K_{OL} value was proportional to $\log m_c$, and $\log m_c$ could be related to $\log P_{OW}$ and pK_a . These results reveal the possibility that the permeation rate using the PCD method can be predicted by measuring the distribution coefficient through the SRM or by using known physical properties, such as P_{OW} and pK_a . The results obtained in this study will aid an efficient design of this system.

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