Adsorption Properties of Aromatic Compounds on Polyethylene as a Membrane Material

Y. KISO,[1] T. KITAO,[2] K. NISHIMURA[2]

[1] Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580 Japan

[2] Department of Architecture and Civil Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580 Japan

ABSTRACT: Membrane fouling is an important problem in microfiltration processes. Although the solute adsorption on the membrane is one of the factors inducing membrane fouling, its evaluation is difficult. In this study we have attempted this evaluation using liquid chromatography with polyethylene as the stationary phase. Polyethylene is a common material of a microfiltration membrane. Aromatic compounds were retained significantly by the polyethylene stationary phase, although small amount of solute loading to the column was allowed. The logarithm of the capacity factor ($\log k'$) for aromatic compounds was linearly correlated with the logarithm of 1-octanol/water partition coefficient ($\log K_{o/w}$), and this indicated that the main controlling factor for the adsorption is the hydrophobic interaction. We also found that alkyl substituents and the nonplanarity of the molecular structures exerted negative effects for the adsorption. Moreover, evaluation of partition coefficient based on the surface area of the stationary phase revealed that polyethylene could adsorb aromatic compounds as much as 15 to 90 times more than octadecylsilane. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1037–1043, 1999

Key words: microfiltration membrane; polyethylene; adsorption; liquid chromatography; aromatic compounds

INTRODUCTION

Microfiltration membrane processes have been used for water and wastewater treatment not only to remove trace-level particulate matter but also to separate biomass material, such as activated sludge. The former is utilized in water treatment and advanced treatment for wastewater.[1–4] The latter is known as the membrane bioreactor process or membrane separation activated sludge process and has recently been developed as an advanced treatment process for wastewater.[5–11] Since solid or sludge concentration in feed solution is very high in this type of processes, membrane fouling is a serious problem observed commonly and results in a remarkable reduction in filtration efficiency.

Membrane fouling is induced by many causes, such as pore plugging with particulate matter, gel layer formation of polymeric or colloidal matter on the membrane surface, or adsorption of solutes on the membrane surface or pore wall. The fouling control techniques are determined by whatever caused the fouling, however, fouling in practice is characterized by complex phenomena of all these factors, and it is not easy to distinguish exactly among them.

Particulate matter accumulated physically on the membrane surface may be removed by mechanical means, so as to increase of the crossflow

Table I   List of Aromatic Compounds and 1-octanol/water Partition Coefficients

Solute	$\log K_{o/w}$ [a]	Solute	$\log K_{o/w}$ [a]
benzene	2.15	*m*-xylene	3.20
naphthalene	3.33	*p*-xylene	3.15
anthracene	4.45	anisole	2.11
pyrene	4.88	nitrobenzene	1.85
biphenyl	4.04	chlorobenzene	2.84
o-terphenyl	5.05[b]	*o*-dichlorobenzene	3.38
m-terphenyl	5.54[b]	*m*-dichlorobenzene	3.38
p-terphenyl	5.67[b]	*p*-dichlorobenzene	3.39
toluene	2.69	phenol	1.46
ethylbenzene	3.15	aniline	0.90
n-propylbenzne	3.68	benzenesulfonic acid	—
o-xylene	3.12		

[a] 1-octanol/water partition coefficient from ref. 17.
[b] Estimated value based on the retention time for the ODS column.

verosity, intermittent filtration, and backwashing. The fouling by gel layer or adsorption, however, occasionally may require chemical cleaning with detergents and/or oxidizing agents. Adsorption may modify the surface character of the membrane, and this may also promote the adsorption of several solutes as well as gel layer formation.

Accordingly, the study and evaluation of the adsorption properties of organic compounds on membrane materials is an important subject in order to control membrane fouling involving aspects such as selection of an appropriate membrane, cleaning agents, and pretreatment of the feed solution.

In our previous works,[12–16] we examined the use of a liquid chromatograph packed with membrane material as the stationary phase. When cellulose acetate (CA), a common reverse osmosis membrane material, was used as the stationary phase in high-performance liquid chromatography (HPLC), it was shown that liquid chromatography (LC) is a very common convenient technique, mainly because many solutes can be tested appropriately; this allows the analysis and evaluation of the most important controlling factors causing the adsorption. In this work, polyethylene, a material commonly used in microfiltration membranes, was used as the stationary phase in LC, and adsorption properties of several organic compounds on the membrane material were examined from their retention behavior.

EXPERIMENTAL

The particulate polymer material for the flat sheet-type microfiltration membrane (nominal pore size: 0.4 μm) was obtained from Kubota Co., Ltd. (Osaka, Japan). This polymeric material is a copolymer of polyethylene and poly(vinyl chloride) but is here called simply polyethylene (PE) because this is the material for the polyethylene membrane purchased by Kubota. The particulate PE was sieved and the fraction of 25–37 μm was packed into a stainless steel HPLC column (4.6 mm i.d. $\times$ 250 mm long). An octadecyl silica (ODS) column (monomeric ODS, 5 μm, 4.6 mm $\times$ 250 mm long, Shinwa Chemical Industries, Ltd., Kyoto, Japan) was also used for comparison with the PE column.

The HPLC apparatus consisted of a 880-PU pump (JASCO, Tokyo, Japan), a sample injector (Rheo-dyne 7125, USA) and a 870-UV detector (JASCO) or a 830-RI detector (JASCO). The column temperature was kept at 30 $\pm$ 1°C with a column oven. Methanol–water solutions were used as the mobile phase: HPLC grade methanol and the deionized water passed through an ODS column. The flow rate was kept at 0.5 or 1.0 mL/min.

All solutes listed in Table I were used as purchased without further purification. Deuterium oxide (99.75%, Merck, Darmstadt, Germany) was used as the unretained solute when the RI detector was used. When the UV detector was used, sodium nitrate was used for the same purpose.

Each solute was dissolved within the mobile phase.

The capacity factor (k') was used as the quantitative index for the adsorption properties.

$$k' = \frac{t_R - t_0}{t_0} \qquad (1)$$

Here, t_R and t_0 are the retention times (min) for organic solutes and the unretained solute, respectively.

RESULTS AND DISCUSSION

Loading Amount

Considering that the microfiltration membrane is used for water treatment, the adsorption properties should be measured in aqueous conditions. However, it was difficult to use water as a mobile phase because of the poor wetting properties of PE. In order to be wet enough, the surface of PE by a mobile phase methanol or methanol–water has to be used. First, the retention properties of aliphatic alcohols were examined with a HPLC equipped with an RI detector. In this case, no significant retention was obtained even for 1-hexanol. On the other hand, benzene and toluene were significantly retained, but very large tailing was observed.

The peak symmetry is affected by the packed condition of the stationary phase, the loading amount to the column, and the retention mechanism. It is well known that overloading gives extreme tailing and short retention times. In inverse gas chromatography, the relationship between loading and peak shape was used for polymer characterization.[18–19] Considering that PE is not a porous material, the most probable factor for the tailing was expected to be the overloading and, thus, the effects of the loading amount on the retention time and the peak shape were examined. The injection volume was kept at 50 μL, and the solute concentrations were varied, maintaining the methanol content of the mobile phase at 80%.

The relationships between the retention time and the concentration are shown in Figure 1. As observed in this figure, even in the case of benzene, whose retention time was but affected by the loading, extreme tailing peaks were obtained in the high concentration range, but under lower concentration conditions symmetric peaks were
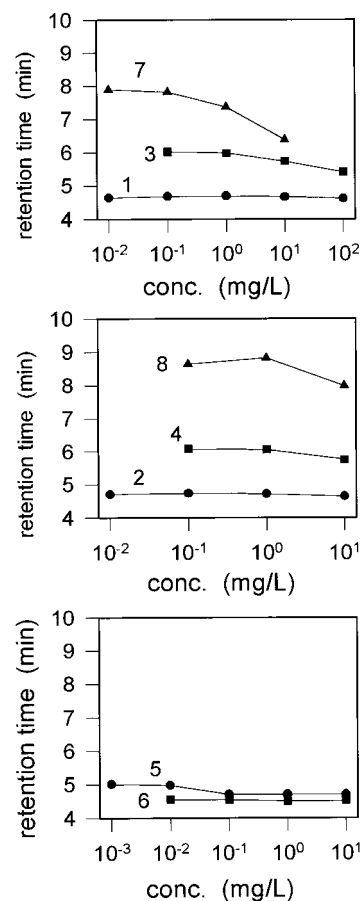

Figure 1 The effects of solute concentration on the retention time. PE column (4.6 mm i.d. × 250 mm long), 30°C; mobile phase: MeOH 80%, flow rate: 1.0 mL/min, column temperature: 30°C; injection volume: 50 μL.

obtained. For the other compounds, decrease of solute concentration results in both in increase of retention times and more symmetric shape of the peaks. These results indicated that loading less than 5 ng of solute was appropriate in order to prevent overloading to the column.

Moreover, it was observed that the solvent for sample preparation affects the retention time as well: The use of methanol solutions resulted in small retention times. In this case, the formation of gradient elution conditions is unavoidable when the sample is loaded to the column, and this may be the main cause for the variance of the retention times. Therefore, the sample solutions were prepared with the mobile phase used for following experiment.

The peak shape is also affected by the retention mechanism, as well as by sample loading. From a macroscopic point of view, the retention mecha-
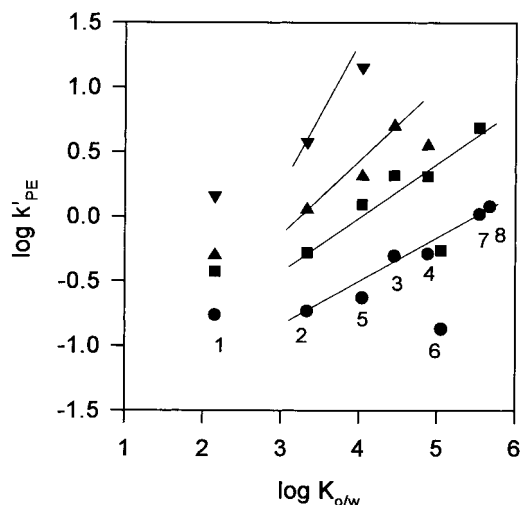
Figure 2 log k' vs. log $K_{o/w}$ (ODS column). Mobile phase: ▼: MeOH 50%, ▲: MeOH 60%, ■: MeOH 70%, ●: MeOH 80%, flow rate: 1.0 mL/min, column temperature: 30°C.

nism for solutes includes both adsorption and absorption: The later indicates that a solute molecule penetrates the polymer matrix. When absorption is the dominant factor, tailing may be promoted. The method used in this work is regarded as inverse LC. Inverse gas chromatography is a well-known inverse technology in the chromatographical field.[18–21] In this case, the retention of a probe molecule may be controlled mainly by absorption within the polymer material (the stationary phase); thus, the retention of the probe molecule is influenced by the change of the structure of the polymer matrix. In the LC system, however, the PE is not swollen by the mobile phases, and this suggests that the composition of the mobile phase exerts very small influence on the structure of PE. Although the effects of absorption are not neglected in this process, it is difficult to make a clear distinction between both absorption and adsorption effects from the retention data alone.

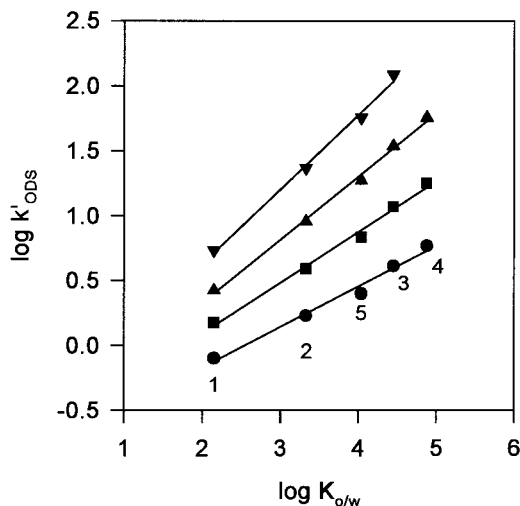### The Effects of Mobile Phase Composition

The effects of methanol content in the mobile phase were examined with polynuclear aromatic hydrocarbons (PAHs). For each mobile phase, the logarithm of the capacity factor (log k') was linearly correlated with the logarithm of 1-octanol/water partition coefficient (log $K_{o/w}$) as shown in Figure 2, where the experimentally nonavailable log $K_{o/w}$ values for compounds such as terphe-

nyls[17] were estimated by the following method: For the compounds whose log $K_{o/w}$ value was known, the retention times were measured with the ODS column, the correlation equation between log k'_{ODS} and log $K_{o/w}$, and the log $K_{o/w}$ values were estimated based on a correlation equation. The relationship between log k'_{ODS} and log $K_{o/w}$ for PAHs is shown in Figure 3.

In the case of the PE column, a linear correlation between log $K_{o/w}$ and log k'_{PE}, with exception of benzene and o-terphenyl, was obtained for each methanol content as shown in Figure 2. It was further observed that the slope of the correlation equation decreases with increase of methanol content of the mobile phase. Since these results are similar to the retention properties in common reverse-phase chromatography, it can be pointed out that the retention by PE column is mainly controlled by hydrophobic interactions. Considering that the membrane is used in an aqueous solution system, these compounds are suggested to be adsorbed very strongly on the PE membrane.

In comparison with other PAHs, benzene and o-terphenyl show a high and a very low log k'_{PE} in each mobile phase, respectively. Considering the benzene did not show any remarkable effect of the loading amount as shown in Figure 1, it can be suggested that benzene has a unique adsorption feature on PE.

On the other hand, o-terphenyl is characterized by significantly nonplanar structure, al-

Figure 3 The effects of mobile phase composition on the retention of PAHs (ODS column). Mobile phase: ▼: MeOH 50%, ▲: MeOH 60%, ■: MeOH 70%, ●: MeOH 80%, flow rate: 1.0 mL/min, column temperature: 30°C.
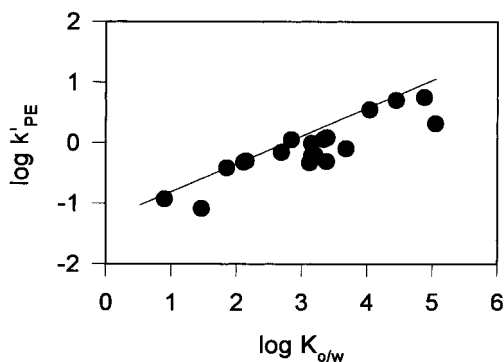
Figure 4 The relationship between log k' and log $K_{o/w}$ (PE column). Mobile phase: MeOH 60%, flow rate: 1.0 mL/min, column temperature: 30°C.

though biphenyl also shows some nonplanarity. The retention properties may be influenced less by solute structure in the case of absorption as the dominant factor than in the case that adsorption is. When PAHs are adsorbed on the PE surface (i.e., no penetration in the polymer matrix occurs), the contact area between the nonplanar solute and the PE surface may decrease, and this may cause a lower retention of o-terphenyl.

Retention Properties of the PE Column

For the case of 60% methanol mobile phase and a PE column, the relationship between log k'_{PE} for all aromatic compounds shown in Table I, and log $K_{o/w}$ is illustrated in Figure 4. For comparison purposes the results for log k'_{ODS} are also shown in Figure 5. The results for benzenesulfonic acid were not plotted in the figures because no retention was observed. Benzenesulfonic acid is considered to be excluded by electric repulsion due to
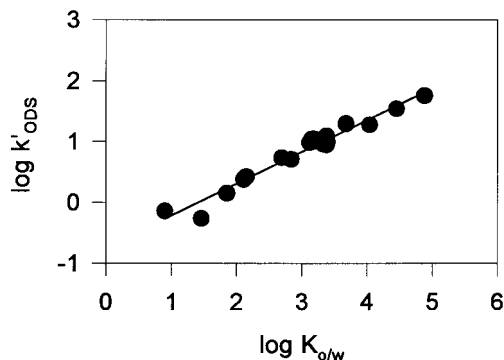
Figure 5 The relationship between log k'_{ODS} and log $k_{o/w}$. Mobile phase: MeOH 60%, flow rate: 1.0 mL/min, column temperature: 30°C.
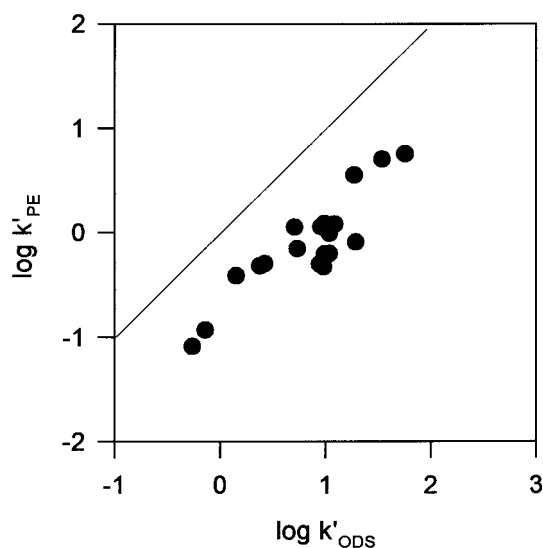
Figure 6 The relationship between log k'_{PE} and log k'_{ODS}. Mobile phase: MeOH 60%, flow rate: 1.0 mL/min, column temperature: 30°C.

both its ionic character and the low permittivity of the stationary phase (PE or ODS). Phenol also showed relatively low retention in each column.

In the case of an ODS column, the correlation equation between log k'_{ODS} and log $K_{o/w}$ for all compounds except phenol was almost linear and similar to the line in Figure 3; here no substituents effects were observed. The line observed in Figure 4 corresponds to the correlation for PAHs except o-terphenyl, and some compounds were plotted at significantly lower values than the mentioned line. The compounds showing lower log k'_{PE} values include the following groups: (1) electrolytes (benzenesulfonic acid, phenol), (2) alkylbenzenes (ethylbenzene, n-propylbenzene), (3) nonplanar PAH (o-terphenyl), and (4) o-disubstituted benzenes (o-xylene, o-dichlorobenzene). The results for alkylbenzenes suggested that aromatic rings may interact specifically with the PE. The effects of o-disubstituted benzenes may thus also be similar to the effects of nonplanar PAH.

Comparison of PE and ODS

In order to evaluate the adsorption capacity of PE we examined to compare the capacity factors for PE and ODS because ODS is a common stationary phase for reverse-phase LC. The capacity factors for PE column (log k'_{PE}) were plotted against to those for ODS (log k'_{ODS}). The results are shown in Figure 6, and the following correlation equation was obtained:

$$\log k'_{PE} = 0.784 \log k'_{ODS} - 0.766 \ (r^2 = 0.7942)$$
(2)

The fact that the values of $\log k'_{PE}$ are lower than those of $\log k'_{ODS}$ indicates an apparently lower adsorption capacity of PE as compared to that of ODS.

Since the capacity factor includes the effect of the surface area of the stationary phase, it is necessary to evaluate this adsorption capacity based on the unit surface area. For this purpose we used the distribution coefficient of solute based on the surface area of the stationary phase (D_s), defined as

$$D_s = \frac{\text{amount of solute per unit surface area}}{\text{amount of solute per unit volume of mobile phase}}$$
(3)

D_s is calculated using experimental data by

$$D_s = \frac{(t_R - t_0)Q}{S_s W}$$

where t_R and t_0 are the retention times (min) for solute and unretained solute, Q is the flow rate of the mobile phase (mL/min). S_s is the specific surface area of the stationary phase (m^2/g), and W is the mass of the stationary phase (g). The masses of PE and ODS in the column were measured after the experiment. The surface area of the ODS was assigned a nominal value of 300 m^2/g, and that for PE was evaluated based on particle size assuming spherical particle character.

The plots of the distribution coefficient for PE, D_s(PE), versus that for ODS, D_s(ODS), are shown in Figure 7. Comparison of the distribution coefficient based on unit surface area clarified that the adsorption capacities for PE were larger by 1.2 to 1.9 log units than those for ODS.

This suggests that in the PE membrane, irreversible fouling may be easily induced by aromatic compounds even at very low concentrations. Moreover, considering that the adsorption is mainly controlled by hydrophobic interactions, the feed solution containing hydrophobic solutes may foul the PE membrane rapidly, and frequent chemical washing or membrane replacement may be required.

CONCLUSIONS

In this study we examined to evaluate the adsorption properties of aromatic compounds on PE used as the microfiltration membrane material.
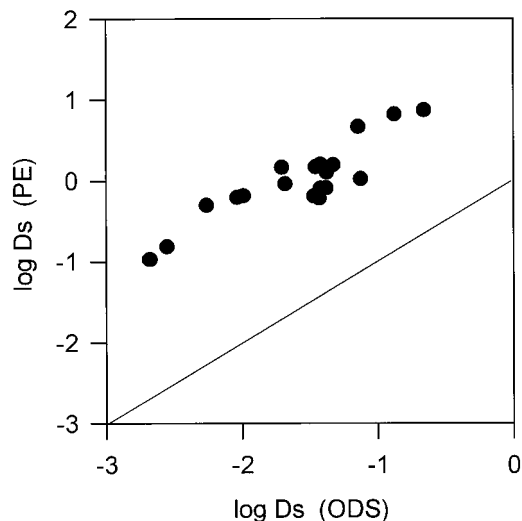
Figure 7   The relationship between $\log D_s$(PE) and $\log D_s$(ODS). Mobile phase: MeOH 60%, flow rate: 1.0 mL/min, column temperature: 30°C.

As the results indicate, the adsorption of aromatic compounds was controlled mainly by hydrophobic interactions, and the effects of alkyl substituent as well as molecular structure characteristics (nonplanarity) were also clarified. Comparison of the retention properties for PE and ODS clarified that PE adsorbed aromatic compounds more than ODS.

The methodology suggested here proved valuable to evaluate the adsorption properties of many solutes. Nevertheless, all membrane materials can not be used as the stationary phase because they are not available in a fine particulate form. Therefore, a future research topic is the preparation of the stationary phases with a variety of membrane materials.

REFERENCES

1. Nakatsuka, S.; Nakate, I.; Miyano, T. Desalination 1996, 106, 55.
2. Kaiya, Y.; Itoh, Y.; Fujita, K.; Takizawa, S. Desalination 1996, 106, 71.
3. Oe, T.; Koide, H.; Hirokawa, H.; Okukawa, K. Desalination 1996, 106, 107.
4. Jacangelo, J. G.; Trussell, R. R.; Watson, M. Desalination 1997, 113, 119.

5. Magara, Y.; Itoh, M. Water Sci Technol 1991, 23, 1583.
6. Chaize, S.; Huyard, A. Water Sci Technol 1991, 23, 1591.
7. Magara, Y.; Nishimura, K.; Itoh, M.; Tanaka, M. Water Sci Technol 1992, 25, 241.
8. Kishino, H.; Ishida, H.; Iwabu, H.; Nakano, I. Desalination 1996, 106, 115.
9. Visvanathan, C.; Yang, B.-S.; Muttamara, S.; Maythanukhraw, R. Water Sci Technol 1997, 36, 259.
10. Seo, G. T.; Lee, T. S.; Moon, B. H.; Choi, K. S.; Lee, D. H. Water Sci Technol 1997, 36, 275.
11. Vera, L.; Villarroel-Lopez, R.; Delagdo, S.; Elmaleh, S. Desalination 1997, 114, 65.
12. Kiso, Y. Bull Chem Soc Jpn 1985, 58, 3637.
13. Kiso, Y. Chromatographia 1986, 22, 55.
14. Kiso, Y.; Kitao, T. Chromatographia 1986, 22, 341.
15. Kiso, Y.; Kitao, T.; Ge, Y.-S.; Jinno, K. Chromatographia 1989, 28, 279.
16. Kiso, Y.; Takayama, K.; Jinno, K. J High Resolution Chromatogr 1989, 12, 169.
17. Hnash, C.; Leo, R. L. Substituent Constants for Correlation Analysis in Chemistry and Biology; Wiley: New York, 1979.
18. Braun, J.-M.; Guilet, J. E. Adv Polym Sci 1976, 21, 107.
19. Gray, D. G. Prog Polym Sci 1977, 5, 1.
20. Dorris, G. M.; Gray, D. G. J Chem Soc Faraday Trans 1 1981, 77, 713.
21. Tsutsumi, K.; Osuga, T. Colloid Polym Sci 1990, 268, 38.