

## Evaluation of interaction between organic solutes and a membrane polymer by an inverse HPLC method

Yoshiaki Kiso<sup>1</sup>, Katsuya Hosogi<sup>1</sup>, Yuki Kamimoto<sup>2</sup> and Yong-Jun Jung<sup>\*3</sup>

<sup>1</sup> Department of Environmental and Life Sciences, Toyohashi University of Technology,  
Tempaku-cho, Toyohashi 441-8586, Japan

<sup>2</sup> EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan

<sup>3</sup> Department of Environmental engineering, Catholic University of Pusan,  
Oryundae-ro, Geumjeong-gu, Busan, 609-757, Korea

(Received February 22, 2014, Revised June 04, 2014, Accepted June 05, 2014)

**Abstract.** Organic compounds are adsorbed on RO/NF membranes, and the adsorption may influence the rejection of organic compounds by the membranes. Because almost RO/NF membranes are composite membranes, the results obtained by adsorption experiment with using membrane pieces are unable to avoid the influence by the support membrane. In this work, the interaction between membrane polymer and organic solutes was examined by an inverse HPLC methodology. Poly (*m*-phenylenetrimesoylate), the constituent of skin layer of RO/NF membranes, was coated on silica gel particles and used as a stationary phase for HPLC. When water was used as a mobile phase, almost hydrophilic aliphatic compounds were not effectively adsorbed on the stationary phase, although hydrophobic compounds were slightly adsorbed. The results indicated that the hydrophilic aliphatic compounds are useful probe solutes to examine the molecular sieving effect of a membrane. When water was used as a mobile phase, the aromatic compounds were strongly retained, and therefore CH<sub>3</sub>CN/H<sub>2</sub>O (30/70) was used as a mobile phase. It was revealed that the adsorption of aromatic compounds was controlled by stacking between solute and polymer and was hindered by non-planar structure and substituents.

**Keywords:** RO/NF membrane; polyamide; adsorption; organic solute; HPLC

---

### 1. Introduction

Membrane separation technologies such as RO and NF membrane processes have high potential for the removal of hazardous organic micro-pollutants (Agenson and Urase 2007, Kimura *et al.* 2003a, Kiso *et al.* 2000, 2001a, b, 2002, Plakas and Karabelas 2008, 2011, Yoon *et al.* 2006, Zhang and Pagilla 2010, Koo *et al.* 2011), and the membrane filtration processes are expected to be employed more widely. Considering the situation, the importance of following subjects is increasing: estimation of removal performance of a membrane for target pollutants, estimation of the effects of co-existing solutes on rejection and water permeability (including fouling), and selection of an appropriate membrane. However, this subject is very difficult, because the controlling factors for the membrane separation of organic pollutants have not been clarified yet.

---

\*Corresponding author, Professor, E-mail: [yjjung@cup.ac.kr](mailto:yjjung@cup.ac.kr)

In the case of non-ionic organic solutes, there is no repulsive force between the solutes and membrane polymer, and molecular sieving effect may mainly control the solute separation. However, this factor is limited to the solutes having no attractive interaction with membrane material. In our previous works (Kiso *et al.* 2010, 2011), with using alcohols as the probe compounds, which are assumed not to be adsorbed on membrane polymer, the pore radii of NF membranes were successfully evaluated, where the pore model incorporated molecular shape parameters (molecular length and molecular width) for organic solutes were employed.

Most of hazardous organic micro-pollutants are low water solubility and hydrophobic, and it was pointed out that these compounds were adsorbed on membrane (Comerton *et al.* 2007, David *et al.* 2006, Jung *et al.* 2005, Kimura *et al.* 2003, Kiso *et al.* 2001a, b, Semião and Schäfer 2013). Adsorption of organic solutes influences solute separation performance and induces fouling. The adsorption of organic solutes was examined on the basis of the results from membrane separation experiments or batch type adsorption experiments with using membrane pieces. Almost all commercially available RO and NF membranes were composite membranes, and it may be unavoidable that the adsorption properties for organic solutes included the influence of support membranes. In order to examine the effects of solute adsorption on membrane, the adsorption experiment should be conducted with skin layer of membrane.

An inverse high performance liquid chromatography (HPLC) may be a useful approach to examine the interaction property between solid and liquid phases, where the term of inverse HPLC means HPLC application to evaluate the property of stationary phase. In our previous works (Kiso 1986, Kiso *et al.* 1989a, b), the inverse HPLC approach was employed for cellulose acetate and polyolefin; cellulose acetate has been used for a wide range of membranes, e.g., RO, NF, UF, and polyolefin for MF membranes. The powdered materials of these membrane polymers were able to be obtained and the fine particle fractions were used as a packing material for HPLC column. On the other hand, polyamide RO/NF membranes are made by surface polymerization on a support membrane, and therefore it is hard to obtain powdered polymer of skin layer.

In this study, poly (*m*-phenylenetrimesoylate: PPT) was coated on silica beads by surface polymerization, and the coated particles were packed into a HPLC column. The adsorption of organic compounds on the membrane surface was simulated on the basis of the retention properties of organic solutes in HPLC system with using water as a mobile phase. In the case of the solutes retained strongly on the stationary phase, CH<sub>3</sub>CN/H<sub>2</sub>O was also used as a mobile phase. The factors influencing the interaction between organic compounds and PPT were discussed based on the HPLC results.

## 2. Materials and methods

### 2.1 Column packing material

The polyamide stationary phase was coated on silica particles by surface polymerization (Kiso *et al.* In Submission) of *m*-phenylenediamine and trimesoylchloride by the following procedure: the silica gel particles (5 μm) used as a carrier for octadecylsilyl (ODS) column were impregnated with aquatic *m*-phenylenediamine (2% (w/v)) solution, and the particles were dropped into the *n*-hexane solution of trimesoylchloride (0.1% (w/v)) under dispersed condition. After the reaction (ca. 30 min), the reaction mixture was filtered, the solids were washed with *n*-hexane and methanol in this order, and finally the particles were dried. The specific surface area was measured

by BET method, and the value was 253 m<sup>2</sup>/g. The particles were packed into a HPLC column (4.6 mm i.d. × 250 mm long).

## 2.2 HPLC measurement

The HPLC system was consisted of a pump (PU-2080Plus, JASCO, Tokyo, Japan), a degasser (DG-2080-53, JASCO, Tokyo, Japan), a sample injector (20 μL, Rheodyne 7125, USA), a column oven (Co-2060Plus, JASCO, Tokyo, Japan), and a RI detector (830-RI, JASCO, Tokyo, Japan) for the aliphatic compounds or a UV-Vis detector (UV-2070, JASCO, Tokyo, Japan) for the aromatic compounds. The HPLC data were analyzed by data processing software (ChromNAV: JASCO, Tokyo, Japan). A column packed with PPT coated silica gel was equipped into the system. A column packed with silica gel particles uncoated with PPT was also prepared.

Distilled-deionized water was used as a mobile phase for hydrophilic organic compounds, and CH<sub>3</sub>CN/water (30/70) was for aromatic compounds, and the flow rate was 0.5 mL/min for each mobile phase. The column temperature was controlled at 15, 22, 30, and 40°C.

The retention property was evaluated with a capacity factor (*k'*). When the retention times of an organic solute and of an unretained compound were *t<sub>R</sub>* and *t<sub>0</sub>*, respectively, the capacity factor (*k'*) was expressed by the following equation

$$k' = \frac{t_R - t_0}{t_0}$$

When pure water was used as the mobile phase, deuterium oxide was used as an unretained solute. On the other hand, when CH<sub>3</sub>CN/H<sub>2</sub>O (30/70) was used as the mobile phase, NaNO<sub>3</sub> was used as an unretained compound.

## 2.3 Organic compounds

The polar aliphatic compounds and the aromatic compounds examined in this work are listed in Tables 1 and 2, respectively, and the logarithmic values of *n*-octanol/water partition coefficient (log *K<sub>o/w</sub>*), which is a typical index for hydrophobicity, were also described in these tables. The polar aliphatic compounds were dissolved into distilled-deionized water: the concentrations were in the range of 0.2-2% w/v. The aromatic compounds were dissolved into methanol at 100 mg/L.

The reagents were used without further purification (reagent grade, NACALAI TESQUE, Kyoto, Japan). The aliphatic compounds were detected by the RI detector, and the aromatic compounds were by the UV-Vis detector ( $\lambda = 220\text{-}374$  nm).

## 2.4 Octanol/water partition coefficient (log *K<sub>o/w</sub>*) measurement

The measurement of log *K<sub>o/w</sub>* was conducted by a shake-flask method in this work because of the following reasons: (1) the experimental data were not available for some compounds used in this work, only the results obtained by a shake-flask method give original log *K<sub>o/w</sub>* values; and (2) the calculated values of log *K<sub>o/w</sub>* for some compounds are unreliable.

Ultrapure water (Milli-Q water) and *n*-octanol (log *K<sub>o/w</sub>* measurement grade: Nacalai Tesque Inc., Kyoto, Japan) were used for the measurement of log *K<sub>o/w</sub>*. Prior to the partition experiment, the ultra pure water and the *n*-octanol were saturated with one another. The initial solute concentrations of *n*-octanol solutions were 50-10000 mg/L, and three initial concentration

Table 1 Aliphatic compounds examined in this study

Compounds	MWt	log $K_{o/w}$	Compounds	MWt	log $K_{o/w}$		
Alcohol			Ester				
1	methyl alcohol	32	-0.77	24	ethylformate	74	0.29*
2	ethyl alcohol	46	-0.31	25	propylformate	88	0.83
3	<i>n</i> -propyl alcohol	60	0.25	26	butylformate	102	1.37
4	<i>n</i> -butyl alcohol	74	0.88	27	ethylpropionate	102	1.21
5	<i>n</i> -pentyl alcohol	88	1.16	28	ethylacetate	88	0.73
6	<i>n</i> -hexyl alcohol	102	2.03	29	propylacetate	102	1.27*
7	<i>iso</i> -propyl alcohol	60	0.05	30	isopropylacetate	102	1.07*
8	<i>iso</i> -butyl alcohol	74	0.76	Amide			
9	<i>sec</i> -butyl alcohol	74	0.61	31	formamide	45	-1.53*
10	<i>tert</i> -butyl alcohol	74	0.35	32	N-methylformamide	59	-0.97
11	ethylene glycol	62	-1.36	33	N,N-dimethylformamide	73	-1.01*
12	glycerol	92	-1.76	34	N,N-diethylformamide	101	-0.38
Ethers			35	acetamide	59	-1.29*	
15	methyl <i>n</i> -propyl ether	74	1.04*	36	N-methylacetamide	73	-1.05
16	methyl <i>n</i> -butyl ether	88	1.58*	37	N-ethylacetamide	87	-0.51
17	1,4-dioxane	88	-0.27	38	N-butylacetamide	115	0.57
18	diethyl ether	74	0.89	39	N,N-dimethylacetamide	87	-0.77
19	di- <i>n</i> -propyl ether	102	2.03	40	N,N-diethylacetamide	115	0.15*
Aldehyde/Ketone			41	N,N-propylacetamide	143	1.07*	
20	formaldehyde	30	0.35	* : measured in this work			
21	propylaldehyde	58	0.59				
22	butylaldehyde	72	0.70*				
23	Methyl ethyl ketone	72	0.29				

solutions, typically 200, 100, and 50 mg/L, were prepared. The partition experiments were carried out by the shake-flask method. One or 2 mL of *n*-octanol solution and 10 or 8 mL of water saturated with *n*-octanol were put into a centrifuge tube (15 mL) made of glass, and the mixture was shaken by a reciprocal shaker for 24 h. in an incubation chamber controlled 25°C. Then, the mixture was stored in the incubation chamber for around 1 week under settling condition.

The solute concentrations in the *n*-octanol and the aqueous layers were analyzed with HPLC by direct injection method (Kiso *et al.* 1996, 1999) under the following conditions: an ODS column (VX-ODS, monomeric ODS, 5  $\mu$ m, 4.6 mm i.d., 250 mm long, Shinwa Chemical Co. Ltd., Kyoto, Japan), the mobile phase of CH<sub>3</sub>CN/H<sub>2</sub>O (CH<sub>3</sub>CN = 30-95%) at flow rate of 1.0 mL/min, and UV detection ( $\lambda$  = 220 or 254 nm). The aqueous solution of 2-5 mL was injected directly into the HPLC system: when 5 mL of aqueous sample was injected, sub  $\mu$ g/L of the concentration of the solute used in this work was detected. On the other hand, the *n*-octanol solution was diluted with methanol followed by the injection of 20  $\mu$ L into the HPLC system. The relative standard

Table 2 Aromatic compounds examined in this study

Compounds				Compounds			
	MWt	$\log K_{o/w}$	$\Delta H$ [kJ/mol]		MWt	$\log K_{o/w}$	$\Delta H$ [kJ/mol]
Polyaromatic hydrocarbon (PAH)				30	<i>o</i> -dichlorobenzene	147	3.38 -18.1
1	benzene	79	2.13 -26.8	31	<i>m</i> -dichlorobenzene	147	3.38 -17.5
2	naphthalene	128	3.30 -17.0	32	<i>p</i> -dichlorobenzene	147	3.39 -18.0
3	anthracene	178	4.45 -19.3	Alkylphenol (AOH)			
4	phenanthrene	178	4.46 -18.9	20	4-ethylphenol	122	2.58 -28.9
5	pyrene	202	4.88 -17.7	21	4- <i>n</i> -butylphenol	150	3.56* -23.2
6	chrysene	228	5.73 -22.1	22	4- <i>tert</i> -butylphenol	150	3.33* -24.7
Aromatic hydrocarbon (AH)				23	4-pentylphenol	164	4.06 -24.6
7	biphenyl	154	4.01 -19.1	24	4-heptylphenol	192	4.15 -22.6
8	2,2'-dimethylbiphenyl	182	5.05* -19.4	25	4- <i>n</i> -octylphenol	206	5.15* -23.5
9	4,4'-dimethylbiphenyl	182	5.09 -19.0	26	4-nonylphenol	220	5.43* -21.7
10	<i>o</i> -terphenyl	230	5.12* -20.2	Alkylphthalate (AP)			
11	<i>m</i> -terphenyl	230	5.63* -20.9	33	dimethyl phthalate	194	1.56 -21.2
12	<i>p</i> -terphenyl	230	6.03 -23.8	34	<i>p</i> -dimethyl phthalate	194	2.25 -16.3
13	triphenylmethane	244	5.46* -20.1	35	diethyl phthalate	222	2.47 -16.3
Alkyl benzene (AB)				36	<i>p</i> -diethyl phthalate	222	3.24* -16.1
14	toluene	92	2.73 -22.3	37	dipropyl phthalate	250	3.27 -15.8
15	ethylbenzene	106	3.15 -20.1	38	diisopropyl phthalate	250	2.83 -14.8
16	<i>n</i> -propylbenzene	120	3.68 -16.1	39	dibutyl phthalate	278	4.72 -16.6
17	<i>o</i> -xylene	106	3.12 -18.3	40	diisobutyl phthalate	278	4.11 -15.6
18	<i>m</i> -xylene	106	3.20 -18.9	41	dicyclohexyl phthalate	330	5.01* -15.5
19	<i>p</i> -xylene	106	3.15 -18.7	42	di(2-ethylhexyl) phthalate	390	7.45 -26.8
Halobenzene (HB)				*: measured in this work			
27	chlorobenzene	113	2.84 -19.0				
28	bromobenzene	157	2.99 -18.0				
29	iodobenzene	204	3.25 -18.0				

deviations of  $\log K_{o/w}$  were less than 5%, and the recoveries of solute in the measurement were in the range of 98-102%.

### 3. Results and discussion

#### 3.1 Aliphatic compounds

The polyaromatic hydrocarbons (PAHs) listed in Table 2 were not retained by the column packed with silica particles uncoated with PPT under the condition of water as a mobile phase. On

the other hand, benzene and toluene were retained by the stationary phase of PPT coated on silica particles. The results indicated that PPT was successfully coated on silica particle. The retention properties of aromatic compounds are to be described later.

Most of polar aliphatic compounds were hardly retained by the PPT column as shown in Fig. 1, where the capacity factor ( $k'$ ) was plotted against  $\log K_{o/w}$ . In the case of alcohols, only 1-hexanol, which is the highest hydrophobic compound among the alcohols, was obviously retained. The ethers showed small or no retention. The carbonyl compounds, such as aldehydes, ketones, esters, were retained by cellulose acetate column (Kiso 1986), but these compounds were not retained by the PPT column. In the case of the amides, however, the capacity factor ( $k'$ ) increased with the increase of  $\log K_{o/w}$ , although the compounds involve carbonyl group. The PPT polymer also involves amide group, and both amide groups in the solute and PPT (polyamide) may interact attractively by hydrogen bonding.

The following findings from the results can be given: hydrophilic aliphatic compounds with the exception of amides do not interact attractively or repulsively with membrane polymers. These

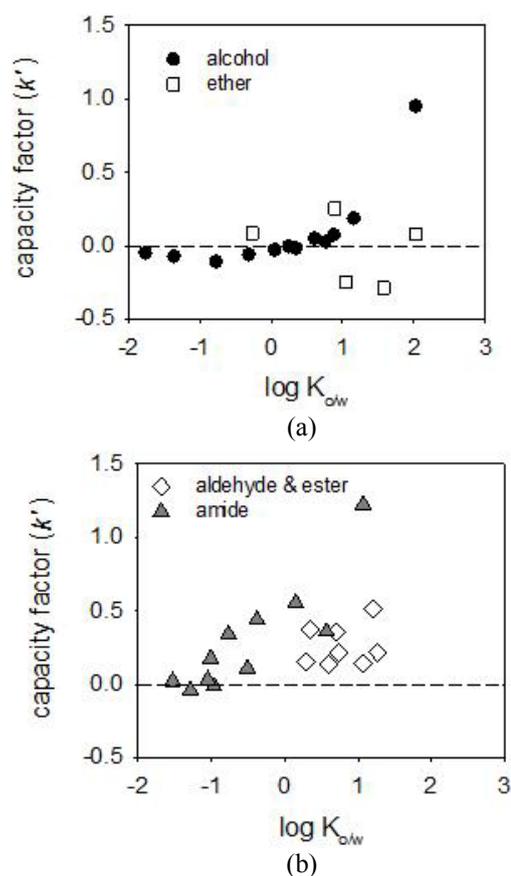


Fig. 1 Plots of capacity factor ( $k'$ ) vs.  $\log K_{o/w}$  (aliphatic compounds)

Stationary phase: PPT; mobile phase: water; flow rate: 0.5 mL/min; column temp.: 30°C

hydrophilic compounds may behave in a similar way of water in a pore of membrane and may be

useful probe compounds to evaluate pore radius by simulation with a pore model.

In our previous works (Kiso *et al.* 2010, 2011), alcohols (including diols and triols) were used as the probe solutes to evaluate the pore radii of RO/NF membranes, and in the simulation model a molecule was approximated as a perpendicular pipe (non-sphere). The results shown in Fig. 1 indicate that more variety of hydrophilic compounds can be used as a probe compound for the examination of molecular sieving effect. When a wide variety of organic compounds are used as a probe solute, the effects of molecular shape and/or functional group on permeation of solute may be possible.

### 3.2 Aromatic compounds

All aromatic compounds examined in this work were retained strongly in the case that water was used as a mobile phase and the adsorption property in aqueous phase could not be examined. Therefore, CH<sub>3</sub>CN/H<sub>2</sub>O (30/70) was used as a mobile phase, and even under the condition, all

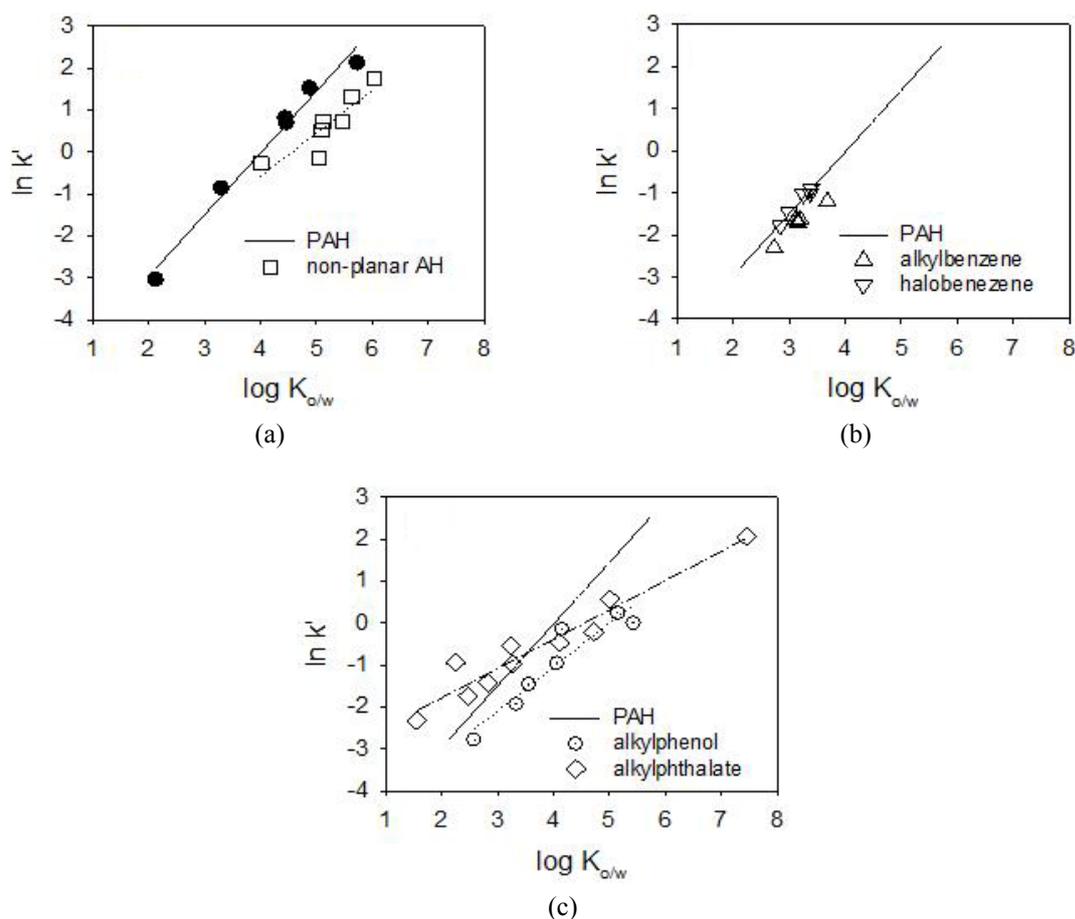


Fig. 2 Plots of capacity factor ( $k'$ ) vs.  $\log K_{o/w}$  (aromatic compounds)  
Stationary phase: PPT; mobile phase: CH<sub>3</sub>CN/water (30/70); flow rate: 0.5 mL/min; column temp.: 30°C

aromatic compounds were retained by the PPT column. In our previous works (Kiso 1986, Kiso *et al.* 1989a, b, 1999), it was indicated that  $\log K_{o/w}$  was a useful descriptor to examine the adsorption properties of organic compounds on membrane polymer such as cellulose acetate or polyolefin. Many researchers also used  $\log K_{o/w}$  for similar purpose. In this study,  $\log K_{o/w}$  was also employed as a descriptor to analyze the retention properties.

In the case of polyaromatic hydrocarbons (AHs), the logarithm of the capacity factor ( $\ln k'$ ) was linearly correlated with  $\log K_{o/w}$  as shown in Fig. 2(a), where the  $\ln k'$  at 30°C was plotted. The result is similar to those for cellulose acetate (Kiso 1986, Kiso *et al.* 1989a, b) and suggests that the adsorption is controlled by hydrophobic interaction. The regression line for PAHs was used as a reference to examine the adsorption properties of the other aromatic compounds.

The results for aromatic hydrocarbons (AHs) were plotted below the regression line for PAHs as shown in Fig. 2(a). PAHs are planar compounds, but AHs are non-planar shape compounds. The results for the AHs suggest that non-planarity may suppress the adsorption. In the cases of the alkylbenzenes (ABs) and the halobenzenes (HBs), the effects of the substituent were not recognized clearly (Fig. 2(b)). On the other hand, the alkylphenols (AOHs) and the alkylphthalates (APs) showed smaller slope of the regression line than that for PAHs (Fig. 2(c)). The alkyl substituents in AOHs and APs are larger than those in ABs, and long alkyl chain may hinder the adsorption between phenyl group and membrane. Whichever a substituents influenced the adsorption, it was clarified that aromatic compounds were strongly adsorbed on PPT, although the polar aliphatic compounds were hardly adsorbed. The important role of phenyl group on the adsorption on the membrane has been suggested by many researchers (Arsuaga *et al.* 2011, Comerton *et al.* 2007, David *et al.* 2006, Kimura *et al.* 2003a, b, Kiso *et al.* 2001a, b, Semião and Schäfer 2013, Shan *et al.* 2009), and it is pointed out that amino acids involving phenyl group were also strongly adsorbed on membrane than other amino acids (Shim *et al.* 2008).

### 3.3 Thermodynamic approach for the adsorption

The retention properties were measured at 4 different temperatures, and the enthalpy change for the adsorption was examined by van't Hoff plots of capacity factors ( $\ln k'$ ).

$$\ln k' = -\frac{\Delta H}{RT} + \text{const}$$

Although many polar aliphatic compounds were not effectively retained, the values of enthalpy change were evaluated for some of the aliphatic compounds: the correlation coefficients for van't Hoff plots were more than 0.9456 (average: 0.9826). The values of  $\Delta H$  were in the range from -9.8 kJ/mol (butyl aldehyde) to -35.8 kJ/mol (N-metylacetamide). Considering the low capacity factors, the values of  $\Delta H$  were not high precise, but it may be possible to examine the effects of functional group on the adsorption. Fig. 3 shows the relationship between  $\log K_{o/w}$  and  $\Delta H$  for alcohols, amides, aldehydes, and esters. A significant correlation was not observed for aldehydes and esters, but in the cases of alcohols and amides,  $\Delta H$  was negatively correlated with  $\log K_{o/w}$ . The increase of  $\log K_{o/w}$  is caused by the increase of alkyl chain in each homologous group, and therefore, the results in Fig. 3 suggest that functional groups of -OH and >NCO- are attracted to amide group in the polymer by hydrogen bonding, and alkyl chain hinder the interaction.

In the case of aromatic compounds, the enthalpy change was calculated for all compounds, and the results are also described in Table 2. The precise  $\Delta H$  values were obtained because of large

capacity factors. The correlation coefficients for vant' Hoff plots were very high (average: 0.9936), although di (2-ethylhexyl) phthalate was low at 0.9447. The values of  $\Delta H$  under the condition of the mobile phase ( $\text{CH}_3\text{CN}/\text{H}_2\text{O}=30/70$ ) were in the range of  $-28.9 \sim -14.8$  kJ/mol.

Fig. 4 shows the plots of  $\log K_{o/w}$  versus  $\Delta H$  for each group. In the case of aromatic hydrocarbons (PAHs, and non-planar AHs), negative correlation was found. The adsorption energy increased with the increase of hydrophobicity or scale of fused ring. On the other hand, the positive correlation was observed for alkylbenzenes and halobenzenes, and this suggests that substituent hindered the attractive interaction between phenyl group and membrane polymer. In the cases of alkylphenols and alkylphthalates, however, significant correlation was not found.

When the aromatic compounds were rearranged in the order of magnitude of  $\Delta H$ ,  $|\Delta H|$  decreased roughly in the following order: AOH > AH/PAH > AB > HB > AP. Relatively large  $|\Delta H|$  values of the alkylphenol may be caused by hydrogen bonding between  $-\text{OH}$  group of AOH and amide group in PPT. On the other hand, the adsorption for alkylphthalates may be hindered by long alkyl chain.

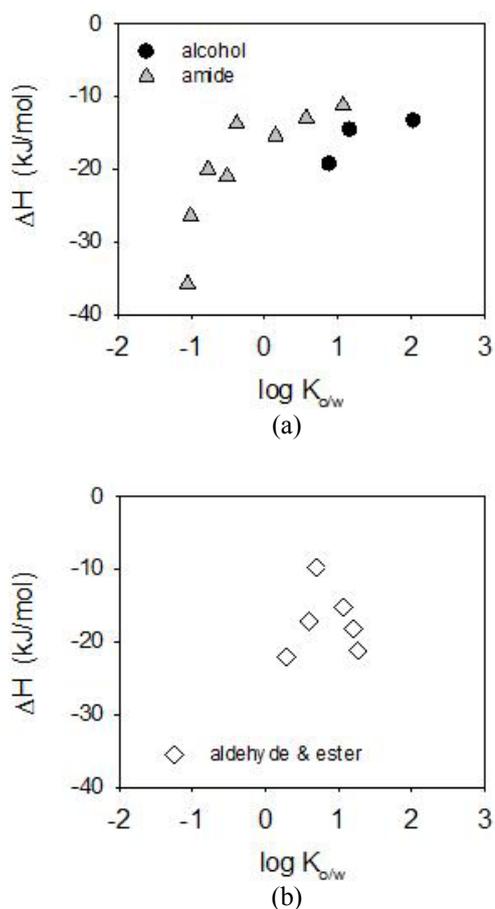


Fig. 3 Relationship between enthalpy change ( $\Delta H$ ) and  $\log K_{o/w}$  (aliphatic compounds)  
Stationary phase: PPT; mobile phase: water

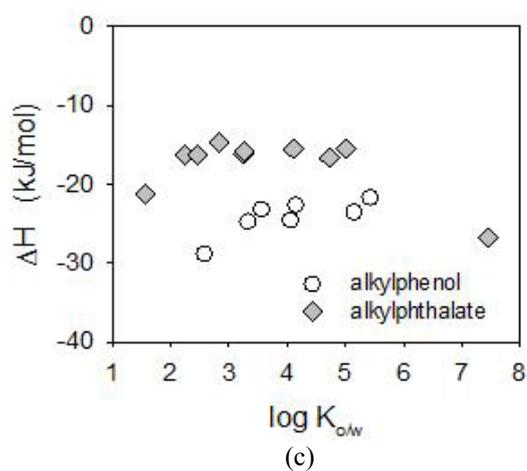
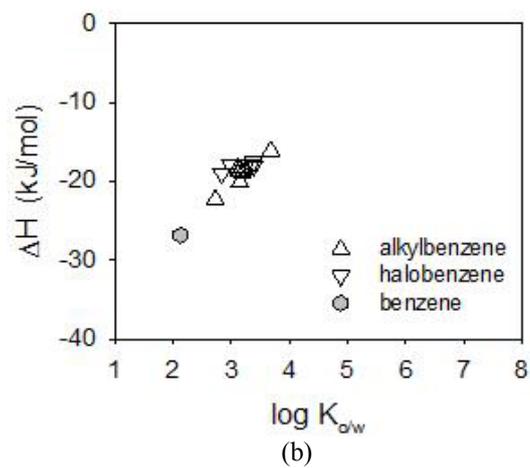
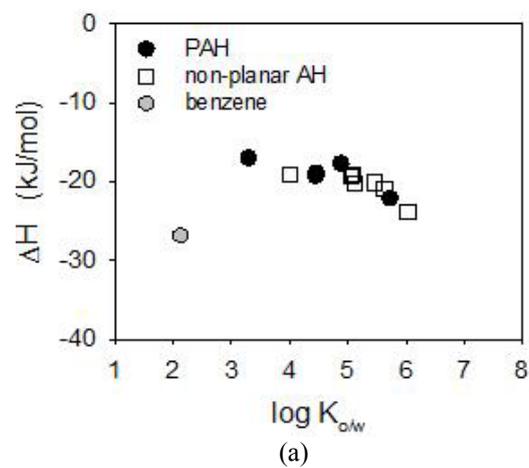


Fig. 4 Relationship between enthalpy change ( $\Delta H$ ) and  $\log K_{ow}$  (aromatic compounds)  
Stationary phase: PPT; mobile phase: CH<sub>3</sub>CN/water (30/70)

Considering the above results, we can conclude that phenyl group interacts specifically with PPT and the interaction is hindered by both non-planar structure and substituents. This suggests that the specific interaction may be caused by stacking of the aromatic ring of solute on the benzene ring in the polyamide.

#### 4. Conclusions

The adsorption properties of organic compounds on poly(*m*-phenylenetrimesoylate: PPT), skin layer of polyamide RO/NF membranes, were successfully examined by an inverse HPLC method, where the silica gel particles coated with PPT were used as a stationary phase. Polar aliphatic compounds were not adsorbed effectively on the polymer, although relatively hydrophobic compounds were adsorbed slightly. The results suggest that the polyamide RO/NF membranes reject hydrophilic aliphatic compounds by molecular sieving mechanism. In addition, it was indicated that the adsorption of the amide compounds was caused by hydrogen bonding between amide groups in both solute and PPT.

Aromatic compounds were strongly adsorbed on PPT in aqueous phase, and therefore CH<sub>3</sub>CN/H<sub>2</sub>O (30/70) was used as a mobile phase. It was revealed that the adsorption of these compounds was controlled by a specific interaction (e.g. stacking) between phenyl groups in both solute and membrane polymer. Non-planar structure and substituents were hindered the adsorption.

Although the fundamental information for adsorption of organic solutes was obtained, the quantitative analysis for the contribution of the solute adsorption remains as an important subject to the estimation of removal performance in membrane separation processes. The adsorption of solutes on support membranes may also influence in membrane separation processes.

#### Acknowledgments

This work was financially supported by the Research Project on Development of Innovative Membrane Separation Technology, sponsored by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

#### References

- Agenson, K.O. and Urase, T. (2007), "Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications", *Sep. Purif. Technol.*, **55**(2), 147-156.
- Arsuaga, J.M., Sotto, A., López-Muñoz, M.J. and Braeken, L. (2011), "Influence of type and position of functional groups of phenolic compounds on NF/RO performance", *J. Membr. Sci.*, **372**(1-2), 380-386.
- Comerton, A.M., Andrews, R.C., Bagley, D.M. and Yang, P. (2007), "Membrane adsorption of endocrine disrupting compounds and pharmaceutically active compounds", *J. Membr. Sci.*, **303**(1-2), 267-277.
- David, A.B., Bason, S., Jopp, J., Oren, Y. and Freger, V. (2006), "Partitioning of organic solutes between water and polyamide layer of RO and NF membranes: Correlation to rejection", *J. Membr. Sci.*, **281**(1-2), 480-490.
- Jung, Y.J., Kiso, Y., Othman, R.A.A.b., Ikeda, A., Min, K.S., Kumano, A. and Arijji, A. (2005), "Rejection properties of aromatic pesticides with a hollow fiber NF membrane", *Desalination*, **180**(1-3), 63-71.
- Kimura, K., Amy, G., Drewes, J.E., Heberer, T., Kim, T.U. and Watanabe, Y. (2003a), "Rejection of organic

- micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes”, *J. Membr. Sci.*, **227**(1-2), 113-121.
- Kimura, K., Amy, G., Drewes, J. and Watanabe, Y. (2003b), “Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection”, *J. Membr. Sci.*, **221**(1-2), 89-101.
- Kiso, Y. (1986), “Factors affecting adsorption of organic solutes on cellulose acetate in an aqueous solution system”, *Chromatographia*, **22**(1-6), 55-58.
- Kiso, Y., Kitao, T., Sheng, G.Y. and Jinno, K. (1989a), “Retention characteristics of aliphatic compounds on cellulose acetate as a stationary phase with an aqueous mobile phase”, *Chromatographia*, **28**(5-6), 279-284.
- Kiso, Y., Takayama, K. and Jinno, K. (1989b), “Cellulose acetates as the stationary phase in microcolumn LC”, *J. High Resolution Chromatography*, **12**(3), 169-173.
- Kiso, Y., Li, H., Shigetoh, K., Kitao, T. and Jinno, K. (1996), “Pesticide analysis by high-performance liquid chromatography using the direct injection method”, *J. Chromatography A.*, **733**(1-2), 259-266.
- Kiso, Y., Kitao, T. and Nishimura, K. (1999), “Adsorption properties of aromatic compounds on polyethylene as a membrane material”, *J. Appl. Polym. Sci.*, **74**(5), 1037-1043.
- Kiso, Y., Nishimura, Y., Kitao, T. and Nishimura, K. (2000), “Rejection properties of non-phenylic pesticides with nanofiltration membranes”, *J. Membr. Sci.*, **171**(2), 229-237.
- Kiso, Y., Kon, T., Kitao, T. and Nishimura, K. (2001a), “Rejection properties of alkyl phthalates with nanofiltration membranes”, *J. Membr. Sci.*, **182**(1-2), 205-214.
- Kiso, Y., Sugiura, Y., Kitao, T. and Nishimura, K. (2001b), “Effects of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes”, *J. Membr. Sci.*, **192**(1-2), 1-10.
- Kiso, Y., Mizuno, A., Othman, R.A.A., Jung, Y.J., Kumano, A. and Arijji, A. (2002), “Rejection properties of pesticides with a hollow fiber NF membrane (HNF-1)”, *Desalination*, **143**(2), 147-157.
- Kiso, Y., Muroshige, K., Oguchi, T., Yamada, T., Hirose, M., Ohara, T. and Shintani, T. (2010), “Effect of molecular shape on the rejection of uncharged organic compounds by nanofiltration membranes and on calculated pore radii”, *J. Membr. Sci.*, **358**(1-2), 101-113.
- Kiso, Y., Muroshige, K., Oguchi, T., Hirose, M., Ohara, T. and Shintani, T. (2011), “Pore radius estimation based on organic solute molecular shape and effects of pressure on pore radius for a reverse osmosis membrane”, *J. Membr. Sci.*, **369**(1-2), 290-298.
- Kiso, Y., Kamimoto, Y., Hosogi, K. and Jung Y.J., “Inverse HPLC approach for the evaluation of repulsive interaction between ionic solutes and a membrane polymer”, *Membr. Water Treat., Int. J.* [In Submission]
- Koo, C.H., Mohammad, A.W. and Suja, F. (2011), “Recycling of oleochemical wastewater for boiler feed water using reverse osmosis membranes – A case study”, *Desalination*, **271**(1-3), 178-186.
- Plakas, K.V. and Karabelas, A.J. (2008), “Membrane retention of herbicides from single and multi-solute media: The effect of ionic environment”, *J. Membr. Sci.*, **320**(1-2), 325-334.
- Plakas, K.V. and Karabelas, A.J. (2011), “A systematic study on triazine retention by fouled with humic substances NF/ULPRO membranes”, *Sep. Purif. Technol.*, **80**(2), 246-261.
- Semião, A.J.C. and Schäfer, A.I. (2013), “Removal of adsorbing estrogenic micropollutants by nanofiltration membranes. Part A—Experimental evidence”, *J. Membr. Sci.*, **431**, 244-256.
- Shan, J.H., Hu, J.Y. and Ong, S.L. (2009), “Adsorption of neutral organic fractions in reclaimed water on RO/NF membrane”, *Sep. Purif. Technol.*, **67**(1), 1-7.
- Shim, Y., Rixey, W.G. and Chellam, S. (2008), “Influence of sorption on removal of tryptophan and phenylalanine during nanofiltration”, *J. Membr. Sci.*, **323**(1), 99-104.
- Yoon, Y., Westerhoff, P., Snyder, S.A. and Wert, E.C. (2006), “Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products”, *J. Membr. Sci.*, **270**(1-2), 88-100.
- Zhang, Y. and Pagilla, K. (2010), “Treatment of malathion pesticide wastewater with nanofiltration and photo-Fenton oxidation”, *Desalination*, **263**(1-3), 36-44.