Separation of Endocrine Disruptors from Aqueous Solutions by Pervaporation: Dioctylphthalate and Butylated Hydroxytoluene in Mineral Water

Akon Higuchi,[1] Boo Ok Yoon,[1] Takayuki Kaneko,[1] Mariko Hara,[1] Maya Maekawa,[2] Takashi Nohmi[2]

[1]*Department of Applied Chemistry, Seikei University, 3–3-1 Kichijoji Kitamachi, Musashino 180-8633, Japan*
[2]*Nohmi Bosai Ltd., 14−4 Nishi-shinjuku 3-chome, Shinjyuku-ku, Tokyo 160-0023, Japan*

Received 4 November 2003; accepted 27 May 2004
DOI 10.1002/app.21093
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We examined the existence of endocrine disruptors in mineral water, ultrapure water, and tap water. GC/MS analysis revealed that dioctylphthalate (di-*n*-octylphthalate and di(2-ethylhexyl)phthalate) in the water was found to be on the order of parts per billion. The dioctylphthalate concentration remained consistent for mineral water of the same brand, regardless of whether it was bottled in a PET bottle or a glass bottle. Therefore, the dioctylphthalate contamination in mineral water originated from the manufacturing line of the mineral water and not as a result of leaching from PET bottles. Butylated hydroxytoluene (BHT), an oxidization prevention agent in plastics, was detected at 2.05 ± 0.1 ppb in the mineral water bottled in glass bottles, but was not detected in the mineral water bottled in PET bottles. BHT contamination in the mineral water in the glass bottles is likely to have originated from the cap of the glass bottles, as the caps were sealed with polyethylene. We further investigated the feasibility of separating dioctylphthalate and BHT from the mineral water by pervaporation using hydrophobic polydimethylsiloxane membranes. We found that trace amounts (on the order of parts per billion) of organic chemicals such as dioctylphthalate and BHT in aqueous solutions can be removed and concentrated by the pervaporation using polydimethylsiloxane membranes. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1737–1742, 2004

Key words: membrane; mineral water; endocrine disruptors; pervaporation; GC-MS

INTRODUCTION

Endocrine disruptors (ED), such as polychlorinated biphenyls (PCB), dioxins, and certain phthalates, exhibit estrogenic activity.[1,2] They adversely affect the development and reproduction of humans and animals,[3,4] and thus their presence in the environment is of major concern.

Zimmerman et al. reported analysis and detection of herbicides (dimethenamid and flufenacet) and their sulfonic and oxanilic acid degradates in a natural water sample taken from near the mouth of the Mississippi River.[5] The ethanesulfonic acid degradates from flufenacet were detected in the samples collected at the peak of the herbicide spring flush in 2000.[5]

Hanaoka et al. measured the concentration of organochlorines in serum and investigated the relationship between the concentration of contaminants in serum and the dietary intake of rural residents in Japan.[6] The residual DDT was found to be positively correlated with the consumption of meat, fish, vegetables, and milk.[6]

Fiedler et al. analyzed the concentration of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofuran, and chlorinated pesticides in Chinese tea (two green teas and two brick teas).[7] The levels of DDT and its metabolites in tea leaves were estimated to be within the limit of safe intake (0.2 mg/kg). However, rather high levels of total polycyclic aromatic hydrocarbons were reported in brick tea compared with green tea.[7]

In this study, we examined the existence of phthalate endocrine disruptors in a number of drinking water samples (commercial mineral water and tap water) and found the dioctylphthalate [di-*n*-octylphthalate (DOP) and di(2-ethylhexyl)phthalate (DEHP)] concentrations to be on the order of parts per billion. We further investigated the feasibility of separating dioctylphthalates from contaminated water samples by pervaporation using hydrophobic polydimethylsiloxane (PDMS) membranes. In the pervaporation process, an aqueous feed solution is brought into contact with one side of a semipermeable membrane, while a vacuum is applied to the other side to maintain a partial pressure. The different species in

Correspondence to: A. Higuchi (higuchi@ch.seikei.ac.jp).
Contract grant sponsor: Salt Science Foundation.

the feed mixture have different affinities for the membrane and different diffusion rates through the membrane. They sorb into the membrane, permeate through it, evaporate into the vapor phase, and are finally removed and condensed.

The pervaporation process has been successfully used in the dehydration of alcohols,[8,9] as well as in the removal of dissolved volatile organic compounds from water.[10–19] Böddeker and co-workers investigated the removal of low-volatility aromatic hydrocarbons [i.e., thymole (MW = 150.2 g/mol) and vanillin (MW = 152.2 g/mol)] from dilute aqueous solutions through polyether-*block*-polyamide membranes by pervaporation.[11,12] In their study, very high separation factors were observed (thymole over water α = 380 and *o*-dichlorobenzene over water α = 1000).[11] In most of the previous studies,[12–17] organic compounds removed from aqueous solutions by pervaporation were volatile organic solvents such as benzene, toluene, chloroform, and trichloroethylene having molecular weights of less than 170 g/mol. Most endocrine disruptors have a high molecular weight (e.g., dioctylphthalate) and a very low vapor pressure (e.g., dioctylphthalate) and are nearly insoluble in water.

We previously reported the removal of endocrine disruptors from extremely dilute aqueous solutions through hydrophobic polydimethylsiloxane membranes by pervaporation.[18,19] EDs such as coplanar PCB, dibenzo-*p*-dioxin, and 1,2-dibromo-3-chloropropane (DBCP) were concentrated 30–1300 times in the permeate.[18,19] A relatively high correlation between the logarithm of the separation factor and p_{vap} (vapor pressure) x log K_{ow} (octanol–water partition coefficient) was found experimentally in the pervaporation of the endocrine disruptors.[19]

Here we report the concentration of dioctylphthalate in commercially available drinking water and in tap water. Moreover, we confirmed that pervaporation using PDMS membranes could be used to successfully remove dioctylphthalate from drinking water with separation factors of 106 ± 10.

EXPERIMENTAL

Materials

Commercially available mineral water [PET bottles: Evian (Calpis Itochu Mineral Water Co., Ltd.), Volvic (Danon Waters of Japan, Co., Ltd.), Crystal Geyser (Otsuka Beverage Co., Ltd.), and Izumono Karadauruou Alkali Ion Natural Water (K F G Co., Ltd.), glass bottle: Evian (Calpis Itochu Mineral water Co., Ltd.)] was used in this study. The brand names of these mineral waters were randomly denoted as Brands A, B, C, and D in this study. Four bottles of each brand of mineral water were purchased from different stores located in Musashino-shi, Tokyo.

A flat-sheet PDMS membrane (SR30, Tigers Polymer, Co., Ltd.) with a thickness of 300 μm was used. Prior to use, the PDMS membrane was rinsed with 2-propanol for 24 h 10 times and then dried subsequently under vacuum for 12 h.

DOP (MW = 390.6 g/mol, vapor pressure = 2.6 $\times$ 10^{-6} Torr at 25°C, octanol–water partition coefficient logK_{ow} = 8.1[20]) and butylated hydroxytoluene (BHT, MW = 220.3 g/mol, vapor pressure = 9.75 $\times$ 10^{-3} Torr at 25°C, logK_{ow} = 5.1[20] were purchased from Wako Pure Chemicals Industries, Ltd. Other chemicals were of reagent grade and were used without further purification.

Analysis of drinking water

A total of 100 mL of commercially available mineral water was extracted with 10 mL of hexane twice. The resulting hexane phase was dehydrated with a suitable amount (about 2.7 g) of anhydrous sodium sulfate. The hexane extract (10 times concentration) was also concentrated by an evaporator in some cases (100 times concentration). Thereafter, the extract was analyzed by a gas chromatograph (GC)/mass spectrometer (MS) (GC/MS-QP5050A, Shimadzu Co.) equipped with a type AOC-20 autosampler (Shimadzu Co.) and a DB-1 capillary column (0.25 mm inner diameter of 30 m, J and W Scientific Co.). For comparison, ultrapure water (MilliQ plus + Elix, Millipore Co.), tap water from the laboratory (Seikei University, Tokyo), and tap water after a cleaning treatment through a water purifier using activated carbon were also used instead of the mineral water in the above procedures. In GC/MS, both the injection and the detection temperatures were set at 300°C. The column temperature was programmed as follows: 70°C for 1 min, heating at 5°C/min up to 300°C, and temperature maintenance at 300°C for 10 min.

Pervaporation

Permeation experiments were performed using a standard pervaporation (PV) apparatus.[13,18,19] The effective membrane area of the PV cell was 15.2 cm^2. The revolution speed of magnetic spinbars in the PV cell was controlled (i.e., 300 rpm in this study) by a magnetic stirrer for agitation of feed solution in the PV cell. The downstream (permeate) pressure was kept below 7 hPa in all experiments. The permeate solution was collected in a cold trap by liquid nitrogen at regular time intervals (1 h) and then analyzed by a gas chromatograph-mass spectrometer mentioned previously. The separation factor (α) of PV was calculated according to Eq. (1),

$$\alpha = X_p/Y_p \,/\, X_f/Y_f, \qquad (1)$$

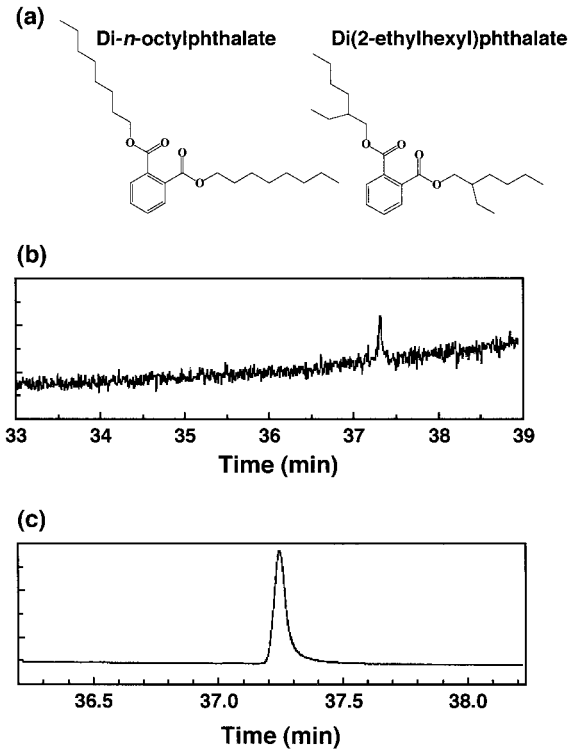

Figure 1 Scheme of dioctylphthalate (a) and chromatograms of extracts from the mineral water containing PET bottles (Brand A) as determined by EI mode (b) and SIM mode (c) in GC/MS measurements.

where X_f and Y_f are the weight fractions of endocrine disruptor (X) and water (Y) in the feed solution, and X_p and Y_p are the weight fractions of the components in the permeate.

The PV cell was wound with a flexible insulated heating sheet and the temperature of the feed solution (T_{feed}) was regulated to be the desired temperature (90°C in this study) using a temperature controller. The temperature of the membrane was regulated to be the same temperature to the feed solution using a flat sheet heater located under the PV cell in this study.[18,19] The vacuum line between the PV cell and the cold trap on the permeate side was wound with flexible insulated heating tapes and the temperature of the vacuum line ($T_{interface}$) was regulated to be the desired temperature (i.e., 150°C in this study) using a temperature controller.[18,19]

RESULTS AND DISCUSSION

Concentration of dioctylphthalate in mineral water

Commercially available mineral water (Brand A) bottled in PET bottles was analyzed by GC/MS to determine whether endocrine disruptors were present as contaminants in the mineral water. Figure 1 shows the chromatograms of extracts from the mineral water (Brand A) as determined by GC/MS analysis. The presence of dioctylphthalate [OP, di-*n*-octylphthalate and di(2-ethylhexyl)phthalate] was confirmed at a retention time of 37.3 min in the extract from mineral water by measurements in both electron ionization (EI) mode and selected ion monitoring (SIM) mode. The dioctylphthalate peak was not seen in the chromatogram of a 10 times concentration of mineral water by hexane extraction in EI mode, likely due to its low detection limit when compared with that of SIM mode. The concentration of dioctylphthalate in the mineral water was estimated as 0.66 ± 0.1 ppb from a 10 times concentration (hexane extraction) and 0.72 ± 0.1 ppb from a 100 times concentration (hexane extraction followed by an evaporation stage to concentrate) in SIM mode. Experimental error was found to be less than 5%, which may be attributed to the use of different concentration methods for the mineral water samples.

The origin of the dioctylphthalate was thought to be either from a plasticizer in the PET bottles or from the manufacturing line of the mineral water. To identify the source of contamination, mineral water bottled in glass bottles was analyzed by GC/MS in parallel. Figure 2 shows a chromatogram of 10 or 100 concentrate extracts from the mineral water (Brand A) contained in glass bottles. Dioctylphthalate was also observed in the mineral water bottled in glass bottles. Therefore, dioctylphthalate contaminants in the mineral water are thought to have originated from the manufacturing line of the mineral water. More interestingly, BHT was detected at a retention time of 17.2 min at a concentration of 2.05 ± 0.1 ppb. This BHT impurity was not, however, detected in the mineral water in PET bottles (Fig. 1). Butylated hydroxytoluene is an oxidization prevention agent used in plastics such as polyethylene. The insides of the caps of the

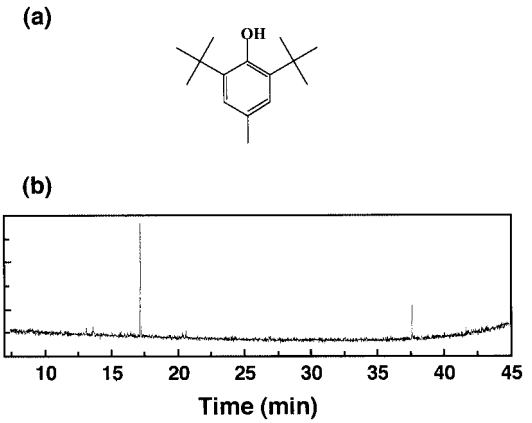

Figure 2 Scheme of BHT (a) and chromatograms of extracts from the mineral water (Brand A) contained in the glass bottles as determined by EI mode in GC/MS measurements (b).

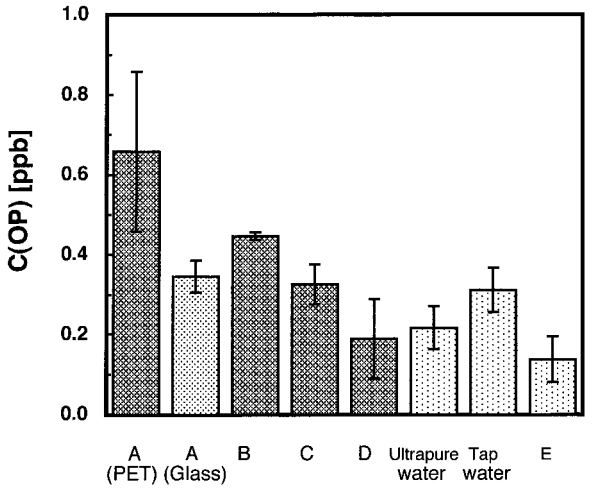

Figure 3 Concentration of dioctylphthalate in drinking water as determined by GC-MS measurements. A, B, C, and D indicate the mineral water in PET bottles (A, B, C, and D) and glass bottle (A). E indicates tap water after cleaning treatment through water purifier.

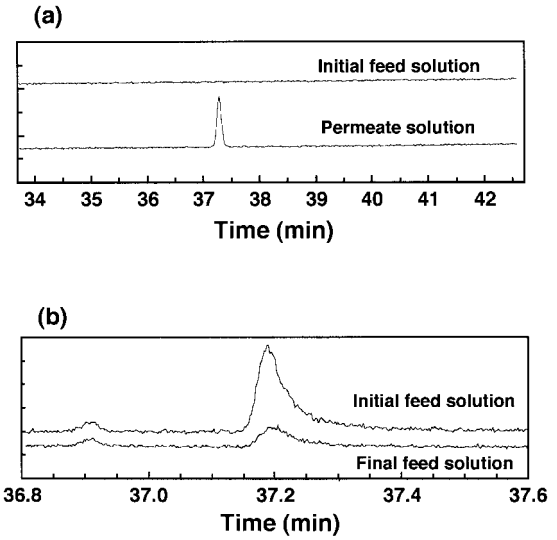

Figure 4 Chromatograms of extracts from the mineral water (Brand A) contained in the PET bottles before and after pervaporation as determined by EI mode (a) and SIM mode (b) in GC/MS measurements.

glass bottles were sealed with plastic, which was identified as polyethylene by attenuated total reflection-infrared red (ATR-IR) spectroscopy measurements (MIRacle, Pike Technologies, Inc., and FT/IR 670, Jasco Co.). Therefore, we were able to conclude that the BHT found in the mineral water in glass bottles originated from the plastic used to seal the caps.

The concentration of dioctylphthalate in mineral water of various brands as well as tap water in the laboratory was analyzed by GC/MS. Figure 3 shows that the concentrations of dioctylphthalate, *C*(OP), in various drinking waters were less than 1.0 ppb. The concentration of dioctylphthalate in Brand A bottled in PET bottles was found to be the highest of the water examined in this study. The concentration of dioctylphthalate in ultrapure water and tap water was relatively low after a cleaning treatment using a water purifier was performed. The additional cleaning treatment performed on the ultrapure water and the tap water used an activated carbon system. Therefore, it is believed that the dioctylphthalate in drinking water would also be reduced if treated with activated carbons, as activated carbons are reported to adsorb the phthalate group of diethylphthalate, dibutylphthalate, and dioctylphthalate.[21]

Although the phthalate group is suspected to be an endocrine disruptor, the upper limit of phthalate present in drinking water has not yet been established and none of the dioctylphthalate concentration levels reported in this study is considered to be illegal.

Removal of dioctylphthalate by PV

The possibility of removing dioctylphthalate from drinking water by pervaporation using PDMS membranes was investigated. Figure 4 shows the chromatograms of mineral water (Brand A) bottled in PET bottles before and after pervaporation. After 10 h of pervaporation, the concentration of dioctylphthalate was reduced to less than 1/10 of the initial concentration. Table I shows the separation factor of dioctylphthalate in pervaporation when several water samples with different dioctylphthalate concentrations were used as the feed solution. It was found that dioctylphthalate was successfully removed from water under pervaporation using a PDMS membrane. The separation factor of dioctylphthalate using the PV method was averaged to be 106 ± 10 in this study.

The possibility of removing BHT by the PV method was also examined in this study. Figure 5 shows the chromatograms of mineral water (Brand A) bottled in glass bottles before and after pervaporation. The BHT peak, previously seen at 17.2 min, was unable to be detected in the final feed solution after 10 h of perva-

TABLE I
Separation Factor of Dioctylphthalate (OP) in the Pervaporation of Various Water through PDMS Membranes

Feed solution	Concentration of OP in initial feed solution (ppm)	α
Mineral water (Brand A) in PET bottle	0.639	106
Mineral water (Brand B) in PET bottle	0.456	108
Mineral water (Brand C) in PET bottle	0.311	102
Mineral water (Brand A) in glass bottle	0.347	98
Ultrapure water	0.210	106
Tap water	0.323	114

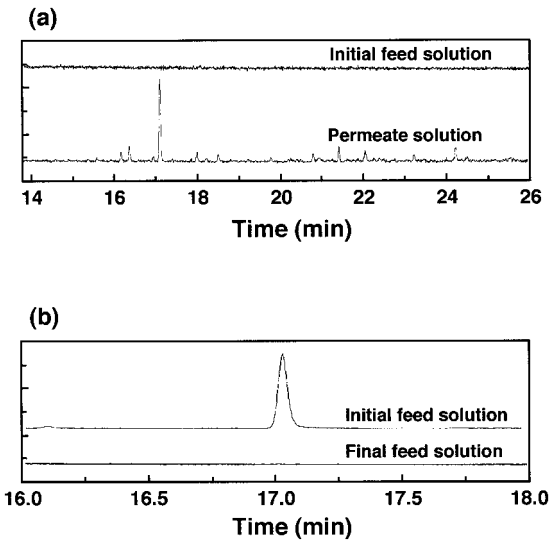

Figure 5 Chromatograms of extracts from the mineral water (Brand A) contained in the glass bottles before and after pervaporation as determined by EI mode (a) and SIM mode (b) in GC/MS measurements.

poration (Fig. 5b), but was shown in permeate (Fig. 5a). The separation factor of BHT was calculated to be 235 ± 15.

We found that trace amounts (on the order of ppb) of organic chemicals such as dioctylphthalate and BHT in aqueous solution can be removed and concentrated by the PV method using hydrophobic PDMS membranes.

In a previous study,[19] we theoretically concluded that the separation factor (α) of EDs was directly related to the product of p_{vap} (the saturated vapor pressure of the endocrine disruptor) and log K_{ow} (the partition coefficient between octanol and water) in the pervaporation of endocrine disruptors contained in aqueous solution through PDMS membranes. Briefly, the relationship was theoretically derived as described below.[19]

The separation factor by pervaporation is described from Eq. (1) by

$$\alpha = [J(\mathrm{ED})/J(\mathrm{H_2O})] \,/\, [X_f/Y_f], \tag{2}$$

where J(ED) and $J(H_2O)$ are the flux of the endocrine disruptor and water, respectively. Because the concentration of endocrine disruptors in the feed solution is dilute (less than 10 ppm), $X_f \ll 1$ and therefore $Y_f \cong 1$. Equation (2) is reduced to Eq. (3).

$$\alpha = [J(\mathrm{ED})/J(\mathrm{H_2O})]/X_f \tag{3}$$

The driving force of solute permeation through the membrane by pervaporation, dp/dx, is described by Raoult's law[22] with the assumption that the vapor pressure of solute on the permeate side is zero due to the vacuum on the permeate side:

$$dp/dx = -X_f \cdot p_{vap}(\mathrm{ED})/L \quad \text{for endocrine disruptor permeation} \tag{4}$$

and

$$dp/dx = -Y_f \cdot p_{vap}(\mathrm{H_2O})/L \quad \text{for } H_2O \text{ permeation,} \tag{5}$$

where L is the membrane thickness, and p_{vap}(ED) and $p_{vap}(H_2O)$ are the saturated vapor pressure of the endocrine disruptor and water, respectively. Since concentration of EDs is dilute, Eq. (5) reduces to Eq. (6).

$$dp/dx = -p_{vap}(\mathrm{H_2O})/L \quad \text{for } H_2O \text{ permeation.} \tag{6}$$

The solubility of an endocrine disruptor in a PDMS membrane, S(ED), from an aqueous dilute solution of endocrine disruptor should be related to the partition coefficient between octanol and water (log K_{ow}) as Eq. (7), because the solubility of an endocrine disruptor, S(ED), in a hydrophobic PDMS membrane is reported to increase with increasing hydrophobicity of the endocrine disruptor,[21] and the hydrophobicity of the solute (endocrine disruptor) increases with an increasing value of log K_{ow} of endocrine disruptors.[21] Thus,

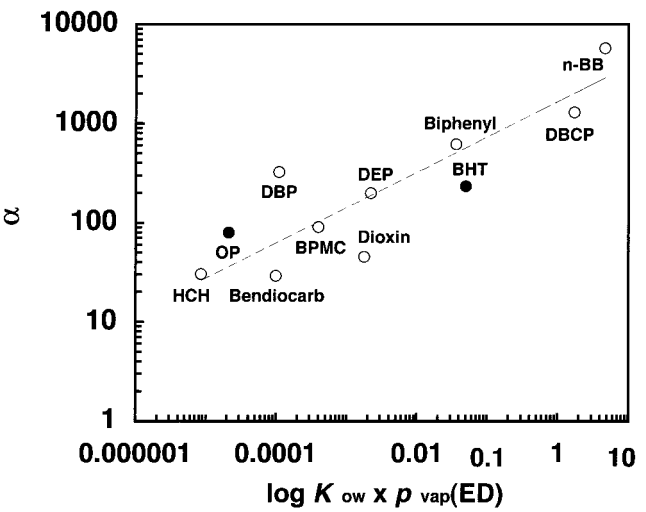

Figure 6 Relationship between the separation factor of endocrine disruptors by pervaporation and log $K_{ow} \cdot p_{vap}$ (ED) based on the theoretical equation of Eq. (10). The separation factors of *n*-butylbenzene (*n*-BB), 1,2-dibromo-3-chloropropane (DBCP), biphenyl, dibenzo-*p*-dioxin (dioxin), diethylphthalate (DEP), dibuthylphthalate (DBP), hexachlorohexane (HCH), 2-*sec*-butylphenylmethyl-carbamate (BPMC) and 2,2-dimethyl-1,3-benzodioxol-4-yl methylcarbamate (bendiocarb) were referred from Ref. 19.

in this study, S(ED) is assumed to be linearly related to log K_{ow} of endocrine disruptors in this study.[19]

$$S(\mathrm{ED}) = \gamma \cdot \log K_{ow}, \quad (7)$$

where γ is a constant.

Combining Eqs. (3), (4), (6), and (7), the separation factor is obtained as Eq. (8).

$$\alpha = [D(\mathrm{ED}) \cdot S(\mathrm{ED}) \cdot p_{vap}(\mathrm{ED})]/ [D(\mathrm{H_2O}) \cdot S(\mathrm{H_2O}) \cdot p_{vap}(\mathrm{H_2O})] = \beta \cdot D(\mathrm{ED}) \cdot \log K_{ow} \cdot p_{vap}(\mathrm{ED}), \quad (8)$$

where $\beta = \gamma / [D(\mathrm{H_2O}) \cdot S(\mathrm{H_2O}) \cdot p_{vap}(\mathrm{H_2O})]$ is a constant, and D(ED) and $D(\mathrm{H_2O})$ are the diffusion coefficients of an endocrine disruptor in the membrane and water in the membrane, respectively. $S(\mathrm{H_2O})$ is the solubility of water in the membrane.

Hence, the separation factor is obtained from Eq. (8) as Eq. (9).

$$\alpha \propto D(\mathrm{ED}) \cdot \log K_{ow} \cdot p_{vap}(\mathrm{ED}) \quad (9)$$

Assuming that the diffusion coefficient of endocrine disruptors in the PDMS membrane, D(ED) is approximately the same for all the endocrine disruptors used in this study [because the molecular weights of endocrine disruptors are similar (approximately 100–400 g/mol)] Eq. (10) is finally obtained.

$$\alpha \propto \log K_{ow} \cdot p_{vap}(\mathrm{ED}) \quad (10)$$

Figure 6 shows the relationship between the separation factor of endocrine disruptors and log $K_{ow} \cdot p_{vap}$ (ED) based on the theoretical equation, Eq. (10). The experimental separation factors of dioctylphthalate and BHT were also found based on Eq. (10). The unknown separation factor of endocrine disruptors in the pervaporation can be estimated from Eq. (10).

CONCLUSION

Dioctylphthalate was detected in mineral water, ultrapure water, and tap water on the order of ppb by GC-MS analysis. Dioctylphthalate was also found in the same brand of mineral water whether it was bottled in PET bottles or glass bottles. Therefore, dioctylphthalate contaminated in the mineral water is thought to have originated from the manufacturing line of the mineral water and not from leaching from PET bottles.

The oxidization prevention agent of plastics, BHT, was detected as 2.05 ± 0.1 ppb in the mineral water in glass bottles and was not detected in the mineral water in PET bottles. BHT concentration of mineral water in the glass bottles is likely to have originated from the cap of the glass bottles, as the inside of the caps was sealed with polyethylene.

We further investigated the feasibility of separating dioctylphthalate and BHT from the mineral water by pervaporation using hydrophobic polydimethylsiloxane membranes. Dioctylphthalate and BHT were successfully removed from the water with separation factor of 106 ± 10 and 235 ± 15, respectively. This is demonstrated that trace amounts (on the order of ppb) of low volatile, high MW, and low water soluble organic chemicals such as dioctylphthalate and BHT in aqueous solutions can be removed from feed solutions and concentrated in permeate by pervaporation using PDMS membranes. The unknown separation factors for endocrine disruptors α(ED) in the pervaporation process can be estimated from the relationship derived in Eq (10) using the known physical parameters of endocrine disruptors (i.e., p_{vap} and log K_{ow}).

References

1. Korach, K. S.; Sarver, P.; Chae, K.; McLachlan, J. A.; McKinney, J. D. Mol Pharmacol 1988, 33, 120.
2. Jobling, S.; Reynolds, T.; White, R.; Parker, M. G.; Sumpter, J. P. Environ Health Perspect 1995, 103, 582.
3. Colborn, T.; Vom Saal, F. S.; Soto, A. M. Environ Health Perspect 1993, 101, 378.
4. Sharpe, R. M.; Skakkebaek, N. F. Lancet 1993, 341, 1392.
5. Zimmerman, L.R.; Schneider, R. J.; Thurman, E. M. J Agric Food Chem 2002, 50, 1045.
6. Hanaoka, T.; Takahashi, Y.; Kobayashi, M.; Sasaki, S.; Usuda, M.; Okubo, S.; Hayashi, N.; Tsugane, S. Sci Total Environ 2002, 286, 119.
7. Fiedler, H.; Cheung, C. K.; Wong, M. H. Chemosphere 2002, 46, 1429.
8. Yoshikawa, M.; Ochiai, S.; Tanigaki, M.; Eguchi, W. J Appl Polym Sci 1991, 43 2021.
9. Uragami, T.; Matsuda, T.; Okuno, H.; Miyata, T. J Membrane Sci 1994, 88, 243.
10. Oliveira, T. A. C.; Scarpello, J. T.; Livingston, A. G. J Membr Sci 2002, 195, 75.
11. Böddeker, K. W.; Bengtson, G. J Membr Sci 1990, 53, 143.
12. Böddeker, K. W.; Gatfield, I. L.; Jähnig, J.; Schorm, C. J Membrane Sci 1997, 137, 155.
13. Hoshi, M.; Saitoh. T.; Yoshioka, C.; Higuchi, A.; Nakagawa, T. J Appl Polym Sci 1999, 74, 983.
14. Ji, W.; Hilaly, A.; Sikdar, S. K.; Hwang, S. T. J Membr Sci 1994, 97, 109.
15. Wijmans, J. G.; Athayde, A. L.; Daniels, R.; Ly, J. H.; Kamaruddin, H. D.; Pinnau, I. J Membr Sci 1996, 109, 135.
16. Schnabel, S.; Moulin, P.; Nguyen, Q. T.; Roizard, D.; Aptel, P. J Membr Sci 1998, 142 129.
17. Yamaguchi, T.; Tominaga, A.; Nakao, S.; Kimura, S. AIChE J 1996, 42, 892.
18. Higuchi, A.; Yoon, B. O.; Asano, T.; Nakaegawa, K.; Miki, S.; Hara, M.; He, Z.; Pinnau, I. J Membr Sci 2002, 198, 311.
19. Yoon, B. O.; Asano, T.; Nakaegawa, K.; Ishige, M.; Hara, M.; Higuchi, A. ACS Symposium Series, 876, 2004, chp. 27.
20. Herbert, B. J.; Dorsey, J. G. Anal Chem 1995, 67, 744.
21. Yoon, B.O.; Koyanagi, S.; Asano, T.; Hara, M.; Higuchi, A. J Membr Sci 2003, 213, 137.
22. Atkins, P. W. Physical Chemistry, 5th ed;., Oxford University Press: Oxford, 1994, pp. 226–274.