

Sorption Behavior of Flavor Compounds into Packaging Films from Ethanol Solution

Masaomi Fukamachi, Toshiro Matsui,* Yoon-Hee Hwang, Mitsuya Shimoda, and Yutaka Osajima

Department of Food Science and Technology, Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812, Japan

The sorption of flavor compounds into low-density polyethylene (LDPE) and ethylene–vinyl alcohol copolymer (EVOH) films was greatly influenced by ethanol concentration, and maximal sorptions were observed at 5–10% (v/v) ethanol for LDPE and 10–20% (v/v) ethanol for EVOH. The sorptions of ethyl hexanoate, octanal, and octanol into LDPE film were ~1.7, 16.5, and 2.5 times higher than those in the 0% (v/v) ethanol solution, respectively (for EVOH film, the sorption increments of these compounds were ~6.2, 3.5, and 4.1 times, respectively). To better understand this phenomenon, the solvent properties of ethanol solutions were investigated. The dielectric constants were roughly unchanged in the range 5–15% (v/v) ethanol. According to the results obtained by ¹H NMR measurement, in which the difference in proton chemical shift from water-*d* (HDO) and ethyl alcohol-*d* (EtOD) became maximum at 23% (v/v) ethanol solution, the structural change of water induced by the addition of ethanol would be great up to 23% (v/v) ethanol. These results accurately reflected the sorption behavior. Therefore, the specific sorption behavior of flavor compounds from an ethanol solution would be brought about by the heterogeneous water–ethanol structure.

Keywords: Sorption; flavor; ethanol solution

INTRODUCTION

The sorption of flavor compounds into packaging polymer has been considered to be a main contributing factor in degradation of flavor or “food quality” during storage (Shimoda et al., 1984; Matsui and Osajima, 1993; Leufvén and Hermansson, 1994). In a series of our studies, we clarified the factors affecting sorption of flavor compounds (Osajima and Matsui, 1993; Matsui et al., 1992). Among these factors, driving potential (i.e., molar heat of vaporization of flavor compounds towards film) was found to be responsible for the sorption process (Matsui et al., 1994). In particular, in aqueous solution, the interaction of flavor with water molecules directly affected the potential (Fukamachi et al., 1994). Thus, to evaluate the sorption behavior of flavor compounds into a packaging film for liquid food, solvent property must be taken into consideration sufficiently.

Recently, the demand for plastic films as interior lining or coating material for paper cartons and metal cans in liquor packaging has increased tremendously because of their low cost and convenience (Oki, 1994; Akutsu, 1994; Omote, 1994). For liquors such as wine, beer, sake, and fruit-flavored alcoholic beverages, acceptable flavor is the most important quality factor (Winterhalter, 1991; Rodriguez et al., 1991; Kamiura and Kaneda, 1992; Sakamoto et al., 1993). Thus, loss or change of flavors by sorption and chemical changes during storage would greatly affect the food quality value. Protection from chemical changes of flavors during storage has been accomplished (Rodriguez et al., 1991) with refrigeration at 4 °C, and exclusion of oxygen. However, there has been no research on the protection from sorption for liquors. Hence, in this work, we

investigated the sorption behavior of flavor compounds from an ethanol solution as a model of alcoholic beverages.

MATERIALS AND METHODS

Materials. Low-density polyethylene (LDPE) film with the thickness of 50 μm was supplied by Showa Denko KK, Oita, Japan, and ethylene–vinyl alcohol copolymer (EVOH) film with the thickness of 35 μm and 32 mol % ethylene contents was supplied by Kuraray Company, Ltd., Osaka, Japan. The volatile compounds and other reagents were all guaranteed reagent grade from Nacalai Tesque Inc., Kyoto, Japan, and used without further purification.

Preparation of Model Flavor Solution. A mixture of homologous volatile compounds (esters, aldehydes, and alcohols with carbon numbers 4–12) was added to the ethanol solutions (300 mL) of various concentrations [0, 5, 10, 15, 20, 40, 60, and 80% (v/v)] to make a 15 ppm flavor solution of each compound. For preparation of a 0% (v/v) ethanol solution, sugar-ester (S-1170, Mitsubishi-Kasei Food Company, Ltd., Tokyo, Japan; hydrophilic–lipophilic balance value of 11) was added as an emulsifier to obtain enough dispersion of volatile compounds in the solution. The solutions were dispersed homogeneously by an ultrasonic wave generator for 10 min. LDPE (4 \times 7 cm) and EVOH (8 \times 10 cm) films were individually immersed in each model flavor solution and stored at 20 °C until the sorption equilibrium was established (~28 days).

Determination of Sorption. Volatile compounds from the sample solution were recovered by an adsorptive column method (Shimoda et al., 1987). Briefly, 100 mL of sample solution was passed through a column (20 mm i.d. \times 250 mm) packed with 30 mL of porous polymer beads (Porapak Type Q; Millipore Corp., Bedford, MA). After the column was washed with 100 mL of deionized water, absorbed compounds were eluted with 100 mL of diethyl ether. Amylbenzene was added into the ether eluents as an internal standard (1.0 μL /100 mL) to quantify the volatile compounds, and the ether eluents were concentrated on a water bath at 42 °C. Before the recovery, sample solutions with an ethanol concentration

* Author to whom correspondence should be addressed [fax (0081)-92-642-3030].

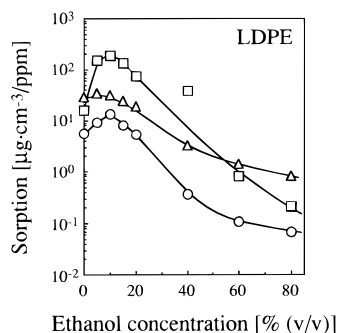


Figure 1. Sorption behavior of ethyl hexanoate (Δ), *n*-octanal (\square), and *n*-octanol (\circ) into LDPE film in ethanol solution.

of $\geq 15\%$ (v/v) were diluted with deionized water to $<10\%$ (v/v) ethanol to prevent the lower recovery of volatile compounds from high ethanol concentration solutions (Shimoda et al., 1987). The volatile compounds that sorbed into film were extracted by immersing the film in 60 mL of diethyl ether for 2 days at 5 °C. After concentration on a water bath at 42 °C, the extracts were analyzed by gas-liquid chromatography (GLC) with a gas chromatograph (GC-14A, Shimadzu Company, Ltd., Kyoto, Japan) connected to an integrator (Chromatopac C-R4A, Shimadzu). A fused silica capillary column coated with 10% (cyanopropyl) phenyl polysiloxane (CBP 10, 0.25 mm i.d. \times 50 m; Shimadzu) was used for separation, and the column temperature was programmed from 60 to 240 °C at a rate of 2 °C min^{-1} . Sorption [$\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$] was calculated by dividing the sorbed volatile compound in film ($\mu\text{g}\cdot\text{cm}^{-3}$) by the concentration (ppm) in flavor solution.

Characteristics of Ethanol Solutions. The dielectric constant of the ethanol solution was measured on a Dielectric Constant Meter (model SS-208, Shibayama Scientific Company, Ltd., Tokyo, Japan) at 20 °C. Before the experiment, a plot of capacitances (pF) of cyclohexanol, acetone, methanol, ethanol, and water in the capacitor against their dielectric constants (Weast, 1988) was found to be linear ($r = 0.994$):

$$y = 0.44x - 23.59 \quad (1)$$

y is the dielectric constant and x is the capacitance. The dielectric constants of the various ethanol solutions were calculated with eq 1.

The ^1H NMR spectra were obtained on a JNM A400 NMR instrument (JOEL) at 30 °C. The operating conditions were as follows: 16 scans were accumulated with 12 Hz of spinning and 3.69 μs of pulse width (35°), and pulsed delay was set at 7.95 s (resolution, 0.49 Hz). The tested ethanol solutions were prepared with D_2O (isotopic purity, 98.5 atom % D; E. Merck AG, Darmstadt, Germany) and EtOD (isotopic purity, 99.5 atom % D; E. Merck AG). The frequency was locked by D_2O , and the chemical shift was standardized by tetramethylsilane (TMS, 99.9%; Nacalai Tesque Inc., Ltd., Kyoto, Japan) in CDCl_3 , where the closed capillary tube (Φ 1.0 mm \times 5 cm) containing TMS was inserted into sample tube (Φ 5 mm).

RESULTS AND DISCUSSION

The sorption behaviors of flavors with various functional groups (ethyl esters, aldehydes, and alcohols) into packaging film were investigated in various ethanol solutions. The effects of ethanol concentration on sorptions of ethyl hexanoate, octanal, and octanol into LDPE and EVOH films at $<80\%$ (v/v) ethanol concentrations are shown in Figures 1 and 2, respectively. Interestingly, the sorptions for LDPE film increased with increasing ethanol concentration, and maximal sorptions were observed at 5–10% (v/v). The sorptions for ethyl hexanoate, octanal, and octanol were increased ~ 1.7 , 16.5, and 2.5 times, respectively, compared with

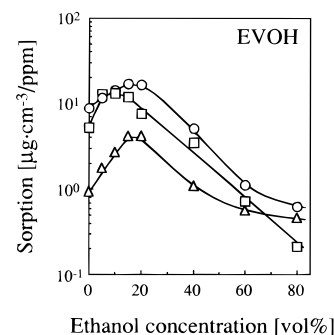


Figure 2. Sorption behavior of ethyl hexanoate (Δ), *n*-octanal (\square), and *n*-octanol (\circ) into EVOH film in ethanol solution.

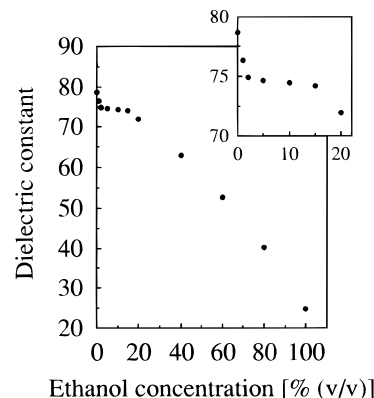


Figure 3. Change in dielectric constants of solution by the addition of ethanol.

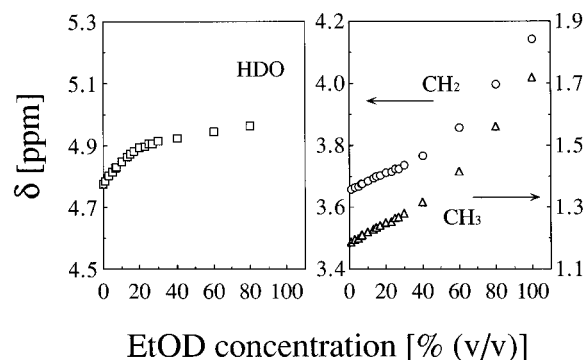


Figure 4. Effect of EtOD concentration on chemical shifts of CH_2 (\circ) and CH_3 (Δ) protons from EtOD and HDO (\square).

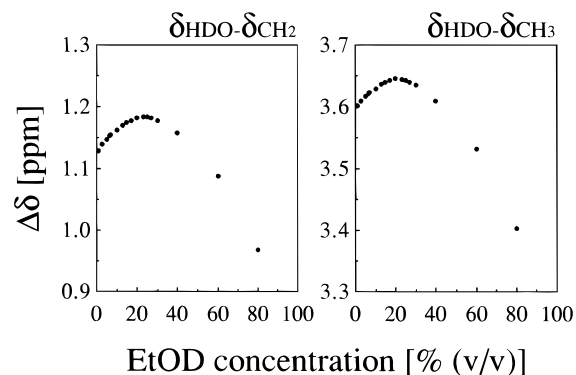


Figure 5. Plots of the difference in chemical shift between CH_3 or CH_2 protons and HDO ($\delta_{\text{HDO}} - \delta_{\text{CH}_3}$ or CH_2) versus EtOD concentration.

in 0% (v/v) ethanol solution. Subsequently, the sorptions decreased remarkably with increasing ethanol concentration. Similar specific sorption behaviors were observed for the EVOH film, with the maximal sorption

Table 1. Sorption [$\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$] into LDPE in Ethanol Solutions at 20 °C after 28 days of Storage

compounds	ethanol concentration [% (v/v)]							
	0 ^a	5	10	15	20	40	60	80
esters								
ethyl butyrate	0.9	1.8	2.1	1.4	1.3	0.3	0.1	0.1
ethyl hexanoate	20.2	33.5	30.9	24.4	18.6	3.3	1.4	0.8
ethyl octanoate	242.3	407.4	339.2	215.6	168.9	14.5	1.6	0.4
ethyl decanoate	318.8	955.7	2104.5	913.6	707.5	70.1	5.8	1.2
aldehydes								
hexanal	4.3	18.9	24.8	18.5	17.8	2.6	0.1	0.1
octanal	11.4	155.2	188.0	134.8	73.9	37.8	0.8	0.2
decanal	35.0	457.1	466.6	86.7	65.3	164.6	15.6	2.6
dodecanal	69.3	1213.6	2098.7	656.7	497.0	66.9	23.1	6.5
alcohols								
hexanol	1.9	1.4	1.1	1.5	1.7	0.1	N.D. ^b	N.D.
octanol	5.5	9.1	13.5	8.2	5.3	0.4	0.1	0.1
decanol	16.1	123.2	207.7	102.9	77.4	2.2	0.4	0.3
dodecanol	12.1	696.7	1572.8	923.1	507.2	8.9	1.1	0.6

^a 0% (v/v) corresponds to 0.3% (w/v) sugar-ester solution. ^b N.D., not detected.

Table 2. Sorption [$\mu\text{g}\cdot\text{cm}^{-3}/\text{ppm}$] into EVOH in Ethanol Solutions at 20 °C after 28 Days of Storage

compound	ethanol concentration [% (v/v)]							
	0 ^a	5	10	15	20	40	60	80
esters								
ethyl butyrate	0.4	0.5	0.7	0.8	0.8	0.3	0.2	0.1
ethyl hexanoate	0.7	1.7	2.7	4.1	4.1	1.1	0.6	0.5
ethyl octanoate	4.7	29.3	28.5	21.2	12.3	1.9	0.5	0.3
ethyl decanoate	17.8	210.8	458.5	213.4	65.6	4.3	0.9	0.6
aldehydes								
hexanal	0.3	1.4	2.6	2.9	0.9	0.8	0.2	0.2
octanal	3.7	12.7	13.0	11.9	7.1	3.3	0.7	0.3
decanal	8.3	15.6	27.8	10.6	7.3	8.5	0.8	0.8
dodecanal	16.3	34.7	60.3	44.7	9.2	8.9	2.2	1.4
alcohols								
hexanol	1.2	2.1	2.6	4.0	3.8	2.1	0.7	0.4
octanol	4.1	11.4	14.3	16.9	16.6	5.1	1.1	0.6
decanol	5.2	53.8	69.1	84.1	66.5	10.0	1.5	1.1
dodecanol	6.3	157.8	220.3	375.8	186.5	15.5	2.3	2.0

^a 0% (v/v) corresponds to 0.3% (w/v) sugar-ester solution.

at 10–20% (v/v) ethanol concentration. The sorptions for ethyl hexanoate, octanal, and octanol were increased ~6.2, 3.5, and 4.1 times, respectively, compared with 0% (v/v) ethanol solution.

The sorption behaviors of all volatile compounds used in this study into LDPE and EVOH films are summarized in Tables 1 and 2, respectively. In each homologous series, more sorption into both films was observed in ethanol solutions with increasing carbon chain length; these results are in good agreement with those in aqueous solution. In addition, sorption of all volatile compounds was maximal at 5–10% (v/v) ethanol concentration for LDPE film and 10–20% (v/v) ethanol concentration for EVOH film. Thus, it may be necessary to take into account any solvent property to explain the specific sorption behavior in ethanol solution.

We have already reported (Fukamachi et al., 1994), that the sorption process was responsible for the interaction of flavor with water molecules. Namely, more sorption was observed with increasing driving potential $[(\delta_s - \delta_v)^2]$. The value of $(\delta_s - \delta_v)^2$ represents the driving potential of flavors towards film; that is, the difference in solubility parameters between flavor (δ_v) and water or solvent (δ_s). Therefore, evaluation of δ_s is necessary to elucidate the specific sorption behaviors in ethanol solutions. The solvent property of the ethanol solution has been investigated in detail, and the change in dielectric constant, as an index of solution polarity, by the addition of ethanol is shown in Figure 3. Interestingly, the dielectric constants decreased with increasing ethanol concentration, but the behaviors

were not uniform with concentration. In particular, in the range 5–15% (v/v) ethanol, the dielectric constants were roughly unchanged. This specific dielectric constant behavior is in agreement with the results of Nishi et al. (1988) who showed that the characteristics of the ethanol–water clustering in the solutions changed in the range 8–22% (v/v) ethanol. Therefore, the sorption behavior shown in Figures 1 and 2 could be brought about by the heterogeneous molecular association of water–ethanol solutions.

Further investigation of the interaction between ethanol and water molecules was made by ¹H NMR measurements. The plots of the observed proton chemical shifts (CH_3 and CH_2 protons from EtOD, and HDO) versus the concentration are shown in Figure 4. Apparently, all protons were shifted toward low magnetic field with concentration. These low-field shifts caused by adding ethanol suggest that each proton was inversely shielded by a newly formed hydrogen bond between ethanol and/or water molecules. The differences in chemical shift ($\Delta\delta$) between CH_3 or CH_2 protons and HDO ($\delta_{\text{HDO}} - \delta_{\text{CH}_3(\text{CH}_2)}$) are shown in Figure 5 ($\Delta\delta$ indicates the difference in the degree of the solvent effect on each other). The $\Delta\delta$ for each proton increased up to 23% (v/v) and then decreased, which clearly reflected the sorption behaviors shown in Figures 1 and 2. This result indicates that up to 23% (v/v), the structural change of HDO induced by the addition of EtOD may be great because the low-field shift of HDO was higher than those of EtOD protons. Consequently, it is suggested that the specific sorption behavior of flavor

compounds (Tables 1 and 2) could be due to the heterogeneous water-ethanol structure.

ABBREVIATIONS USED

LDPE, low-density polyethylene; EVOH, ethylene-vinyl alcohol copolymer; EtOD, ethyl alcohol-*d*; D₂O, deuterium oxide; NMR, nuclear magnetic resonance.

LITERATURE CITED

- Akutsu, M. Changes of plastic bottles. *JPI J.* **1994**, *32*, 496–505.
- Fukamachi, M.; Matsui, T.; Shimoda, M.; Osajima, Y. Derivation of thermodynamic sorption equation of flavors with packaging films (2). *J. Agric. Food Chem.* **1994**, *42*, 2893–2895.
- Kaneura, M.; Kaneda, H. Off-Flavors in Beer. In *Off-Flavors in Foods and Beverages*; Charalambous, G., Ed.; Elsevier Science: Amsterdam, The Netherlands; 1992; p 433.
- Leufvén, A.; Hermansson, C. The sorption of aroma components from tomato juice by food-contact polymers. *J. Sci. Food Agric.* **1994**, *64*, 101–105.
- Matsui, T.; Nagashima, K.; Fukamachi, M.; Shimoda, M.; Osajima, Y. Application of solubility parameter in estimating sorption behavior of flavor into packaging film. *J. Agric. Food Sci.* **1992**, *40*, 1902–1905.
- Matsui, T.; Osajima, Y. Sorption of flavors into plastic films used for interior can coating. *J. Iron Steel* **1993**, *79*, 1138–1144.
- Matsui, T.; Fukamachi, M.; Shimoda, M.; Osajima, Y. Derivation of thermodynamic sorption equation of flavors with packaging films (1). *J. Agric. Food Chem.* **1994**, *42*, 2889–2892.
- Nishi, N.; Koga, K.; Ohshima, C.; Yamamoto, K.; Nagashima, U.; Nagami, K. Molecular association in ethanol-water mixtures studied by mass spectrometric analysis of clusters generated through adiabatic expansion of liquid jets. *J. Am. Chem. Soc.* **1988**, *110*, 5246–5255.
- Oki, Y. Changes in metal and composite containers. *JPI J.* **1994**, *32*, 476–488.
- Omote, K. Changes in paper containers for liquid foods. *JPI J.* **1994**, *32*, 506–513.
- Osajima, Y.; Matsui, T. Dynamic approach to the sorption of flavors into a food packaging film. *Anal. Sci.* **1993**, *9*, 753–763.
- Rodriguez, M.; Sadler, G. D.; Sims, C. A.; Braddock, R. J. Chemical changes during storage of an alcoholic orange juice beverage. *J. Food Sci.* **1991**, *56*, 475–479.
- Sakamoto, K.; Shimoda, M.; Osajima, Y. Concentration in Porapak Q column of volatile compounds in sake for analysis. *Nippon Nogeikagaku Kaishi* **1993**, *67*, 685–692.
- Shimoda, M.; Nitanda, T.; Kadota, N.; Ohta, H.; Suetsuna, K.; Osajima, Y. Adsorption of satsuma mandarin juice aroma on plastic films. *J. Jpn. Soc. Food Sci. Technol.* **1984**, *31*, 697–703.
- Shimoda, M.; Hirano, K.; Osajima, Y. Concentration of volatile components in foods with porous polymer column. *Bunseki Kagaku* **1987**, *36*, 792–797.
- Weast, R. C. In *CRC Handbook of Chemistry and Physics*, 1st student ed.; CRC: Boca Raton, FL: 1988; pp E44–46.
- Winterhalter, P. 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) formation in wine. 1. Studies on the hydrolysis of 2,6,10,10-tetramethyl-1-oxaspiro[4.5]dec-6-ene-2,8-diol rationalizing the origin of TDN and related C13 norisoprenoids in riesling wine. *J. Agric. Food Chem.* **1991**, *39*, 1825–1829.

Registry No. Supplied by the Author: Polyethylene, 9002-88-4; ethylene-vinyl alcohol copolymer, 25067-34-9; ethanol, 64-17-5; ethyl hexanoate, 123-66-0; octanal, 124-13-0; octanol, 111-87-5; ethyl alcohol-*d*, 925-93-9; deuterium oxide, 7789-20-0.

Received for review October 23, 1995. Revised manuscript received April 10, 1996. Accepted June 28, 1996.®

JF950707I

® Abstract published in *Advance ACS Abstracts*, August 15, 1996.