Reversible selectivity of water/organic solvent mixtures in poly(lactic acid) film

Ryo Iida, Tomoki Yonezu, Yasuaki Shinkawa, Kazukiyo Nagai

Department of Applied Chemistry, Meiji University, 1-1-1 Higashi-Mita, Tama-Ku, Kawasaki, 214-8571, Japan
Correspondence to: K. Nagai (E-mail: nagai@meiji.ac.jp or nagai@shikon.meiji.ac.jp)

ABSTRACT: The separation properties of water/organic solvent mixtures in poly(lactic acid) (PLA) films were investigated. The organic solvent flux increased linearly as the feed concentration increased, whereas the water flux was almost constant up to a feed concentration of 30 wt %. Interestingly, the permselectivity of PLA films was reversed from organic solvent selectivity to high water selectivity depending on the type of organic solvent. The permselectivity was strongly correlated with the solution concentration at which the solvent-induced crystallization of the PLA films occurred. The selectivity of permeation, solution, and diffusion in water/organic solvent mixtures was determined by the expanded free volume of the PLA films as a result of the interaction between PLA and the water/organic solvent mixture. The permeability behavior of water/organic solvent mixtures in PLA films was very complex. However, it was found that this behavior could be predicted through immersion tests. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 43822.

INTRODUCTION

Poly(lactic acid) (PLA) is an environmentally friendly plastic made from plants, such as corn and sugar cane. PLA is competitively priced in plant-based plastics markets. This plastic is mainly used as a packaging material because of its high transparency and good moldability associated with a low melting point.[1] We focused on the application of PLA to beverage plastic bottles. Beverages contain various flavor components, such as ester, carboxylic acid and alcohol, and the permeability behavior of these components is an important property in the material design of PLA to prevent flavor change. As flavor components, organic solvents are normally present in water; therefore, water/organic solvent binary systems should be treated to clarify their permeability behaivior. The permeability of water/ethanol mixtures in PLA films was described in our previous study.[2] The permeability of other water/organic solvent mixtures possibly differs from that of water/ethanol mixtures. In this study, three typical organic solvents, namely, n-butyl acetate, ethyl acetate, and acetic acid, were selected as flavor components in beverages. We have used a pervaporation (PV) method to measure the solution permeability. The PV method can be performed under a condition similar to that of plastic bottle application, that is, sample films are in contact with a given feed solution at room temperature and pressure.[3]

The concentration of flavor compounds in beverages is generally very low.[4,5] However, in this study, the PV measurements were

conducted in a larger range of feed concentrations to reveal the permeability behavior of water/organic solvent mixtures. The solvent-induced crystallization of amorphous PLA was described in our previous study.[6] This phenomenon causes the material deterioration, such as cloudiness and low density. These properties are fatal features of packaging materials. Therefore, we identified the crystallization concentration of PLA through immersion tests, and the PV measurements were performed in a range of feed concentrations at which PLA films maintain an amorphous state.

This study investigated the separation properties of water/organic solvent mixtures in PLA films and the effect of the type of organic solvent on the permeability behaviors of water/organic solvent mixtures. This study provides the reference for the material design of PLA.

EXPERIMENTAL

Film Preparation

The PLA films were the same samples employed in our previous study.[7] The PLA polymer used in this study was a 4032D product (NatureWorks LLC, Minnetonka). The isomer ratio (L:D) ranged from 96.0:4.0 to 96.8:3.2. To prepare the PLA films, 2 wt % dichloromethane solution was casted onto a flat-bottomed Petri dish in a glass bell-type vessel and then dried it at room temperature and atmospheric pressure. The solvent was allowed to evaporate for 48 h. The dried PLA films were then thermally treated
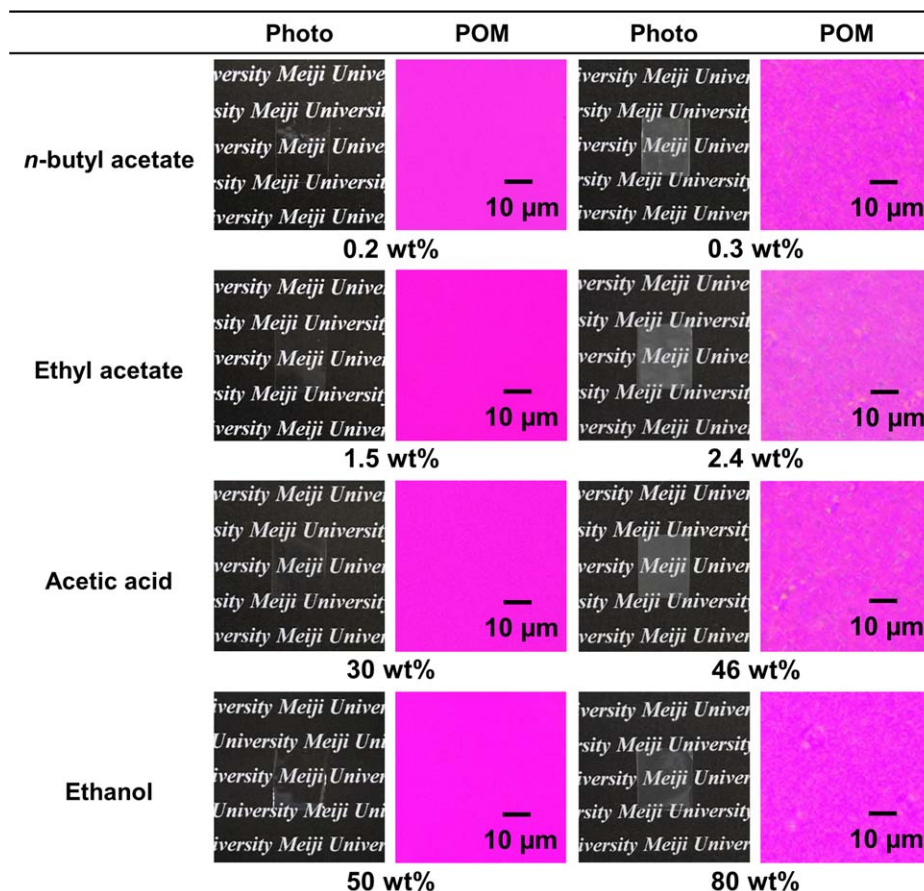
Figure 1. Photographs and POM images of PLA films after immersion tests. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in vacuum for 48 h at 70 °C to completely eliminate the residual solvent and to obtain amorphous PLA films. The thermally treated PLA films were then cooled at room temperature and atmospheric pressure. Proton nuclear magnetic resonance (^{1}H-NMR; JNM-ECA500, JEOL Ltd., Tokyo, Japan) analysis confirmed that the residual solvent was removed. The thickness of the films used in this study varied from 35 to 45 μm, and the uncertainty of the thickness of each film was ±1 μm.

Immersion Tests

The immersion tests were performed for 48 h at 25 ± 1 °C. The concentration of the water/organic solvent mixtures was changed stepwise. The organic solvents used in the tests were dichloromethane, 1,4-dioxane, ethyl acetate, methyl acetate, n-butyl acetate, ethyl formate, acetonitrile, N,N-dimethylformamide, acetic acid, ethanol, and methanol.

PV Measurement

The PV measurements were conducted in accordance with the method expounded in the literature.[3] The water/organic solvent mixtures were prepared as the feed solution at a specified concentration. The feed stream was continuously flowed over the film surface at a constant temperature of 25 ± 1 °C. The feed solution was stirred at 200 rpm to reduce the concentration polarization layer. The effective area of the round film was 18.1 cm². After steady state conditions were achieved, the per-

meated vapor was collected using liquid nitrogen at 5 mmHg for 4 h. The composition of the feed solution and the permeated mixture was determined using a gas chromatograph (GC-18A, Shimadzu Co., Kyoto, Japan). TC-1701 (GL Sciences Inc., Tokyo, Japan) was used as a column, and a hydrogen flame ionization detector was used as a detector. The flux (kg/m²/h) and water/organic solvent permselectivity (α_P) were calculated using eqs. (1) and (2):

$$\text{Flux} = \frac{Q}{A \cdot t} \tag{1}$$

$$\alpha_P = \frac{P_w/P_{org}}{F_w/F_{org}} \tag{2}$$

where Q is the weight of the permeate (kg), A is the film area (m²), and t is the operating time (h). P_w and P_{org} are the weight fractions of water and organic solvent in the permeate, respectively, and F_w and F_{org} are the weight fractions of water and organic solvent in the feed, respectively.

Swelling and Sorption Measurement

The degree of swelling by the water/organic solvent mixture was measured at 25 ± 1 °C. The films were soaked in each solution until sorption equilibrium was achieved. The surfaces of the films were wiped off, and their weight was immediately measured. The films were then dried through evaporation until the

Table I. Crystallization Concentration of PLA Films with Water/Organic Solvent Mixtures at 25 °C

Organic solvent	$|\delta_{h,PLA}-\delta_{h,org}|$	Crystallization concentration (wt %)
Dichloromethane	0.1	0.5
1,4-dioxane	0.1	26
Ethyl acetate	0.1	2.4
Methyl acetate	0.3	5.4
n-butyl acetate	1.0	0.3
Ethyl formate	1.1	3.0
Acetonitrile	1.2	8.2
N,N-dimethylformamide	4.0	68
Acetic acid	6.2	46
Ethanol	12.1	80
Methanol	15	76

Figure 2. Relationship between crystallization concentration and $|\delta_{h,PLA}-\delta_{h,org}|$.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sorbate was eliminated completely, and the weight of the dry films was measured. The degree of swelling was calculated using eq. (3):

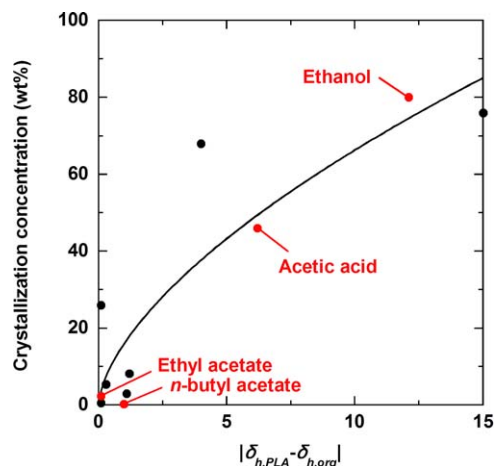$$S = \frac{W_S - W_D}{W_D} \times 100 \tag{3}$$

where S is the degree of swelling (wt %), W_S is the weight of the swollen film (g), and W_D is the weight of the dry film (g). The measurement of W_S was repeated until a constant weight was obtained. The composition of water/organic solvent mixtures sorbed in the film at equilibrium was analyzed. The surface of the equilibrated film was wiped off, and the sorbate was evaporated by heating at 100 °C in vacuum for more than 2 h. The sorbed mixtures were collected using liquid nitrogen, and their composition was determined using the gas chromato-

graph.[8] The water/organic solvent solubility selectivity (α_S) was calculated using eq. (4):

$$\alpha_S = \frac{M_w/M_{org}}{F_w/F_{org}} \tag{4}$$

where M_w and M_{org} are the weight fractions of water and organic solvent sorbed in the film, respectively.

The average diffusion coefficient ($\bar{D}$) was calculated in accordance with Aptel's research.[9] The flux (J) was defined as in eq. (5):

$$J = \frac{\bar{D}C_1}{l} = \frac{\bar{D}kS}{l} \tag{5}$$

where C_1 is the feed concentration, l is the film thickness. k was obtained using eq. (6):

Table II. Permeation Data of Water/Organic Solvent Mixtures in PLA Films at 25 °C

Feed concentration (wt %)	Total flux (kg/m²/h)	Water flux (kg/m²/h)	Organic solvent flux (kg/m²/h)	α_P (water/ organic solvent)
Water[a]	$4.87 \pm 0.12 \times 10^{-3}$	$4.87 \pm 0.12 \times 10^{-3}$	N/A	N/A
n-butyl acetate 0.01 wt %	$5.53 \pm 0.37 \times 10^{-3}$	$5.53 \pm 0.37 \times 10^{-3}$	$5.85 \pm 0.36 \times 10^{-6}$	$0.97 \pm 0.34 \times 10^{-1}$
n-butyl acetate 0.1 wt %	$5.97 \pm 0.39 \times 10^{-3}$	$5.91 \pm 0.42 \times 10^{-3}$	$5.55 \pm 2.94 \times 10^{-5}$	$1.15 \pm 0.43 \times 10^{-1}$
n-butyl acetate 0.2 wt %	$6.03 \pm 0.81 \times 10^{-3}$	$5.91 \pm 0.79 \times 10^{-3}$	$1.13 \pm 0.64 \times 10^{-4}$	$1.05 \pm 0.30 \times 10^{-1}$
Ethyl acetate 0.1 wt %	$5.21 \pm 0.61 \times 10^{-3}$	$5.19 \pm 0.62 \times 10^{-3}$	$1.87 \pm 0.33 \times 10^{-5}$	$2.98 \pm 0.94 \times 10^{-1}$
Ethyl acetate 0.5 wt %	$4.94 \pm 0.75 \times 10^{-3}$	$4.89 \pm 0.74 \times 10^{-3}$	$5.55 \pm 1.24 \times 10^{-5}$	$4.15 \pm 0.79 \times 10^{-1}$
Ethyl acetate 1.0 wt %	$5.65 \pm 0.48 \times 10^{-3}$	$5.53 \pm 0.45 \times 10^{-3}$	$1.25 \pm 0.24 \times 10^{-4}$	$4.20 \pm 0.56 \times 10^{-1}$
Ethyl acetate 1.5 wt %	$5.53 \pm 1.07 \times 10^{-3}$	$5.34 \pm 1.02 \times 10^{-3}$	$1.51 \pm 0.40 \times 10^{-4}$	$5.18 \pm 1.38 \times 10^{-1}$
Acetic acid 1 wt %	$5.58 \pm 0.40 \times 10^{-3}$	$5.58 \pm 0.40 \times 10^{-3}$	$1.08 \pm 0.60 \times 10^{-6}$	$5.69 \pm 2.15 \times 10$
Acetic acid 10 wt %	$5.43 \pm 0.61 \times 10^{-3}$	$5.42 \pm 0.61 \times 10^{-3}$	$6.79 \pm 1.94 \times 10^{-6}$	$9.01 \pm 3.43 \times 10$
Acetic acid 20 wt %	$5.57 \pm 0.45 \times 10^{-3}$	$5.55 \pm 0.45 \times 10^{-3}$	$1.93 \pm 0.34 \times 10^{-5}$	$7.39 \pm 0.98 \times 10$
Acetic acid 30 wt %	$5.65 \pm 0.31 \times 10^{-3}$	$5.61 \pm 0.31 \times 10^{-3}$	$3.91 \pm 0.59 \times 10^{-5}$	$6.31 \pm 0.99 \times 10$
Ethanol 10 wt %[a]	$5.50 \pm 0.34 \times 10^{-3}$	$5.50 \pm 0.34 \times 10^{-3}$	$0.15 \pm 0.02 \times 10^{-7}$	$4.47 \pm 0.90 \times 10^4$
Ethanol 30 wt %[a]	$5.68 \pm 0.23 \times 10^{-3}$	$5.68 \pm 0.23 \times 10^{-3}$	$0.61 \pm 0.06 \times 10^{-7}$	$3.91 \pm 0.55 \times 10^4$
Ethanol 50 wt %[a]	$3.64 \pm 0.40 \times 10^{-3}$	$3.64 \pm 0.40 \times 10^{-3}$	$2.42 \pm 0.28 \times 10^{-7}$	$2.14 \pm 0.74 \times 10^4$

[a] Data from Ref. 2.

$$\frac{1}{k} = \frac{S}{d_s} + \frac{100}{d_m} \tag{6}$$

where d_s and d_m are the densities of the sorbed liquid and the film, respectively. In a water/organic solvent binary mixture, the flux of water and organic solvent are expressed as in eqs. (7) and (8):

$$J_w = \frac{\bar{D}_w C_w}{l} = \frac{\bar{D}_w k S_w}{l} \tag{7}$$

$$J_{org} = \frac{\bar{D}_{org} C_{org}}{l} = \frac{\bar{D}_{org} k S_{org}}{l} \tag{8}$$

The water/organic solvent diffusivity selectivity (α_D) was calculated using eq. (9):

$$\alpha_D = \frac{\bar{D}_w}{\bar{D}_{org}} \tag{9}$$

Characterization Analysis

The characterization data were determined in the film state for at least three samples to confirm the reproducibility of the experimental results.

Orthoscope observation was performed using an Olympus BX-51 polarization microscope (POM; Olympus Inc., Tokyo Japan)
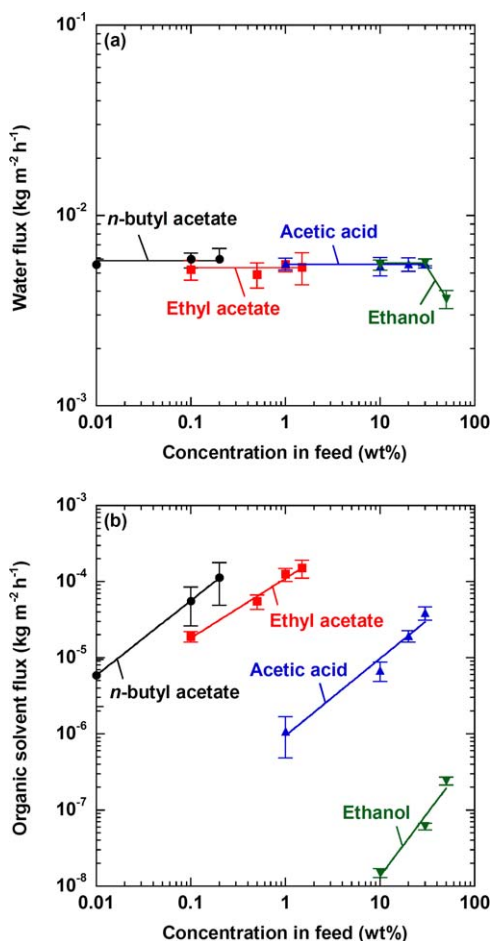

Figure 4. Permselectivity of PLA films as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

under cross Nicol condition. Polarization images were observed under a colored additive at 530 nm using a sensitive color plate.

The thermal analysis data were obtained using a Diamond differential scanning calorimeter (DSC; Perkin-Elmer, Inc., Shelton). The sample pan-kit alum (Perkin-Elmer, Inc., Shelton) was made of aluminum. These data are used to discuss crystalline structures and crystallinity. The first heating scan data, that is, before annealing, represent the optimum condition relative to the second heating scan data. Heat scan was performed from 20 to 200 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The glass transition temperature (T_g) was determined as the middle point of endothermic transition. The crystallization temperature (T_c) and melting temperature (T_m) were

Figure 3. Flux of (a) water and (b) organic solvent in PLA films at 25 °C as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
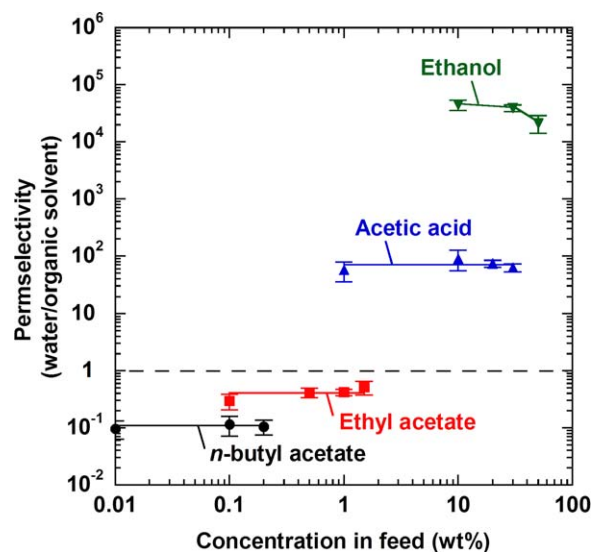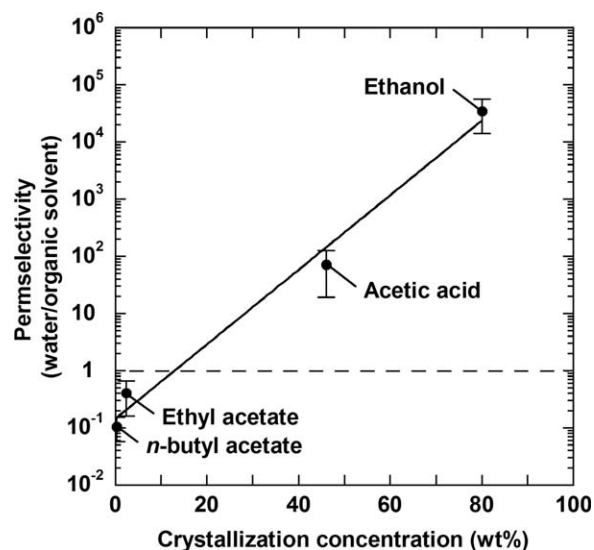

Figure 5. Relationship between permselectivity and crystallization concentration.

Applied Polymer
JOURNAL OF

Table III. Solution and Diffusion Data of Water/Organic Solvent Mixtures in PLA Films at 25 °C

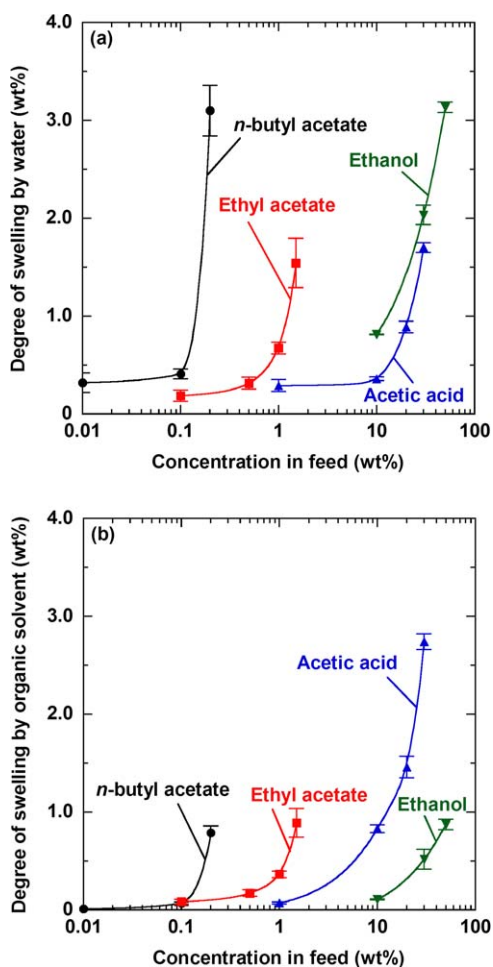| Feed concentration (wt %)	Degree of swelling (wt %)	Concentration in film (wt %)	α_S (water/ organic solvent)	α_D (water/ organic solvent)	$\bar{D}_W$ (cm²/s)	$\bar{D}_{org}$ (cm²/s)
Water[a]	0.28 ± 0.07	N/A	N/A	N/A	$6.20 \pm 0.15 \times 10^{-8}$	N/A
n-butyl acetate 0.01 wt %	0.32 ± 0.10	2.2 ± 0.4	$4.53 \pm 0.94 \times 10^{-3}$	$2.14 \pm 0.43 \times 10$	$1.51 \pm 0.13 \times 10^{-7}$	$7.34 \pm 2.19 \times 10^{-9}$
n-butyl acetate 0.1 wt %	0.48 ± 0.05	14.1 ± 4.0	$6.37 \pm 1.82 \times 10^{-3}$	$1.76 \pm 0.58 \times 10$	$1.22 \pm 0.11 \times 10^{-7}$	$7.17 \pm 1.52 \times 10^{-9}$
n-butyl acetate 0.2 wt %	3.89 ± 0.32	20.3 ± 0.3	$7.88 \pm 0.15 \times 10^{-3}$	$1.33 \pm 0.02 \times 10$	$0.17 \pm 0.01 \times 10^{-7}$	$1.31 \pm 0.02 \times 10^{-9}$
Ethyl acetate 0.1 wt %	0.27 ± 0.08	36.5 ± 4.9	$0.18 \pm 0.04 \times 10^{-2}$	$1.62 \pm 0.33 \times 10^{2}$	$2.71 \pm 0.21 \times 10^{-7}$	$1.71 \pm 0.23 \times 10^{-9}$
Ethyl acetate 0.5 wt %	0.49 ± 0.09	35.0 ± 11.3	$0.81 \pm 0.19 \times 10^{-2}$	$0.57 \pm 0.15 \times 10^{2}$	$1.48 \pm 0.14 \times 10^{-7}$	$2.65 \pm 0.39 \times 10^{-9}$
Ethyl acetate 1.0 wt %	1.04 ± 0.09	35.3 ± 14.1	$1.37 \pm 0.45 \times 10^{-2}$	$0.34 \pm 0.10 \times 10^{2}$	$0.85 \pm 0.11 \times 10^{-7}$	$2.55 \pm 0.49 \times 10^{-9}$
Ethyl acetate 1.5 wt %	2.43 ± 0.40	31.1 ± 10.3	$3.61 \pm 1.45 \times 10^{-2}$	$0.17 \pm 0.08 \times 10^{2}$	$0.29 \pm 0.05 \times 10^{-7}$	$1.91 \pm 0.54 \times 10^{-9}$
Acetic acid 1 wt %	0.36 ± 0.07	27.2 ± 10.7	$0.26 \pm 0.10 \times 10^{-1}$	$2.16 \pm 0.99 \times 10^{3}$	$2.07 \pm 0.47 \times 10^{-7}$	$0.99 \pm 0.31 \times 10^{-10}$
Acetic acid 10 wt %	1.18 ± 0.06	69.8 ± 3.0	$0.48 \pm 0.07 \times 10^{-1}$	$1.87 \pm 0.26 \times 10^{3}$	$1.40 \pm 0.17 \times 10^{-7}$	$0.76 \pm 0.07 \times 10^{-10}$
Acetic acid 20 wt %	2.34 ± 0.17	62.2 ± 15.6	$1.33 \pm 0.65 \times 10^{-1}$	$0.60 \pm 0.27 \times 10^{3}$	$0.69 \pm 0.26 \times 10^{-7}$	$1.19 \pm 0.20 \times 10^{-10}$
Acetic acid 30 wt %	4.45 ± 0.13	61.7 ± 2.6	$2.66 \pm 0.29 \times 10^{-1}$	$0.23 \pm 0.02 \times 10^{3}$	$0.30 \pm 0.02 \times 10^{-7}$	$1.31 \pm 0.06 \times 10^{-10}$
Ethanol 10 wt %[a]	0.92 ± 0.10	11.6 ± 0.6	0.86 ± 0.04	$4.87 \pm 0.25 \times 10^{4}$	$6.05 \pm 0.04 \times 10^{-8}$	$1.25 \pm 0.07 \times 10^{-12}$
Ethanol 30 wt %[a]	2.55 ± 0.40	20.3 ± 4.3	1.74 ± 0.46	$2.49 \pm 0.06 \times 10^{4}$	$2.55 \pm 0.13 \times 10^{-8}$	$1.05 \pm 0.21 \times 10^{-12}$
Ethanol 50 wt %[a]	4.01 ± 0.36	21.8 ± 1.0	3.60 ± 0.21	$0.37 \pm 0.01 \times 10^{4}$	$0.72 \pm 0.01 \times 10^{-8}$	$1.98 \pm 0.09 \times 10^{-12}$

[a] Data from Ref. 2.

Figure 6. Degree of swelling by (a) water and (b) organic solvent in PLA films at 25 °C as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

determined as the maximum values of each peak. The crystallinity ($X_{c\text{-}DSC}$) was estimated using eq. (10):

$$X_{c\text{-}DSC} = \frac{\Delta H_m + \Delta H_c}{\Delta H_m^0} \times 100 \qquad (10)$$

where ΔH_m and ΔH_c are the enthalpies (J/g) of the melting and crystallization of a polymer, respectively, and ΔH_m^0 is the enthalpy (93 J/g) of the PLA (*L*-donor 100%) crystal with an infinite crystal thickness.[10]

RESULTS AND DISCUSSION

Immersion Tests

The crystallization concentration was determined as the feed concentration at which spherocrystals were clearly observed in the POM images. Figure 1 shows the photographs and POM images of the PLA films at the feed concentrations before and after crystallization occurred. The PLA films were crystallized at 0.3 wt % *n*-butyl acetate, 2.4 wt % ethyl acetate, and 46 wt % acetic acid. Therefore, the PV measurements were performed in the range of the feed concentration of 0.01–0.2 wt % *n*-butyl acetate, 0.1–1.5 wt % ethyl acetate, and 1–30 wt % acetic acid.
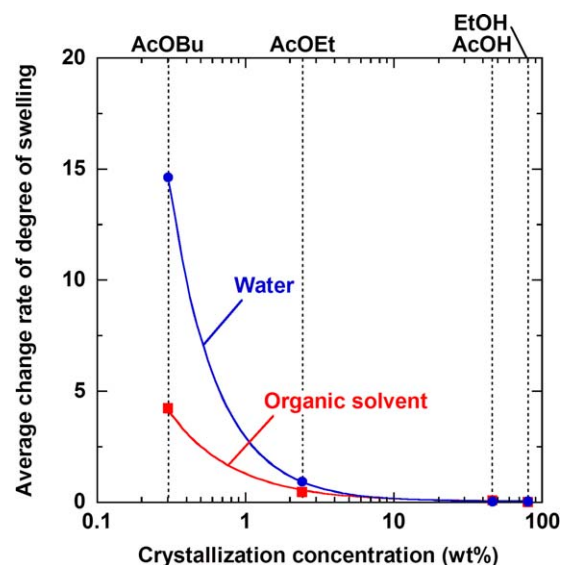

Figure 7. Relationship between average change rate of degree of swelling and crystallization concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Solvent-induced crystallization occurs via the following mechanism. The diffusion of a solvent in a polymer enhances the mobility of polymer chains through the interaction between the polymer and the solvent. As a result, the polymer forms a crystal structure which is a thermodynamically stable arrangement. Thus, the solvent that strongly interacts with the polymer induces polymer crystallization. In our pervious study, the solubility and solvent-induced crystallization of PLA was reported using the Hansen solubility parameter (HSP).[6] HSP is expressed as eq. (11):

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (11)$$

where δ_t is the total HSP, δ_d is the dispersion component, δ_p is the polar component, and δ_h is the hydrogen bonding
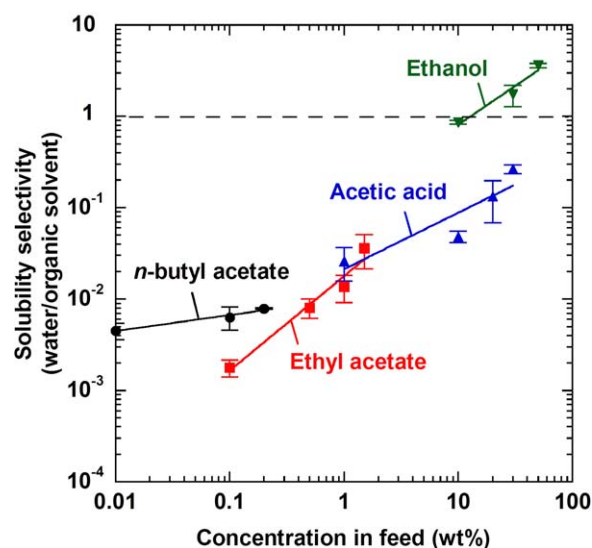

Figure 8. Solubility selectivity of PLA films as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
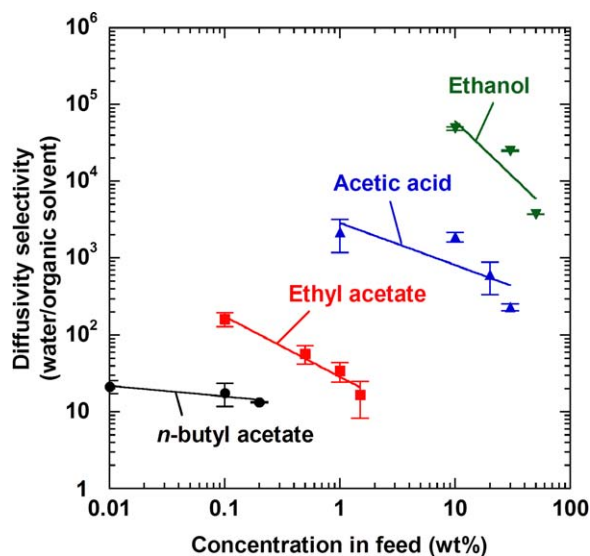
Figure 9. Diffusivity selectivity of PLA films as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

component. The previous study also revealed that the strength of the interaction between PLA and organic solvent increases as the difference between δ_h of PLA ($\delta_{h,PLA}$) and δ_h of the organic solvent ($\delta_{h,org}$) decreases. Table I shows $|\delta_{h,PLA}-\delta_{h,org}|$ and the crystallization concentration of the PLA films. Figure 2 shows the relationship between the crystallization concentration and $|\delta_{h,PLA}-\delta_{h,org}|$. The crystallization concentration decreased as $|\delta_{h,PLA}-\delta_{h,org}|$ decreased. However, this relationship remarkably varied, possibly because $|\delta_{h,PLA}-\delta_{h,org}|$ is an approximate measure of the affinity between PLA and organic solvent. This parameter also does not involve the effect of the interaction between water and organic solvent on the crystallization of PLA. In the case of the hydrophobic polymer such as PLA, the crystallization concentration was considered an accurate mea-
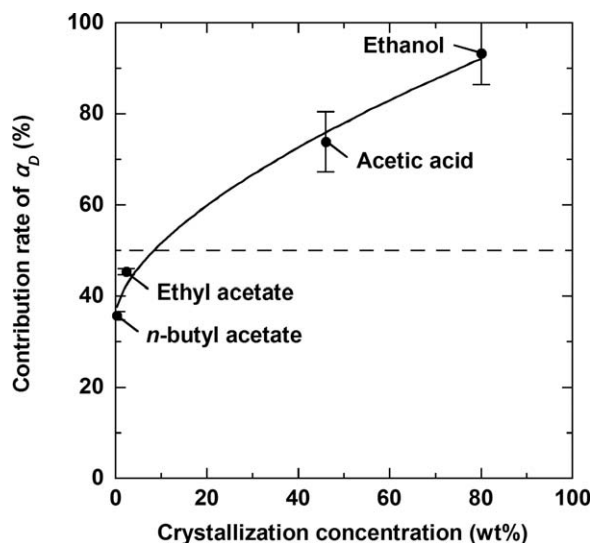

Figure 10. Relationship between contribution rate of diffusivity selectivity and crystallization concentration.
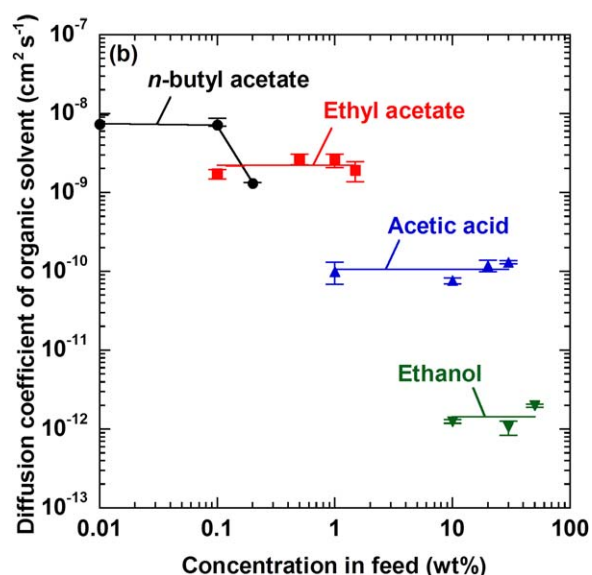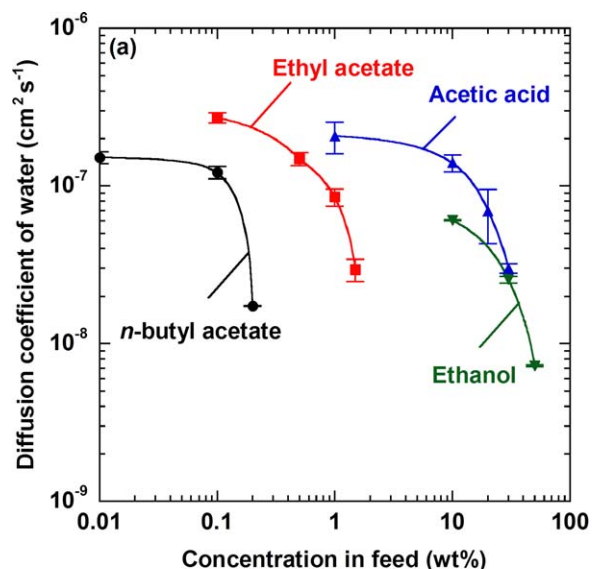

Figure 11. Diffusion coefficients of (a) water and (b) organic solvent as a function of feed concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sure of the affinity between the polymer and the water/organic solvent mixture.

PV

Table II summarizes the results of the PV measurements. Figure 3 shows the flux of water [Figure 3(a)] and organic solvent [Figure 3(b)]. As the feed concentration increased, the water flux was almost constant up to 30 wt % regardless of the type of organic solvent. By contrast, the water flux in water/ethanol decreased at 50 wt %. This decrease was caused by the hydration between water and ethanol molecules, as demonstrated in our previous study.[2] The organic solvent flux increased linearly as the feed concentration increased [Figure 3(b)]. The relationship between α_P and the feed concentration is shown in Figure 4. α_P in water/n-butyl acetate and water/ethyl acetate was
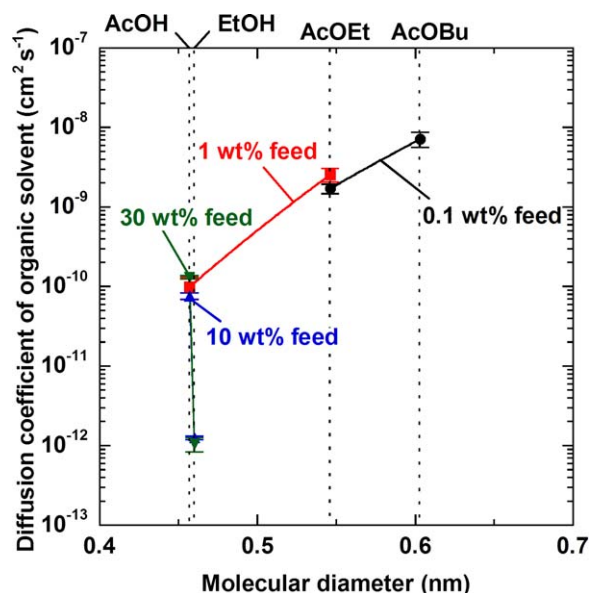
Figure 12. Relationship between diffusion coefficient of organic solvent and molecular diameter. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

less than 1 in all the feed concentrations; this finding indicated organic solvent permselectivity. By contrast, α_P in water/acetic acid and water/ethanol was greater than 1 in all the feed concentrations; this finding indicated water permselectivity. Polymer films generally exhibit either water permselectivity or organic solvent permselectivity regardless of the type of organic solvent. By contrast, in Figure 4, the permselectivity of the PLA films significantly changed from organic solvent selectivity to high water selectivity depending on the type of organic solvent. Therefore, this permselectivity reversal is a characteristic property of PLA film. The relationship between α_P and the crystallization concentration is shown in Figure 5. The logarithm of α_P was proportional to the crystallization concentration. Therefore, it was found that α_P of PLA film can be predicted by applying a simple method, namely, the immersion test. The permeability was investigated in detail on the basis of the solution-diffusion model.

Sorption and Diffusion

The degree of swelling and the results of the sorption measurements are summarized in Table III. Figure 6 shows the degree of swelling by water [Figure 6(a)] and organic solvent [Figure 6(b)]. As the feed concentration increased, the degree of swelling by water and organic solvent increased regardless of the type of organic solvent. The δ_h of PLA, n-butyl acetate, ethyl acetate, acetic acid, ethanol, and water are 7.3, 6.3, 7.2, 13.5, 19.4, and 42.4 MPa$^{1/2}$, respectively.[6] The difference between the δ_h of PLA and that of organic solvent is smaller than that between PLA and water. In other words, PLA exhibits a stronger interaction with organic solvent than with water. Therefore, the sorption amount of organic solvent increased because of the strong interaction between PLA and the organic solvent. By contrast, the sorption amount of water also increased as the proportion of water in the feed solution decreased regardless of the hydrophobicity of PLA. To clarify the factor, we calculated

the average change rate of the degree of swelling. The relationship between the average change rate of degree of swelling and the crystallization concentration is shown in Figure 7. The average change rate of degree of swelling by water and organic solvent increased markedly as the crystallization concentration decreased. Furthermore, the average change rate of degree of swelling by water exhibited a higher degree of increase than that of organic solvent. Indeed, the sorption amount of water increased as the feed concentration increased. The factor is considered as follows: first, the sorption amount of organic solvent in the PLA films increased as the strength of the interaction between PLA and organic solvent increased. The organic solvent then expanded the free volume of the PLA films; as a result, water molecules were preferentially sorbed in the PLA films.

Table III and Figures 8 and 9 show α_S and α_D, respectively. In Figure 8, α_S in water/n-butyl acetate, water/ethyl acetate, and water/acetic acid was less than 1 in all the feed concentrations; this finding indicated organic solvent selectivity. By contrast, α_S in water/ethanol was less than 1 at 10 wt % but was greater than 1 at 30–50 wt %. This finding indicated the change from water selectivity to organic solvent selectivity. α_S in all the mixtures increased as the feed concentration increased. The strength of the interaction between PLA and the water/organic solvent mixture exhibited the following pattern: n-butyl acetate > ethyl acetate > acetic acid > ethanol. α_S had been predicted to exhibit the same pattern. However, α_S in water/ethyl acetate and water/acetic acid was on the same approximate straight line. α_S in water/n-butyl acetate was higher than the extrapolated approximate straight line in water/ethyl acetate. This trend can be explained as follows: water was preferentially sorbed in the PLA films as the strength of the interaction between PLA and the water/organic solvent mixture increased. In Figure 9, α_D was greater than 1 in all the feed concentrations regardless of the
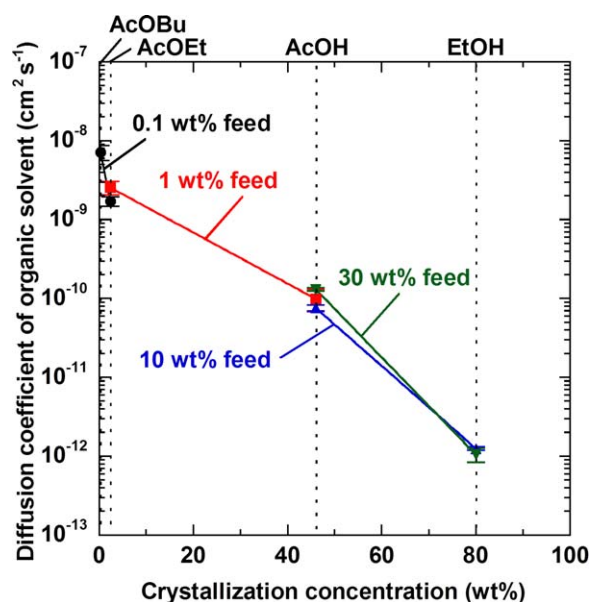

Figure 13. Relationship between diffusion coefficient of organic solvent and crystallization concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal Properties of PLA Films before and after PV Measurements

Feed concentration (wt %)	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	$X_{c\text{-}DSC}$ (%)
Non[a]	60.3 ± 2.1	N/A	N/A	N/A	N/A	0.0
Water[b]	60.3 ± 0.5	115.7 ± 0.3	148.9 ± 0.3	−7.7 ± 0.4	8.5 ± 0.2	0.9 ± 0.2
n-butyl acetate 0.01 wt %	59.6 ± 3.0	122.7 ± 1.9	149.5 ± 0.6	−7.4 ± 1.1	8.0 ± 1.1	0.6 ± 0.1
n-butyl acetate 0.1 wt %	58.6 ± 2.7	121.2 ± 1.2	148.7 ± 0.5	−11.2 ± 3.1	12.3 ± 2.6	1.2 ± 0.6
n-butyl acetate 0.2 wt %	59.1 ± 1.1	119.9 ± 4.2	147.8 ± 1.4	−10.9 ± 3.4	11.7 ± 3.9	0.9 ± 0.6
Ethyl acetate 0.1 wt %	59.1 ± 1.5	120.5 ± 0.5	148.7 ± 1.9	−11.1 ± 3.7	12.4 ± 3.9	1.4 ± 0.5
Ethyl acetate 0.5 wt %	58.7 ± 0.7	120.0 ± 1.6	147.5 ± 1.0	−6.6 ± 0.4	7.9 ± 0.3	1.5 ± 0.2
Ethyl acetate 1.0 wt %	58.0 ± 1.3	121.1 ± 0.6	148.7 ± 2.6	−8.3 ± 0.4	9.1 ± 0.5	0.9 ± 0.4
Ethyl acetate 1.5 wt %	57.9 ± 1.1	119.8 ± 1.4	147.5 ± 0.4	−7.5 ± 2.1	9.04 ± 3.1	1.7 ± 1.1
Acetic acid 1 wt %	62.0 ± 0.3	121.6 ± 0.6	147.5 ± 0.7	−6.0 ± 2.1	6.8 ± 1.5	0.9 ± 0.7
Acetic acid 10 wt %	61.3 ± 1.0	121.8 ± 1.9	147.1 ± 0.4	−5.7 ± 0.6	6.7 ± 0.9	1.1 ± 0.7
Acetic acid 20 wt %	61.8 ± 1.0	120.5 ± 0.5	147.2 ± 0.1	−6.3 ± 1.5	7.5 ± 0.9	1.2 ± 0.6
Acetic acid 30 wt %	58.9 ± 0.9	120.9 ± 0.5	148.5 ± 0.3	−8.0 ± 0.3	9.5 ± 0.8	1.7 ± 0.5
Ethanol 10 wt %[b]	60.4 ± 2.4	116.2 ± 0.5	149.2 ± 0.1	−5.9 ± 0.6	7.5 ± 0.5	1.7 ± 0.1
Ethanol 30 wt %[b]	58.6 ± 1.4	115.8 ± 0.5	148.3 ± 0.4	−6.0 ± 0.4	7.7 ± 0.2	1.8 ± 0.1
Ethanol 50 wt %[b]	60.2 ± 0.4	115.5 ± 0.4	147.8 ± 0.1	−3.3 ± 0.4	4.7 ± 0.1	1.5 ± 0.1

[a] Data from Ref. 7.
[b] Data from Ref. 2.

type of organic solvent; this finding indicated water selectivity. α_D decreased as the feed concentration increased. α_D exhibited the following pattern: ethanol > acetic acid > ethyl acetate > n-butyl acetate. In the film separation based on the solution-diffusion model, the permeability is expressed as the product of solubility and diffusivity. To clarify whether the permeability of water/organic solvent mixtures was strongly dependent on either the solubility or the diffusivity, we calculated the contribution rate of α_D to $\alpha_S \times \alpha_D$ using eq. (12):

$$\text{Contribution rate of } \alpha_D = \frac{\sqrt{(\log \alpha_D)^2}}{\sqrt{(\log \alpha_S)^2} + \sqrt{(\log \alpha_D)^2}} \times 100 \quad (12)$$

The relationship between the contribution rate of α_D and the crystallization concentration is shown in Figure 10. The contribution rate of α_D decreased as the crystallization concentration decreased. The contribution rate of α_D in water/n-butyl acetate and water/ethyl acetate was less than 50%; this finding indicated the large contribution of the solubility. By contrast, the contribution rate of α_D in water/acetic acid and water/ethanol was greater than 50%; this finding indicated the large contribution of the diffusivity. Therefore, the large change in the contribution of the solubility and the diffusivity, which was dependent on the type of organic solvent, resulted in the permselectivity reversal of the PLA films. The high water permselectivity in water/acetic acid and water/ethanol was caused by the high diffusivity selectivity. Accordingly, the diffusivity of water and organic solvent was investigated.

$\bar{D}_w$ and $\bar{D}_{\text{org}}$ are summarized in Table III. Figure 11 shows $\bar{D}_w$ [Figure 11(a)] and $\bar{D}_{\text{org}}$ [Figure 11(b)]. $\bar{D}_w$ was higher than $\bar{D}_{\text{org}}$ regardless of the type of organic solvent. In Figure 11(b), $\bar{D}_{\text{org}}$ was

almost constant without depending on the feed concentration except at 0.2 wt % n-butyl acetate. By contrast, $\bar{D}_{\text{org}}$ in water/n-butyl acetate was almost constant up to 0.1 wt % but decreased at 0.2 wt %. $\bar{D}_{\text{org}}$ exhibited the following pattern except at 0.2 wt % n-butyl acetate: n-butyl acetate > ethyl acetate > acetic acid > ethanol. The diffusivity of a penetrant in a polymer film generally increases as the penetrant size increases. The molecular diameter of the penetrant can be calculated from its density and molecular weight in the liquid state.[11] The molecular diameter of water, acetic acid, ethanol, ethyl acetate, and n-butyl acetate are 0.311, 0.457, 0.460, 0.546, and 0.603 nm, respectively. Figure 12 shows that $\bar{D}_{\text{org}}$ was not correlated with molecular diameter. Figure 13 shows that $\bar{D}_{\text{org}}$ increased linearly as the crystallization concentration decreased. Therefore, the diffusivity of organic solvents depended not on their molecular size but on their affinity with PLA because the organic solvents, which strongly interact with PLA, expanded the free volume in the PLA films. By contrast, $\bar{D}_w$ decreased as the feed concentration increased regardless of the type of organic solvent [Figure 11(a)], and $\bar{D}_{\text{org}}$ of n-butyl acetate decreased at 0.2 wt % [Figure 11(b)]. These decreases could be attributed to the interaction between water and organic solvent molecules or the solvent-induced crystallization of the PLA films. In our previous study, we concluded that, in water/ethanol mixtures, the interaction between water and ethanol molecules interrupts the diffusion of water molecules in the PLA films.[2] The effect of water/organic solvent mixtures on the crystal structure of the PLA films was also investigated in this study.

Film Characterization

T_g, T_c, T_m, ΔH_c, and ΔH_m were determined using the DSC thermograms of the PLA films. Table IV shows the thermal properties of the PLA films before and after the PV measurements. T_g of the

PLA films before and after the PV measurements was 57.9–62.0 °C, which are within the range of the values reported in the literature: 55–69 °C.[1,12–17] $X_{c\text{-}DSC}$ before the PV measurements was 0.0%, and $X_{c\text{-}DSC}$ after the PV measurements was 0.6–1.8%. The PLA films were slightly crystallized by the permeation of water/organic solvent mixtures, but the crystallinity was independent of the type of organic solvent and the feed concentration. This result suggested that the interaction between PLA and the water/organic solvent mixture hardly affected the permeability behavior. Therefore, the decrease in the diffusivity of water and n-butyl acetate was caused by the diffusion of water and organic solvent molecules disturbed by their interaction. The decrease of $\bar{D}_{org}$ in water/n-butyl acetate is considered to be caused by the significant increase of sorption amount at 0.2 wt %.

CONCLUSIONS

The separation properties of water/organic solvent mixtures in PLA films and the effect of the type of organic solvent on the permeability behavior of water/organic solvent mixtures were investigated. The water flux was almost constant up to 30 wt % regardless of the type of organic solvent. By contrast, the organic solvent flux increased linearly as the feed concentration increased. Interestingly, the permselectivity of the PLA films was reversed from organic solvent selectivity to high water selectivity depending on the type of organic solvent. As the strength of the interaction between PLA and the water/organic solvent mixture increased, the solubility selectivity initially decreased and then increased; and the diffusivity selectivity monotonically decreased. The permeability, solubility, and diffusivity of water/organic solvent mixtures in PLA films were determined by the change in the free volume of the films. The change in their free volume was caused by the interaction between PLA and the water/organic solvent mixture. The diffusion coefficients of water and n-butyl acetate decreased as the feed concentration increased. Based on the result of DSC measurements, these decreases were attributed to the interaction between water and organic solvent molecules in the PLA films. Thus, the permeability behavior of water/organic solvent mixtures in PLA films was complex. However, we found that the permeability behavior can be predicted through immersion tests. This study will contribute to the material design of PLA to obtain the flavor barrier properties required for applications in beverage plastic bottles.

REFERENCES

1. Komatsuka, T.; Kusakabe, A.; Nagai, K. *Desalination* **2008**, *234*, 212.

2. Shinkawa, Y.; Hayashi, Y.; Sato, S.; Nagai, K. *J. Appl. Polym. Sci.* **2015**, *132*, DOI: 10.1002/app.42031.

3. Driolli, E.; Giorno, L. *Comprehensive Membrane Science and Engineering*; Elsevier: Oxford, **2010**; Vol. *2*, p 243.

4. Charalambous, H. *Analysis of Foods and Beverages: Headspace Techniques*; Academic Press: New York, **1978**; p 229.

5. Rose, A. H. *Alcoholic Beverages*; Academic Press: New York, **1977**; Vol. *1*, Chapters 2–3, p 43.

6. Sato, S.; Gondo, D.; Wada, T.; Kanehashi, S.; Nagai, K. *J. Appl. Polym. Sci.* **2013**, *129*, 1607.

7. Sawada, H.; Takahashi, Y.; Miyata, S.; Kanehashi, S.; Sato, S.; Nagai, K. *Trans. Mater. Res. Soc. Jpn.* **2010**, *35*, 241.

8. Ulutan, S.; Nakagawa, T. *J. Membr. Sci.* **1998**, *143*, 275.

9. Aptel, P.; Cuny, J.; Jozefonvicz, J.; Morel, G.; Neel, J. *J. Appl. Polym. Sci.* **1974**, *18*, 365.

10. Fischer, E. W.; Sterzel, H. J.; Wegner, G. *Kolloid-Z. Z. Polym.* **1973**, *251*, 980.

11. Berens, A. R.; Hopfenberg, H. B. *J. Membr. Sci.* **1982**, *10*, 283.

12. Duek, E. A. R.; Zavaglia, C. A. C.; Belangero, W. D. *Polymer* **1999**, *40*, 6465.

13. Lee, J. H.; Park, T. G.; Park, H. S.; Lee, D. S.; Lee, Y. K.; Yoon, S. C.; Nam, J. D. *Biomaterials* **2003**, *24*, 2773.

14. Sarazin, P.; Roy, X.; Favis, B. D. *Biomaterials* **2004**, *25*, 5965.

15. Tsuji, H.; Suzuyoshi, K. *Polym. Degrad. Stabil.* **2002**, *75*, 347.

16. Weir, N. A.; Buchanan, F. J.; Orr, J. F.; Farrar, D. F.; Boyd, A. *Biomaterials* **2004**, *25*, 3939.

17. Yao, F. L.; Bai, Y.; Chen, W.; An, X. Y.; Yao, K. D.; Sun, P. C.; Lin, H. *Eur. Polym. J.* **2004**, *40*, 1895.