

pH of Solution Greatly Affects Sorption of Ionizable Compounds into Low-Density Polyethylene Film

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Sorption of ionizable compounds of pyridines and aromatic carboxylic acids into low-density polyethylene (LDPE) film was investigated as a function of pH ranging from 4 to 7. The sorptions for pyridines were increased with increasing pH. Within the range examined, pH 7 was observed to promote the highest degree of sorption. When the pH increased by one unit from 6 to 7, the sorptions for 2-propylpyridine and 2,4,6-trimethylpyridine were both increased ~3.8 and 10.5 times, respectively. At pH 4, the sorption for the pyridines entirely disappeared. In contrast, the sorptions for aromatic carboxylic acids increased with decreasing pH. Within the range examined, pH 4 was observed to promote the highest degree of sorption. The magnitude of sorption for pyridines and carboxylic acids apparently depended on the affinity (δ_c) of these compounds for LDPE film. Another factor affecting the sorption at various pHs was the pK_a of these compounds; the sorption greatly decreased with the ionization degree of these compounds. To elucidate the phenomena, the following thermodynamic sorption equation was applied: $S = S_0\gamma \exp\{V_v\{(\delta_w - \delta_v)^2 - \delta_c^2\}/RT\}$. The plots of $\ln S$ for pyridines vs the term of the equation gave an insufficient relationship ($r = 0.519$). In contrast, taking into account the ratio (χ_i) of concentration of un-ionized compound to total concentration, the improvement for the equation was made: $S' = S/\chi_i = S_0\gamma \exp\{V_v\{(\delta_w - \delta_v)^2 - \delta_c^2\}/RT\}$. The plots of $\ln S'$ vs the term of the equation gave a better relationship ($r = 0.884$). Furthermore, the equation was also applicable for the sorption behavior of carboxylic acids into LDPE ($r = 0.769$).

KEYWORDS: Sorption; pH; plastic film

INTRODUCTION

Plastic materials for food, cosmetic, or pharmaceutical packaging have some advantages due to their low cost, heat stability, and convenience as compared with other ones such as glass, metal, and paper. Especially, polyolefins such as polyethylene (PE) and polypropylene (PP) have a widespread use in various packaging because of freedom from toxic monomers and flexibility (1). The increasing use of plastics in their packaging has led to the need for more information about the interactions between the plastics and the packed product.

A direct interaction of volatile compounds with packaging film greatly affects the quality of products. Especially, flavor that is a candidate for determining food quality is liable to deteriorate by the sorption into the film during storage (2, 3). Many studies on sorption of flavors into film have been performed (4–6). In addition, the sorption of volatile compounds into polymers also causes a serious problem linked to the

recycling of packaging polymers under the influence of environmental considerations. If sorbed volatile compounds (especially, unpleasant odor compounds) remain in packaging polymers after the washing procedure, they will be resorbed into the product that has been refilled into the polymer, causing off-flavors.

In our series of studies, we have investigated the practical sorption phenomena of various volatile compounds and then clarified the factors affecting the sorption of compounds **1**, **7**, and **8**. Among the factors, the affinity between film and flavor (1) and driving potential (i.e., molar heat of vaporization of flavor compounds toward film) (7) were found to be responsible for the sorption process. Finally, regarding the energy of sorption as a difference between film–flavor affinity and driving potential of flavors toward film, we have successfully derived a thermodynamic sorption equation for the vapor phase as well as for the aqueous phase to predict sorption behavior (7). In addition, we have demonstrated the factors affecting the interaction between volatile compounds and the films in aqueous solution (7). It was found that ethanol was one of the sorption-promoting factors up to 20% ethanol concentration, and ionic surfactant (emulsifier), such as sodium lauryl sulfate, also

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affected the sorption (9). In contrast, we have reported that the pH of the flavor solution (pH 3–7) did not affect the sorption of ethyl esters into PE film (10). The opposite result by Leufven and Hermansson (11) led us to a further investigate the pH, in which increasing sorption of aldehydes was observed at pH 5. The conflict would be due to nonconsideration of the molecular property of volatile compounds in various pHs.

For better understanding of the effect of pH on the sorption of volatile compounds into a packaging film, the sorption of some ionizable compounds was investigated in this paper, because the ionizable compounds would be directly affected by the pH. The determination of the sorption behaviors of ionizable flavor and other organic compounds has an important significance in the quality control of food, pharmaceutical, and other packaging materials. In this study, pyridines and carboxylic acids were selected as model compounds to clarify the sorption behaviors of cationic (weak base) and anionic (weak acid) volatile compounds, and five pyridines and five carboxylic acids were used to investigate the effect of their molecular properties on the sorption. In addition, we derived a modified thermodynamic sorption equation to predict the sorption in various pHs.

MATERIALS AND METHODS

Materials. Low-density polyethylene (LDPE) film with the thickness of 40 μm and the density of 0.928 g/cm^3 were supplied by Showa Denko KK, Oita, Japan. Pyridines (pyridine, 2-methylpyridine, 2-ethylpyridine, 2-propylpyridine, and 2,4,6-trimethylpyridine), carboxylic acids (benzoic acid, *o*-tolylacetic acid, 3-phenylpropionic acid, 4-phenylbutyric acid, and 3-(*p*-tolyl)propionic acid) and other reagents were all guaranteed reagent grade from Nacalai Tesque Inc. (Kyoto, Japan), and used without further purification.

Preparation of Model Sample Solution. A mixture of homologous compounds (pyridines and carboxylic acids) was added to 300 mL of MacIlvaine buffer (pH: 4, 5, 6, 7) to make a 200 ppm sample solution of each compound. As an emulsifier 0.2% (w/v) poly(oxyethylene) (POE) was selected to obtain sufficient dispersion of the compounds in the solution, because nonionic surfactants had little effects on the sorption of volatile compounds into the film different from ionic surfactant such as sodium dodecyl sulfate (SDS). The solution was dispersed homogeneously by an ultrasonic wave generator for 10 min. LDPE (6 \times 6 cm) films were individually immersed in each model solution and stored in the dark until the sorption equilibrium was established. The store temperature was set at 37 $^{\circ}\text{C}$ to achieve the sorption equilibrium in a short period (in this experiment, 28 days' storage).

Determination of Sorption. The compounds in 300 mL of sample solution were recovered by liquid–liquid extraction with 300 mL of diethyl ether. Before the extraction, 5% NaHCO_3 (for pyridine) or 1 M HCl (for carboxylic acid) was added to each sample solution to convert a compound to an un-ionized form. The compounds sorbed into film were extracted by immersing the film in 60 mL of diethyl ether for 2 days at room temperature. The extract was evaporated to dryness on a water bath at 42 $^{\circ}\text{C}$ and was resolved in 100 μL of acetone. The determination of pyridines was performed by gas–liquid chromatography (GLC; GC-18A, Shimadzu Co., Ltd., Kyoto, Japan) connected to an integrator (Chromatopac C–R5A, Shimadzu). A fused silica capillary column coated with cross-linked 20 M poly(ethylene glycol) (DB-WAX; 0.32 mm i.d. \times 60 m; J&W Science, Folsom, CA) was used for separation, and the column temperature was set at 120 $^{\circ}\text{C}$. Both the injection and the detection temperatures were set at 250 $^{\circ}\text{C}$. The determination of carboxylic acids was performed by reverse-phase HPLC (Shimadzu LC-9A instrument; column, Cosmosil 5C18-ARII, 4.6 \times 250 mm) under room temperature at the isocratic mode of 25% acetonitrile in 0.1% trifluoroacetic acid at a flow rate of 1.0 mL/min (254 nm).

In this study, we defined the unit of the sorption as ($\mu\text{g}/\text{cm}^3/\text{ppm}$); i.e., the sorption was determined as the amount (μg) of sorbed compound in the film per unit volume (cm^3) under 1 ppm of

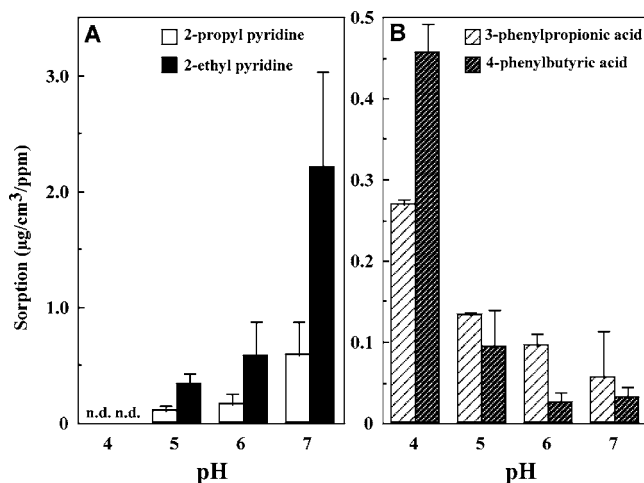


Figure 1. Sorption behaviors of pyridines (2-ethylpyridine, $pK_a = 5.76$; 2-propylpyridine, $pK_a = 5.73$) (A) and carboxylic acids (3-phenylpropionic acid, $pK_a = 4.78$; 4-phenylbutyric acid, $pK_a = 4.86$) (B) into LDPE film in MacIlvaine buffers at pH 4, 5, 6, and 7. Data represent the mean \pm SD ($n = 4$).

concentration difference across the film and calculated by dividing the sorbed compound in film ($\mu\text{g}/\text{cm}^3$) by the concentration (ppm) in sample solution.

Estimation of Solubility Parameter. The solubility parameter (SP) value is defined as the square root of cohesive energy density (CED) (12)

$$\text{SP value}/\text{MPa}^{1/2} = (\text{CED})^{1/2} = (\Delta E/V)^{1/2} \quad (1)$$

where ΔE (J/cm^3) is the energy of vaporization (cohesive energy) and V (cm^3/mol) is the molar volume. The SP values for film (δ_f) and compound (δ_c) were calculated using the Fedors parameter (13)

$$\delta = (\Sigma\Delta E_i/\Sigma\Delta v_i)^{1/2} \quad (2)$$

where $\Sigma\Delta E_i$ and $\Sigma\Delta v_i$ are the sums of the vaporization energy and the molar volume of the atom or group, respectively. Then, the SP values are divided into polar and nonpolar components by application of the homomorph concept (14) as described previously (1). A homomorph is a hydrocarbon counterpart of the same size and shape; for example, the homomorphs of benzene and ethanol are cyclohexane and propane, respectively. According to this concept, one can calculate the δ_p value in the total SP value (δ_t) from the following equation:

$$\delta_p = (\delta_t^2 - \delta_{np}^2)^{1/2} \quad (3)$$

RESULTS AND DISCUSSION

We primarily clarified whether the sorption of ionizable compounds into LDPE film is affected by pH. Pyridines with a pK_a value of 4.95–7.98 and carboxylic acids with a pK_a value of 4.08–4.89 were used in this experiment. All pK_a values for pyridines and carboxylic acids at 37 $^{\circ}\text{C}$ were calculated by using Marvin software (version 3.5.1, ChemAxon Ltd., Hungary) (15). **Figure 1A** shows the effect of pH on sorptions of 2-ethylpyridine ($pK_a = 5.76$) and 2-propylpyridine ($pK_a = 5.73$) into LDPE film at pH 4, 5, 6, and 7. As a result, the pH of the sample solution greatly affected the sorption of both pyridines. A marked increase in sorption was observed with increasing pH, and, at pH 7, the sorption was dramatically increased compared to those in other pHs. Additionally, the sorptions at pH 7 drastically increased by a factor of ca. 3.6 compared with those at pH 6. This suggests that pK_a would be a candidate factor in determining the magnitude of sorption. Interestingly, the sorptions at pH 4 entirely disappeared (**Table 1**). **Figure 1B**

Table 1. Relationship between Sorption and δ_c Values for LDPE Film at 37 °C

compounds	pK_a^a	LDPE				δ_c (MPa ^{1/2})
		sorption ($\mu\text{g}/\text{cm}^3/\text{ppm}$)				
		pH 4	pH 5	pH 6	pH 7	
pyridines						
pyridine	4.95	nd ^b	0.034	nd	0.042	14.45
2-methylpyridine	5.93	nd	0.046	0.043	0.147	13.99
2-ethylpyridine	5.76	nd	0.108	0.159	0.580	13.00
2-propylpyridine	5.73	nd	0.331	0.578	2.209	12.20
2,4,6-trimethylpyridine	7.98	nd	0.013	0.030	0.315	13.43
carboxylic acids						
benzoic acid	4.08	0.133	0.020	0.006	0.007	18.38
<i>o</i> -tolylacetic acid	4.68	0.124	0.048	0.038	0.020	16.55
3-phenylpropionic acid	4.78	0.269	0.132	0.096	0.056	16.10
4-phenylbutyric acid	4.86	0.455	0.094	0.025	0.031	15.23
3- <i>p</i> -tolylpropionic acid	4.89	0.451	0.138	0.033	0.013	15.66

^a pK_a value at 37 °C. ^b nd, not detected.

shows the pH effect on sorptions of 3-phenylpropionic acid ($pK_a = 4.78$) and 4-phenylbutyric acid ($pK_a = 4.86$) into LDPE film. Contrary to the sorption behaviors for pyridines, the sorptions for carboxylic acids were increasing with decreasing pH, and, at pH 4, the sorption dramatically increased compared to those in other pHs. The sorptions for 3-phenylpropionic acid and 4-phenylbutyric acid were increased ~ 2.0 and 4.8 times, respectively, when the pH decreased by one unit from 5 to 4. These results strongly revealed that a factor affecting sorption is a pK_a of sorbing compound.

As far as the authors are concerned, there were only a few reports on the effect of pH on sorption. Leufven and Hermansson (11) have reported an increase in sorption of some tomato flavor compounds by PE and ethylene/vinyl alcohol copolymer (EVOH) at pH 5. However, they did not refer to the underlying mechanism of promoting sorption at pH 5. Thus, it was the first finding that pK_a or ionization of the sorbing molecule was highly associated with the sorption process at various pHs.

Film-flavor affinity is a very important factor with respect to the sorption of flavors. In the present study, the two-dimensional approach (the δ_c concept), proposed by Chen (16), based on the affinity of flavor for film was applied to clarify the sorption behavior for pyridines and carboxylic acids. The δ_c concept has been applied to describe the degree of affinity of diverse polymer-solvent (volatile compound) systems in our previous study (6). According to this theory, polymer-flavor compatibility (δ_c) contributes to the mixing energy caused by dispersion forces and dipole forces. Thus, the δ_c value can be represented as the two-dimensional distance between the SP (δ_i) values of the polymer (δ_1) and the volatile compound (δ_2). When δ_i is subdivided into δ_p and δ_{np} components, the δ_c value is calculated as

$$\delta_c = [(\delta_{1np} - \delta_{2np})^2 + (\delta_{1p} - \delta_{2p})^2]^{1/2} \quad (4)$$

where δ_{1np} (δ_{1p}) and δ_{2np} (δ_{2p}) are the nonpolar (polar) components of δ_1 and δ_2 , respectively. Therefore, the higher δ_c value indicates the lower affinity of the polymer-volatile compound. In addition, it has been shown that the sorptions of flavors into the film in the aqueous phase depend on the δ_c value; the logarithms of the solubility coefficient decreased linearly with an increase in δ_c value. **Table 1** summarizes the sorption behaviors of all compounds used in this study and the related δ_c values. Considering the specific sorption behavior as a function of the δ_c value, the sorptions of all compounds increased with a decrease in the δ_c value. To elucidate the relationship between sorption and the δ_c value in detail, the

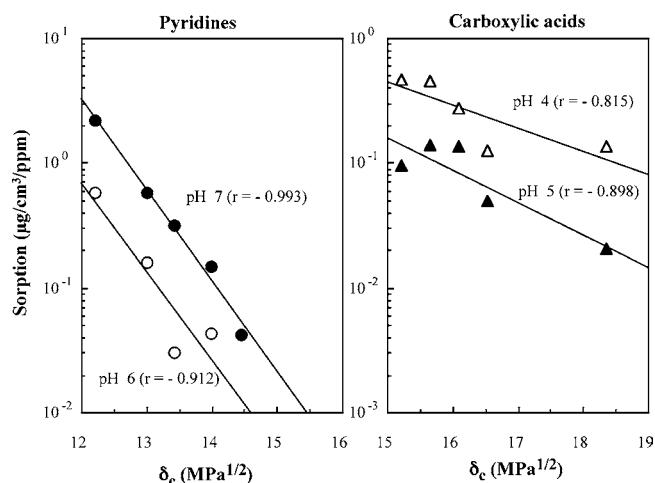


Figure 2. Sorption behaviors of pyridines (pH 6 and 7) and carboxylic acids (pH 4 and 5) as a function of δ_c value.

semilogarithmic plots of the sorption of pyridines and carboxylic acids for LDPE film against the δ_c value are made (**Figure 2**). For pyridines, close negative relationships with a slope of -0.71 ($r = -0.912$) and -0.73 ($r = -0.993$) were observed at pH 6 and 7, respectively, between the logarithms of the sorption of pyridines and the δ_c value. For carboxylic acids, close negative relationships were also observed at pH 4 and 5, and their slopes were -0.18 ($r = -0.815$) and -0.26 ($r = -0.898$), respectively. These results suggest that the sorption apparently depends on the polarity and molecular size of the compounds at a given pH. In addition, the slopes of these lines may give useful information concerning affinity dependence on the sorption of these compounds for LDPE film; a large negative slope indicates that sorption is remarkably influenced by affinity (δ_c). Thus, the results showed that the sorptions of pyridines would be influenced by δ_c greater than that of carboxylic acids. On the other hand, insufficient fitness of the lines was observed at pH 5 for pyridines ($r = -0.721$) and at pH 6 and 7 for carboxylic acids (pH 6, $r = -0.687$; pH 7, $r = -0.666$) (data not shown). These results suggest that ionization of the compounds would directly affect the affinity of the compounds for LDPE film.

Thus, providing that the ionizable compound that is involved in sorption would be restrictedly an un-ionized form, we estimated an un-ionized ratio of added compound according to the Henderson-Hasselbalch equation:

Figure 3 shows the replot of the sorption of pyridines and carboxylic acids obtained in Table 1 as a function of un-ionized ratio. As a result, the sorptions of pyridines and carboxylic acids

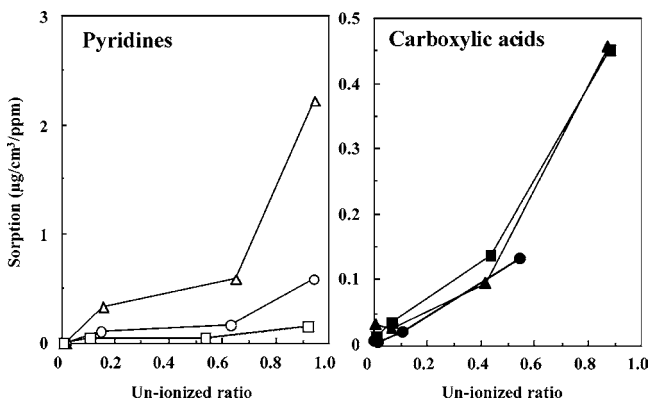


Figure 3. Sorption behaviors of pyridines and carboxylic acids as a function of their un-ionized ratios. Pyridines: 2-ethylpyridine (○), 2-propylpyridine (△), and 2-methylpyridine (□). Carboxylic acids: benzoic acid (●), 4-phenylbutyric acid (▲), and 3-*p*-tolylpropionic acid (■).

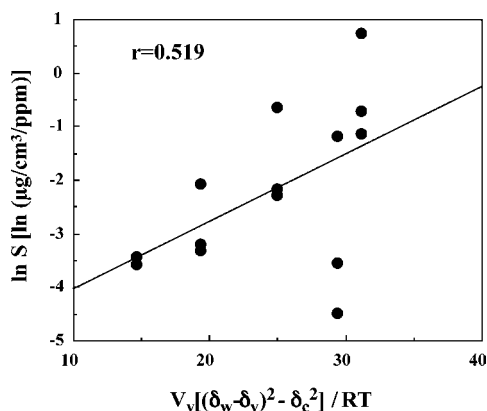


Figure 4. Relationship between the term $V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT$ and $\ln S$ of pyridines.

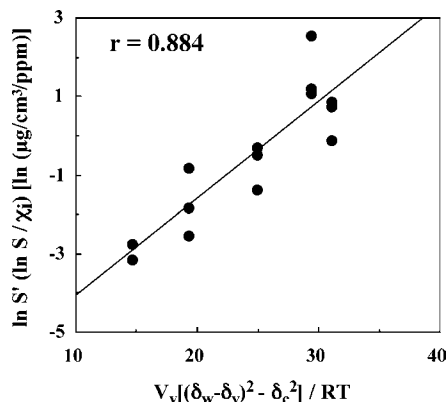


Figure 5. Relationship between the term $V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT$ and $\ln S'$ ($\ln S/\chi_i$) of pyridines.

increased with increasing un-ionized ratio. These specific behaviors suggest that the un-ionized form would be involved in sorption into the LDPE film.

Our next trial was to predict the specific sorption behavior in various pHs. According to our proposed sorption concept for the aqueous phase (7), sorption of the solute (volatile compound) into film was found to obey the following equation:

$$S = S_0 \exp(-\Delta H_S/RT) \\ = S_0 \gamma \exp[V_v \{(\delta_w - \delta_v)^2 - \delta_c^2\}/RT] \quad (5)$$

where S_0 and S_0' are the frequency factors, ΔH_S , is the molar

heat of sorption, V_v is the molar volume of the volatile compound, and γ is the constant characteristic of the polymer property. The sorption concept was applied to the sorption of pyridines and carboxylic acids. **Figure 4** represents the plots of $\ln S$ for pyridines into the LDPE film against the term of eq 5. As a result, insufficient correlation was observed for pyridines ($r = 0.519$). This was due to nonconsideration for the ionization of pyridines. The sorption (solubility coefficient, S) of the compound into the film is usually calculated at an added amount. As described above, however, the actual amount of the compound involved in the sorption process was nearly identical to the amount of the un-ionized form of the compound. Hence, taking into account the ratio (χ_i) of un-ionized species to total compound, the improvement for the eq 5 was made.

$$S' = S/\chi_i = S_0 \gamma \exp[V_v \{(\delta_w - \delta_v)^2 - \delta_c^2\}/RT] \quad (6)$$

Figure 5 represents the plots of $\ln S'$ ($\ln S/\chi_i$) for pyridines into the LDPE film against the term of eq 6. As a result, the plots gave a better relationship ($r = 0.884$) compared with the plots shown in **Figure 4**. Similarly, the improvement in the correlation was observed in the plots for carboxylic acids ($r = 0.769$). The sorption in eq 6 is not an adequate one for the prediction of the sorption of ionizable compounds, and additional factors would be needed. By a further approach, it would be possible to develop the sorption equation for ionizable compounds.

In conclusion, it was found that the pH of the solution greatly affected sorption of ionizable compounds into plastic film. The sorption depends on the affinity of these compounds for LDPE film, and the un-ionized form of the compounds was a candidate for sorption. Taking into account the un-ionized ratio of the compound at pHs, the thermodynamic sorption of eq 6 was derived. The equation was useful for better understanding of sorption behaviors of a variety of ionizable compounds under the pH of the packed food.

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