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Application of the Solubility Parameter in Estimating the Sorption Behavior of Flavor into Packaging Film

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In order to estimate the sorption behaviors of flavors into film packaging, a two-dimensional approach based on the affinity of flavor for film was performed. When the solubility parameter (SP) value is divided into polar and nonpolar components, the affinity can be represented as a two-dimensional distance (δ_c) between two SP values of film and flavor. On the basis of this δ_c concept, the sorptions of flavors into MDPE and EVOH films in the aqueous phase were proved to depend on the δ_c value; the logarithms of the solubility coefficient decreased linearly with an increase in δ_c value, i.e., about one-sixth decrease for one δ_c value. In addition, a large negative slope of the line indicated that the sorption was remarkably influenced by affinity (δ_c).

INTRODUCTION

Plastic materials for food packaging have some advantages due to their low cost, heat stability, and convenience as compared with other ones such as glass, metal, and paper (Hotchkiss, 1988). Therefore, the usage of various plastics for food packaging has been in great demand. Especially, polyolefins such as polyethylene (PE) and polypropylene (PP) have a widespread use as food contact polymers because of freedom from toxic monomers and flexibility. As opposed to their prevalence, a serious problem has been raised concerning deterioration of intrinsic food flavors by plastic films (Reid et al., 1980; Farrell, 1988). This phenomenon may be predominantly brought about by sorption of flavors into interior linings because the film has been directly contacted with foodstuffs over long period storage (Shimoda et al., 1984; Sadler and Braddock, 1991).

Amerongen (1950) has proposed that the sorption of gases to polymer (in this case, film) proceed according to the following four steps: adsorption on the surface of the film, cohesion, absorption (solubility) into, and diffusion in it. Based on this concept, the present authors have quantitatively dealt with the sorption behaviors of flavors into interior linings. The results already made clear are as follows: more sorption is observed with an increase in carbon atoms in a homologous series; functional groups greatly affect the sorption regardless of their carbon chain length (Shimoda et al., 1987; Matsui et al., 1989); sorptions of flavors into films with distinct polarity are quite different (Ikegami et al., 1991).

It has been considered that the affinity of flavor for film would greatly affect the magnitude of sorption (Becker et al., 1983; Matsui et al., 1992). Thus, we have tried to predict the sorption behaviors of flavors for various packaging films on the basis of the affinity concept derived from the solubility parameter.

MATERIALS AND METHODS

Materials. Middle-density polyethylene (MDPE) film with the thickness of 30 μm was manufactured by Showa Denko KK, Oita, and ethylene–vinyl alcohol (EVOH) copolymer films composed of five different ethylene contents (38, 47, 58, 64, and 88 mol %) with thickness of 25 μm were supplied by Kuraray Co., Ltd., Kurashiki. The physical properties of these films are listed in Table I.

Preparation of Model Flavor Solution. The volatile compound was added to a solution (300 mL) of 0.3 w/v % sugar-ester (S-1170, Mitsubishi-Kasei Food Co., Ltd., Tokyo) as an emulsifier to make a 10 ppm flavor solution and dispersed homogeneously by an ultrasonic wave generator for 15 min. Film samples (MDPE, 5.5 × 6 cm; EVOH, 15 × 24 cm) were immersed in this model flavor solution and stored at 20 °C until the equilibrium of sorption was achieved (in this experiment, about a 56-day storage).

The volatile compounds used in this experiment were all guaranteed reagent grade from Nakarai Chemicals Co., Ltd., Kyoto, and were used without further purification.

Recovery of Volatile Compounds. The sorbed film was immersed in 50 mL of diethyl ether and allowed to stand for 2 days. After concentration under a stream of nitrogen gas, the extracts were analyzed by gas–liquid chromatography. The analysis was performed on a Shimadzu GC-9A gas chromatograph connected to a Shimadzu Chromatopac C-R3A integrator. A fused silica capillary column, 0.25-mm i.d. × 50 m, coated with 10% (cyanopropyl)phenyl polysiloxane (CPB10) was used for separation. The column was programed from 60 to 240 °C at 2 °C/min, inlet and detector were maintained at 250 °C, and carrier (He) flow rate was 0.82 mL/min. The quantification of volatile compounds was carried out using 1.0 μg/100 mL of amylbenzene as an internal standard.

Estimation of Solubility Parameter. According to Mangaraj (1963), the solubility parameter (SP) indicates the polymer–solvent compatibility. Thus, the concept may be available for predicting the cohesive property (in other words, sorption) of flavor compound for films. The SP value is defined as the square root of cohesive energy density (CED) (Barton, 1985)

$$\text{SP value } (\delta) = (\text{CED})^{1/2} = (\Delta E/V)^{1/2}\ [\text{MPa}^{1/2}] \tag{1}$$

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 volatile compound and film were calculated on the basis of the Fedors' parameter concept (1974) which can be used for polar and nonpolar materials

$$\delta = \left(\sum \Delta e_i / \sum \Delta v_i\right)^{1/2} \tag{2}$$

where $\sum \Delta e_i$ and $\sum \Delta v_i$ are the sum of vaporization energy and molar volume of atom or group, respectively.

Then, the SP value obtained from eq 2 was divided into polar (δ_p) and nonpolar (δ_{np}) components in order to evaluate the intermolecular forces responsible for sorption. The δ_{np} values have been determined by application of the homomorph concept

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Table I. Characteristics of MDPE and EVOH Films

	ethylene content, mol %					
	EVOH					MDPE
	38	47	58	64	88	100
density, g/cm^3	1.154	1.115	1.082	1.050	0.933	0.944
T_g,[a] °C	56.4	48.1	39.5	37.6		
T_m,[b] °C	173.5	157.5	142.8	142.3	108.4	127.5
ΔH,[c] J/g	77.3	75.6	65.6	73.2	97.1	106.6

[a] T_g, glass transition temperature. [b] T_m, melting temperature. [c] ΔH, heat of fusion.

Table II. Solubility Parameter (SP) Values of Flavor Compounds

	SP, MPa$^{1/2}$		
compound	δ_t[a]	δ_{np}[b]	δ_p[c]
decane	15.8	15.8	0
d-limonene	16.9	15.9	5.6
myrcene	16.6	15.2	6.7
ethyl octanoate	18.3	15.8	9.2
decanal	18.8	15.9	10.0
nerol	19.6	15.4	12.1
decanol	20.5	15.9	12.9

[a] δ_t, total SP value. [b] δ_{np}, nonpolar component of δ_t. [c] δ_p, polar component of δ_t.

Table III. Solubility Parameter (SP) Values of EVOH and MDPE Films at 0% RH[a]

	SP, MPa$^{1/2}$		
ethylene content, mol %	δ_t	δ_{np}	δ_p
38	27.6	16.7	22.0
47	26.2	16.8	20.1
58	24.6	16.9	17.9
64	23.7	17.0	16.5
88	19.6	17.4	9.0
100 (MDPE)	16.5	16.5	0

[a] All symbols are the same as in Table II.

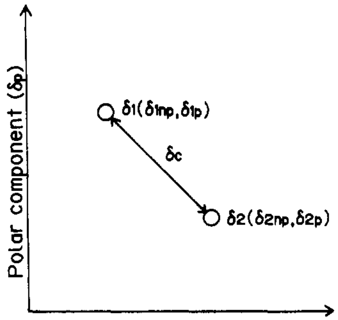

Figure 1. Evaluation of polymer–flavor affinity. δ_1, SP value of polymer; δ_2, SP value of flavor; δ_{1np} (δ_{2np}), nonpolar component of δ_1 (δ_2); δ_{1p} (δ_{2p}), polar component of δ_1 (δ_2); δ_c, two-dimensional distance between δ_1 and δ_2.

Table IV. Relationship between Sorption and δ_c Values for MDPE and 38 mol % EVOH Films at 20 °C

	MDPE		EVOH	
compound	δ_c[a]	S[b]	δ_c	S[b]
decane	0.7	5593	21.9	2.0
d-limonene	5.6	3739	16.3	10.9
ethyl octanoate	9.1	2065	12.8	21.7
decanal	10.1	1695	11.8	36.7
nerol	12.1		9.9	68.9
decanol	12.9	107	9.0	78.4

[a] δ_c (MPa$^{1/2}$), two-dimensional distance between two δ_t values defined in Figure 1. [b] S (μg·cm^{-3}·ρ^{-1}/10 ppm), solubility coefficient.

(Blanks and Prausnitz, 1964). 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:

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

RESULTS AND DISCUSSION

Tables II and III summarize the δ_t, δ_{np}, and δ_p values of volatile compounds and MDPE and EVOH films used in this study. In Table II, the compound with an unsaturated bond and oxygen had higher δ_t and δ_p values than the corresponding homomorph, indicating the increase of polarity or intermolecular force. Not listed in the table, in a homologous series, the δ_{np} value increased with increasing carbon atoms, while the δ_t value decreased. The calculated δ_t and δ_p values relating to EVOH films composed of ethylene and vinyl alcohol units increased with the decrease in ethylene content (Table III), which indicates the increase in cohesive forces between polymer chains. The behaviors were in fair agreement with those of glass transition temperature (T_g) shown in Table I.

The SP value (δ_t) is widely used in predicting the compatibility or affinity of polymer–solvent (volatile compound) systems (Koenhen and Smolders, 1975). It is, however, quite difficult to describe the degree of affinity in diverse systems from the corresponding δ_t values themselves. Therefore, in order to numerize the degree of affinity and represent the sorption characteristics of flavors into films, we have used the two-dimensional method proposed by Chen (1971). 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 δ_t values of polymer (δ_1) and volatile compound (δ_2), as shown in Figure 1. When δ_t is subdivided into δ_p and δ_{np} components, the δ_c value is calculated as

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

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 previous papers (Matsui et al., 1992; Shimoda et al., 1988), we have demonstrated that polar compounds had lower sorptions into polyethylene in aqueuous phase: hydrocarbons > ethyl esters > aldehydes > alcohols. These results revealed that the sorption apparently depends on the polarity of volatile compound. Table IV shows the sorption behaviors of flavor compounds composed of 10 carbon atoms into MDPE and 38 mol % EVOH films in aqueous phase and the related δ_c values. In an MDPE film, the maximum sorption was observed for decane, while in EVOH film for decanol, the behavior was distinct in terms of the property of film. With respect to the δ_c, the value for MDPE with low polarity increased with the polarity of flavors, while for EVOH with higher polarity the opposite results were obtained. Considering the specific sorption behavior as a function of δ_c, the sorption was ascertained to depend on the δ_c (film–flavor affinity); for both films investigated, the sorption increased with a decrease in δ_c value. Hence, the application of δ_c could be effective in estimating the sorption behaviors of flavors for each film. In this study, a direct comparison of sorption amount among MDPE and EVOH films may be impossible due to their differences of physical properties such as free volume, orientation, and so on. In addition, the effect of water absorption on the δ_t value of EVOH

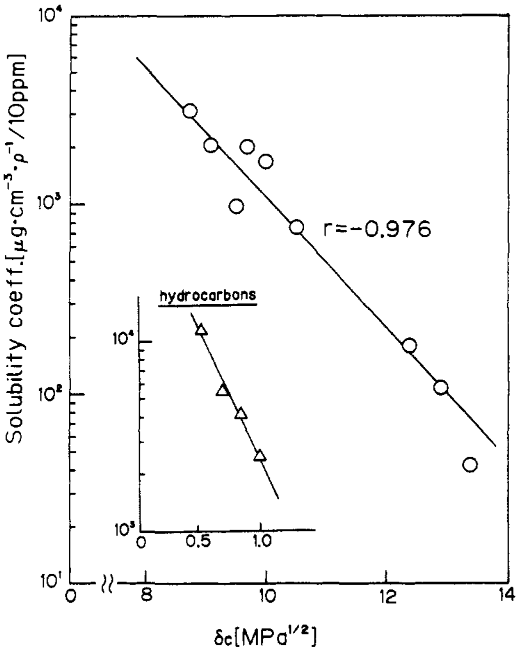

Figure 2. Sorption behaviors of volatile compounds for MDPE film in the aqueous phase at 20 °C as a function of δ_c value. Volatile compound: *n*-hydrocarbons (8–11 carbon atoms), ethyl esters (7–11), *n*-aldehydes (8–11), *n*-alcohols (9–11), terpenes (*d*-limonene, nerol, and α-terpineol).

film is not negligible; the actual δ_t value of EVOH film in aqueous sorption measurement (100% RH) has a lower one due to the lowering of hydrogen force by water than the value at 0% RH shown in the table. However, even if the δ_t value of EVOH film were different, one could make a relative evaluation for sorption, because the δ_c is derived from the solubility parameters due to dispersion forces and dipole forces, not to hydrogen forces (Chen, 1971).

In order to elucidate the relationship between sorption and δ_c value in detail, the semilogarithmic plots of the solubility coefficient for MDPE film against the δ_c value are made (Figure 2). Volatile compounds used in this experiment were aliphatic hydrocarbons (8–11 carbon atoms), ethyl esters (7–11 carbon atoms), aldehydes (8–11 carbon atoms), alcohols (9–11 carbon atoms), and terpenes (*d*-limonene, nerol, and α-terpineol). As in Figure 2, there existed a close negative relationship with a slope of −0.37 (r = −0.976) between the logarithms of solubility coefficients of all compounds except hydrocarbons and the δ_c values; the sorption decreased about one-sixth-fold for one value. The slope of the line may give a useful information concerning affinity dependence on sorption of flavor for a film; a large negative slope indicates that sorption is remarkably influenced by affinity (δ_c). It was, therefore, confirmed that the δ_c parameter may be available for evaluating the magnitude of sorption for MDPE film. Unfitness of the line for hydrocarbons has been assumed to be caused by their higher chemical potentials compared to those for oxygen-containing compounds in aqueous solution.

Similar attempts were made for five grades of EVOH films (38, 47, 58, 64, and 88 mol %) as shown in Figure 3. For each film, all plots of flavors composed of 10 carbon atoms gave a straight line. The negative slopes of these lines were −0.13, −0.08, −0.04, −0.03, and −0.02 for 38, 47, 58, 64, and 88 mol % EVOH films, respectively. These results suggested that for EVOH films with a lower ethylene content, into which the flavors had lower sorptions, the greater influence of affinity on sorption may be expected. Consequently, it has been proved that the sorption in the aqueous phase always decreases with increasing δ_c or lowering of affinity even if the characteristics of sorbed film were different.

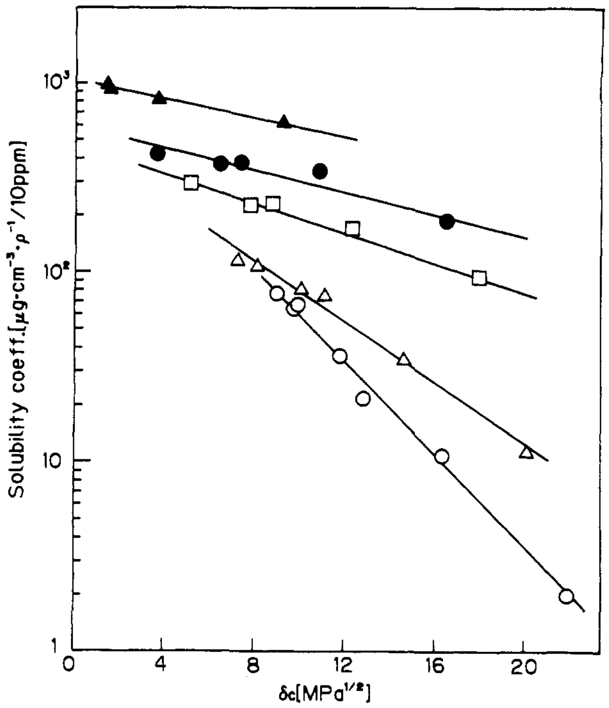

Figure 3. Relationships between the δ_c values and solubility coefficients of volatile compounds for EVOH films at 20 °C. Volatile compound: decane, ethyl octanoate, decanal, decanol, *d*-limonene, nerol; ethylene content of EVOH, 38 mol % (○), 47 mol % (△), 58 mol % (□), 64 mol % (●), 88 mol % (▲).

In conclusion, the application of the δ_c concept could successfully estimate the sorption behaviors of flavors into various films in aqueous phase.

ABBREVIATIONS USED

MDPE, middle-density polyethylene; EVOH, ethylene–vinyl alcohol copolymer; SP, solubility parameter.

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Registry No. $CH_3(CH_2)_8CH_3$, 124-18-5; $CH_3(CH_2)_6CO_2Et$, 106-32-1; $CH_3(CH_2)_8CHO$, 112-31-2; $(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OH$, 106-25-2; $CH_3(CH_2)_9$-OH, 112-30-1; polyethylene, 9002-88-4; ethylene–vinyl alcohol copolymer, 25067-34-9; *d*-limonene, 5989-27-5.