

# Derivation of Thermodynamic Sorption Equation of Flavors with Packaging Films. 1<sup>†</sup>

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The sorption equation of flavors with packaging film to extend for various flavors and polymers was derived by improving the proposed  $\delta_c$  concept. On the basis of the findings that the sorptions depend on both the  $\delta_c$  values between film and flavors with similar chemical potential and their molar heat of vaporization ( $\Delta H_{vap}$ ), the following thermodynamic sorption equation was derived:  $S = S_0 \exp \gamma [V_v(\delta_v^2 - \delta_c^2)/RT]$ . For aqueous phase the plots of  $\ln S$  vs the term of the equation gave an adequate but insufficient relationship ( $r = 0.802$ ), resulting from the influence of any interaction force from solution on the magnitudes of physical adsorption and condensation of flavors on film surface. On the other hand, for vapor phase the same plots gave a quite sufficient correlation ( $r = 0.967$ ). Therefore, in the prediction of the sorption behaviors for vapor phase the derived sorption equation may be more useful and effective.

**Keywords:** Sorption; flavor; prediction

## INTRODUCTION

Degradations of flavors by food packaging during storage are the greatest problems in providing high-quality food. Among them, loss or change of flavors by oxidation and sorption into film would be the contributing factors. (Osajima and Matsui, 1993; Manheim and Havkin, 1981). For the oxidative changes, protection is possible through the addition of an antioxidizing agent such as ascorbic or erysorbic acid and the degassing of solution or substitution for nitrogen (Hotchkiss, 1988). However, these methods cannot cope with the sorption degradation by packaging films, especially interior linings mostly consisting of polyolefins, into which the majority of flavors in citrus juice are sorbed over a short period of storage (Shimoda et al., 1984). To elucidate this problem, it is necessary to develop less sorbed films or to select more favorable film material in which to pack food with the help of the predicted magnitude of sorption of flavors that greatly contribute to the food.

In a series of our studies, we have primarily tried to investigate the practical sorption phenomena of various volatile compounds [reviewed in Osajima and Matsui (1993) and Matsui and Osajima (1993)]. Among the factors affecting the sorption already clarified, the affinity of flavor for film was proved to be attributed to the magnitude of sorption (Matsui et al., 1992a). Further investigation was performed to estimate the sorption behaviors of flavors on the basis of our proposed affinity concept in which the affinity was represented as a two-dimensional distance ( $\delta_c$ [MPa<sup>1/2</sup>]) between two solubility parameter (SP) values of film and flavor divided into polar and nonpolar components (Matsui et al., 1992b). When this  $\delta_c$  concept was applied, the sorption behaviors of flavors with similar chemical

potential into middle-density polyethylene (MDPE) and ethylene-vinyl alcohol (EVOH) copolymer films could be predicted, although the applicable flavors were restrictive.

For permanent gases, Salame (1986) has already derived the empirical permeability equation as a Permachor value of polymer ( $\pi$ ). Though the Permachor equation is very effective for estimating permanent gas permeability as well as diffusion and solubility properties of polymers, a direct application for flavors with various molecular properties may be inadequate due to any interaction or swelling between polymer and flavor. Also, Paik and Tigani (1992, 1993a,b) have tried to predict the sorption of flavors with attention to the first step of sorption process, *i.e.*, adsorption on the surface of film similar to our  $\delta_c$  concept, but their derived concepts based on the difference of cohesive energy (enthalpy in mixing) or dielectric constant (force attraction or repulsion) gave little useful information.

The difficulty in predicting sorption behaviors of flavors is presumed to lie in the omission of some factors concerned in the sorption process. We have tried to establish the thermodynamic sorption equation of flavors with packaging film by improving the  $\delta_c$  concept so as to extend it to various flavors and polymers.

## MATERIALS AND METHODS

**Materials.** Low-density polyethylene (LDPE) film with the thickness of 40  $\mu\text{m}$  was supplied by Showa Denko KK, Oita, Japan, and used as a sample film to perform the derivation of sorption equation in this study.

**Determination of the Magnitude of Sorption.** The solubility ( $S$ ), diffusion ( $D$ ), and permeability ( $P$ ) coefficients of volatile compounds into LDPE film for vapor and aqueous phases were determined by the permeation apparatus based on the isobaric method. Detailed procedures were described elsewhere (Shimoda et al., 1987; Matsui et al., 1989). Briefly, the permeation of a volatile compound through a sample film was continuously detected by GC (Shimadzu GC-6A, equipped with a flame ionization detector, FID), and the coefficients were calculated from the obtained differential permeation curve. For both phases, experimental runs were carried out at 25 °C and 50 mL/min of downstream carrier gas flow rate. For aqueous phase, the volatile compounds were added to a

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0.3 w/v % sugar-ester solution (S-1170, Mitsubishi-Kasei Food Co., Ltd., Tokyo) to make a 200 ppm flavor solution. The volatile compounds used in this study were all guaranteed reagent grade from Nacalai Tesque Inc., Kyoto, and used without further purification.

**Estimation of Solubility Parameter.** The solubility parameter (SP) values for film and flavor were calculated on the basis of the Fedors's (1974) parameter concept and further divided into polar and nonpolar components by application of the homomorph concept (Blanks and Prausnitz, 1964).

#### DERIVATION OF THERMODYNAMIC SORPTION EQUATION

According to the Arrhenius-type relationship (Krevlen, 1990), sorption (solubility) of solvent into polymer can be represented as follows:

$$S = S_0 \exp(-\Delta H_s/RT) \quad (1)$$

where  $S_0$  is the frequency factor and  $\Delta H_s$  the molar heat of sorption. Thus, provided that  $\Delta H_s$  can be estimated or defined correctly, the plots of  $\ln S$  against  $\Delta H_s$  would give a straight line, following the prediction of sorption behaviors of flavors.

On the basis of the regular solution theory (Hildebrand, 1929), free energy change in sorption ( $\Delta G_s$ ) corresponds to the enthalpy in sorption because the change in entropy is considered to be negligible. Thus, we defined the  $\Delta G_s$  as the molar heat of sorption ( $\Delta H_s$ ). Gee (1947) proposed that  $\Delta H_s$  is the sum of the molar heat of condensation ( $\Delta H_v$ ) of volatile compound and of mixing ( $\Delta H_m$ ):

$$\Delta H_s = \Delta H_v + \Delta H_m \quad (2)$$

Hildebrand correlated the enthalpy of mixing ( $\Delta h_m$ ) with cohesive energy densities of polymer ( $\delta_f$ ) and volatile compound ( $\delta_v$ ) (Hildebrand et al., 1970)

$$\Delta h_m = \phi_f \phi_v (X_f V_f + X_v V_v) (\delta_f - \delta_v)^2 \quad (3)$$

$$\phi_f = X_f V_f / (X_f V_f + X_v V_v) \quad (4)$$

$$\phi_v = X_v V_v / (X_f V_f + X_v V_v) \quad (5)$$

where  $\phi_f$  and  $\phi_v$  are the volume fractions,  $X_f$  and  $X_v$  are the mole fractions, and  $V_f$  and  $V_v$  are the molar volumes of polymer (f) and volatile compound (v), respectively. To derive the enthalpy of mixing ( $\Delta H_m$ ) per unit mole of volatile compound, eq 3 is differentiated by the mole fraction ( $X_v$ ) of volatile compound:

$$(\partial \Delta h_m / \partial X_v)_{X_f} = \Delta H_m = V_v \phi_f^2 (\delta_f - \delta_v)^2 \quad (6)$$

Taking into account that the change in volume of mixing is negligible (Hildebrand et al., 1970),  $\phi_f \approx 1$ . Therefore, eq 6 reduces to

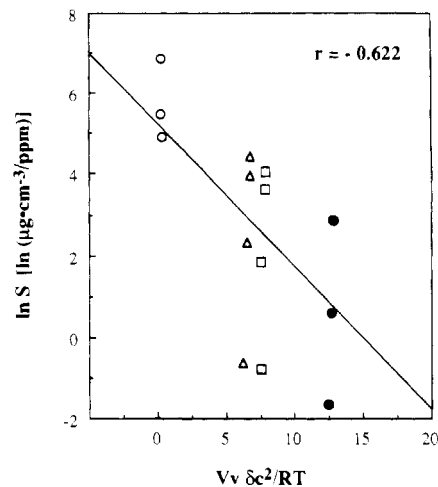
$$\Delta H_m = V_v (\delta_f - \delta_v)^2 \quad (7)$$

which corresponds to the Flory-Huggins parameter ( $\chi$ ) (Mizerovskii and Belova, 1987).

By assuming that  $\Delta H_s$  is only dependent on  $\Delta H_m$ , the following equation is obtained:

$$S = S_0 \exp[-V_v (\delta_f - \delta_v)^2 / RT] \quad (8)$$

Paik and Tigani (1993a) demonstrated that the application of the term  $(\delta_f - \delta_v)^2$  could not be successful in



**Figure 1.** Relationship between the term  $V_v \delta_c^2 / RT$  and sorption of volatile compounds into LDPE film at 25 °C for aqueous phase. Volatile compound: *n*-hydrocarbons (○, 6–10 carbon atoms); ethyl esters (△, 4–10); *n*-aldehydes (□, 4–10); *n*-alcohols (●, 4–10).

estimating the sorption behaviors for various polymers. The poor relationship between  $(\delta_f - \delta_v)^2$  and  $\ln S$  would be caused by incomplete treatment of mutual molecular interaction forces. We introduced the proposed  $\delta_c$  concept (Matsui et al., 1992b) into eq 8, which was defined as a two-dimensional distance between the total SP ( $\delta_c$ ) values of the film [ $\delta_f$ ; ( $\delta_{fp}$ ,  $\delta_{fnp}$ )] and volatile compound [ $\delta_v$ ; ( $\delta_{vp}$ ,  $\delta_{vnp}$ )] on the assumption that the  $\delta_c$  contributes to the mixing energy caused by the dispersion and dipole forces:

$$\delta_c = [(\delta_{vp} - \delta_{fp})^2 + (\delta_{vnp} - \delta_{fnp})^2]^{1/2} \quad (9)$$

The term  $(\delta_f - \delta_v)^2$  in eq 7 is replaced by  $\delta_c$

$$\Delta H_m = V_v \delta_c^2 \quad (10)$$

Combining eq 10 with eq 1 yields

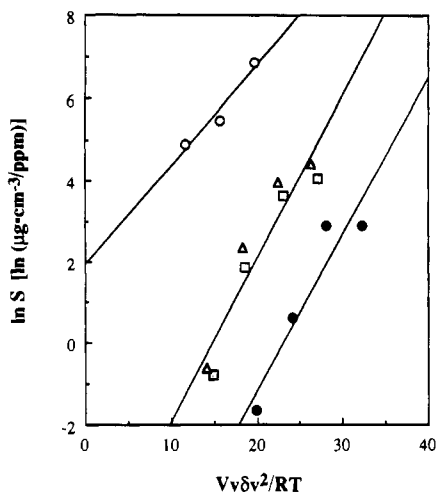
$$S = S_0 \exp \gamma (-V_v \delta_c^2 / RT) \quad (11)$$

where  $\gamma$  is the constant characteristic of polymer property. As shown in Figure 1, the plots of  $V_v \delta_c^2 / RT$  vs  $\ln S$  for *n*-hydrocarbons, ethyl esters, *n*-aldehydes, and *n*-alcohols for aqueous phase resulted in poor correlation. However, it is apparent that for the compounds composed of the same number of carbon atoms there existed a good negative relationship, indicating that the  $\delta_c$  concept may be applicable to compounds with similar chemical potentials. Hence, the introduction of another factor, *e.g.*, chemical potential in a given phase, into eq 11 must be needed for the derivation of a sorption equation applicable to all volatile compounds.

We have already made clear that the sorption depends on the boiling point of the sorbed compound in diverse phases (Osajima and Matsui, 1993). This finding suggested that the molar heat of vaporization ( $\Delta H_{vap}$ ) might be involved in the sorption process. Taking into account that

$$\delta_v^2 = (\Delta H_{vap} - RT) / V_v \quad (12)$$

(Hildebrand et al., 1970), we obtain the equation



**Figure 2.** Relationship between the term  $V_v \delta_v^2 / RT$  and sorption of volatile compounds into LDPE film at 25 °C for aqueous phase. Symbols are as in Figure 1.

$$\begin{aligned} S &= S_0 \exp \gamma(-\Delta H_{\text{vap}}/RT) \\ &= S_0 \exp \gamma(-V_v \delta_v^2 / RT - 1) \\ &= S_0' \exp \gamma(-V_v \delta_v^2 / RT) \end{aligned} \quad (13)$$

Certainly, for each homologous series the sorption in aqueous solutions depended on the  $V_v \delta_v^2 / RT$  values as shown in Figure 2; the greater was  $\Delta H_{\text{vap}} / RT$ , the more sorption was observed. This implies that the  $\Delta H_{\text{vap}}$  of volatile compound may be a "driving potential" in the magnitudes of physical adsorption and condensation of the compound on film surface.

To derive the sorption equation, we have combined the  $\delta_c$  concept with the molar heat of vaporization. As mentioned above,  $\Delta H_s$  is the sum of  $\Delta H_v$  of volatile compound and  $\Delta H_m$ . Since  $\Delta H_v$  is negative in an exothermic process with the same numerical value as  $\Delta H_{\text{vap}}$ ,  $\Delta H_v$  is expressed by

$$\Delta H_v = -\Delta H_{\text{vap}} = -(V_v \delta_v^2 + RT) \quad (14)$$

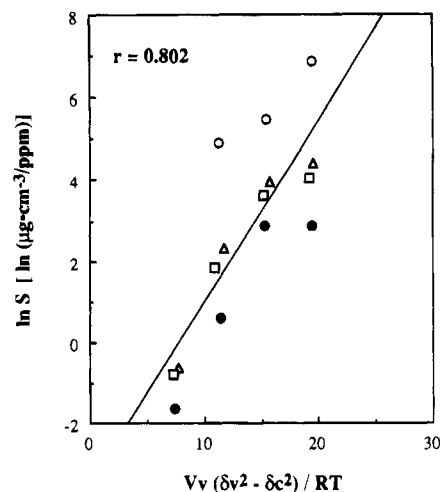
By introducing eqs 10 and 14 into eq 2, the equation obtained is

$$\Delta H_s = V_v \delta_c^2 - (V_v \delta_v^2 + RT) \quad (15)$$

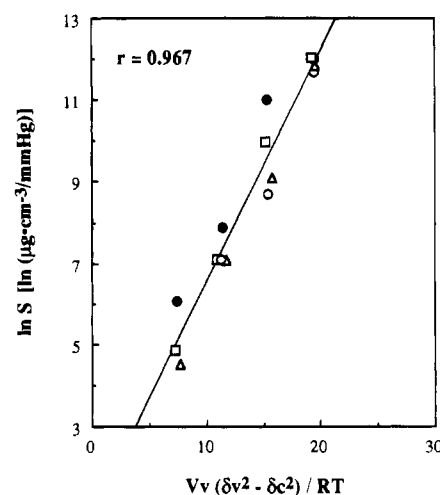
and the concept of our derived  $\Delta H_s$  is consistent with that of Salame (1986), where the heat of solution (in this case,  $\Delta H_s$ ) is the difference between the cohesive energy of polymer and the Lennard-Jones potential of permanent gas. Accordingly, by use of eqs 1 and 15 we have

$$\begin{aligned} S &= S_0 \exp(-\Delta H_s / RT) \\ &= S_0 \exp \gamma[-(V_v \delta_c^2 - (V_v \delta_v^2 + RT)) / RT] \\ &= S_0' \exp \gamma[V_v (\delta_v^2 - \delta_c^2) / RT] \end{aligned} \quad (16)$$

Figure 3 represents the plots of  $\ln S$  against the term of eq 16 for aqueous phase. As a result, a more adequate improvement in the correlation was observed ( $r = 0.802$ ) as compared with the plots shown in Figures 1 ( $r = -0.622$ ) and 2 ( $r = 0.148$ ). However, the sorptions for each homologous series significantly increased with a decrease in their polarity, contributing to the insufficient correlation. This was assumed to be caused by the effect of any interaction forces from solution on driving potential of flavors. To support this assumption, vapor phase investigations were made (Figure 4), in



**Figure 3.** Relationship between the term  $V_v (\delta_v^2 - \delta_c^2) / RT$  and sorption of volatile compounds into LDPE film at 25 °C for aqueous phase. Symbols are as in Figure 1.



**Figure 4.** Relationship between the term  $V_v (\delta_v^2 - \delta_c^2) / RT$  and sorption of volatile compounds into LDPE film at 25 °C for vapor phase. Symbols are as in Figure 1.

which there is no molecular interaction between volatile compounds and water and/or surfactant in solution. As shown in Figure 4, a sufficient correlation ( $r = 0.967$ ) was obtained between  $\ln S$  and the term  $V_v (\delta_v^2 - \delta_c^2) / RT$ . Hence, it was proved that the insufficient correlation observed by plotting for aqueous phase (Figure 3) was attributed to another factor that affected the driving potential of flavors toward film.

Consequently, with respect to the prediction of the vapor phase sorption behaviors of flavors, the derived sorption eq 16 is the most useful and effective one. A further approach to derive the sorption equation for aqueous phase is described in the accompanying paper.

#### ABBREVIATIONS USED

LDPE, low-density polyethylene; SP, solubility parameter.

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#### LITERATURE CITED

Blanks, R. F.; Prausnitz, J. M. Thermodynamics of Polymer Solubility in Polar and Nonpolar Systems. *Ind. Eng. Chem. Fundam.* 1964, 3, 1-8.

- Fedors, R. F. Methods for Estimating both Solubility Parameters and Molar Volumes of Liquid. *Polym. Eng. Sci.* **1974**, *14*, 147-154.
- Gee, G. Some Thermodynamic Properties of High Polymers, and Their Molecular Interaction. *Q. Rev.* **1947**, *1*, 265-298.
- Hildebrand, J. H. Solubility. XII. Regular Solutions. *J. Am. Chem. Soc.* **1929**, *51*, 66-80.
- Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold: New York: 1970; Chapter 6.
- Hotchkiss, J. H. An Overview of Food and Food Packaging Interactions. In *Food and Packaging Interactions*; Hotchkiss, J. H., Ed.; American Chemical Society: Washington, DC, 1988; pp 1-10.
- Krevelen, D. W. *Properties of Polymers*; Elsevier Scientific Publishing: Amsterdam, 1990; Chapter 18.
- Manheim, C. H.; Havkin, M. Shelf-Life of Aseptically Bottled Orange Juice. *J. Food Process. Preserv.* **1981**, *5*, 1-6.
- Matsui, T.; Osajima, Y. Sorption of Flavors into Plastic Films Used for Interior Can Coating. *J. Iron Steel* **1993**, *79*, 1138-1144.
- Matsui, T.; Shimoda, M.; Osajima, Y. A Simple Method for Measuring Sorption of Flavor Compounds in Aqueous Solutions into Polyethylene Film. *J. Jpn. Soc. Food Sci. Technol.* **1989**, *36*, 52-54.
- Matsui, T.; Ono, A.; Shimoda, M.; Osajima, Y. Thermodynamic Elucidation of Depression Mechanism on Sorption of Flavor Compounds into Electron Beam Irradiated LDPE and EVA Films. *J. Agric. Food Chem.* **1992a**, *40*, 479-483.
- Matsui, T.; Nagashima, K.; Fukamachi, M.; Shimoda, M.; Osajima, Y. Application of the Solubility Parameter in Estimating the Sorption Behavior of Flavor into Packaging Film. *J. Agric. Food Chem.* **1992b**, *40*, 1902-1905.
- Mizerovskii, L. N.; Belova, O. V. Calculation of Solubility Parameters for Binary Liquid Mixtures and for Copolymers. *Vsokomol. Soyed.* **1987**, *A29*, 1236-1241.
- Osajima, Y.; Matsui, T. Dynamic Approach to the Sorption of Flavors into a Food Packaging Film. *Anal. Sci.* **1993**, *9*, 753-763.
- Paik, J. S. Comparison of Sorption in Orange Flavor Components by Packaging Films Using the Headspace Technique. *J. Agric. Food Chem.* **1992**, *40*, 1822-1825.
- Paik, J. S.; Tigani, M. A. Application of Regular Solution Theory in Predicting Equilibrium Sorption of Flavor Compounds by Packaging Polymers. *J. Agric. Food Chem.* **1993a**, *41*, 806-808.
- Salame, M. Prediction of Gas Barrier Properties of High Polymers. *Polym. Eng. Sci.* **1986**, *26*, 1543-1546.
- 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.; Matsui, T.; Osajima, Y. Behavior of Diffusion, Permeation and Sorption of Flavor Compounds in Vapor Phase with Polyethylene Film. *J. Jpn. Soc. Food Sci. Technol.* **1987**, *34*, 402-406.
- Tigani, M. A.; Paik, J. S. Use of Dielectric Constants in the Prediction of Flavour Scalping. *Packag. Technol. Sci.* **1993b**, *6*, 203-209.

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