

# Derivation of Thermodynamic Sorption Equation of Flavors with Packaging Films. 2<sup>†</sup>

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A further approach to derive the thermodynamic sorption equation for aqueous phase was performed by estimating the molar heat of sorption ( $\Delta H_s$ ) accurately. On the basis of the findings that the sorption of a volatile compound depends on both its molar heat of mixing into film and its enthalpy change toward film, the following equation could be successfully derived:  $S = S_0 \exp \gamma [V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT]$ . The plots of  $\ln S$  into LDPE film vs the term of the equation gave more adequate improvement in the correlation ( $r = 0.968$ ). Taking into account the volatility ( $\alpha$ ) of a volatile compound from solution, further improvement of the equation was made:  $S = \alpha S_0 \exp \gamma [V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT]$ . The plots of  $\ln S/\alpha$  vs the term of the equation for both sugar-ester and SDS solutions gave a sufficient correlation ( $r = 0.959$ ). Furthermore, the equation could be sufficiently applied to various polymers (PP,  $r = 0.931$ ; EVA,  $r = 0.963$ ; EVOH,  $r = 0.932$ ).

**Keywords:** Sorption equation; flavor; solubility parameter

## INTRODUCTION

In our preceding paper (Matsui et al., 1994), we have elucidated the thermodynamic sorption behaviors of flavors into packaging film. Among the factors affecting sorption, the affinity between film and flavor (Matsui et al., 1992) and the molar heat of vaporization (Osajima and Matsui, 1993) were found to be responsible for the sorption process. Hence, regarding the energy of sorption as a difference between film-flavor affinity and driving potential of flavors toward film, we have succeeded in deriving the sorption equation for vapor phase to predict the sorption behaviors and design more favorable packaging film.

On the other hand, the derivation for aqueous phase was unsuccessful because any interactions between flavor and solution were not considered. In this paper, a further approach for aqueous phase to derive the thermodynamic sorption equation is described. An attempt to apply the derived equation for various packaging films is also described.

## MATERIALS AND METHODS

**Materials.** Low-density polyethylene (LDPE), polypropylene (PP), and ethylene-vinyl acetate copolymer (EVA) with 15 wt % vinyl acetate content films were supplied by Showa Denko KK, Oita, Japan, and ethylene-vinyl alcohol copolymer (EVOH) film with 32 mol % ethylene content was supplied by Kuraray Co., Ltd., Osaka, Japan. The thicknesses of LDPE, PP, EVA, and EVOH films were 40, 50, 50, and 50  $\mu\text{m}$ , respectively. The volatile compounds used in this study were all guaranteed reagent grade from Nacalai Tesque Inc., Kyoto, and used without further purification.

**Determination of the Magnitude of Sorption.** The solubility ( $S$ ), diffusion ( $D$ ), and permeability ( $P$ ) coefficients of volatile compounds into LDPE film for aqueous phase were determined at 25 °C by the proposed permeation apparatus

(Matsui et al., 1989a). Volatile compound was added to a 0.3 w/v % sugar-ester solution (S-1170, Mitsubishi-Kasei Food Co., Ltd., Tokyo) or a 1.0 w/v % sodium lauryl sulfate (SDS) solution (Nacalai Tesque) to make a 200 ppm flavor solution.

The sorption determination for PP, EVA, and EVOH films was performed by the immersed method described elsewhere (Fukamachi et al., 1993). Briefly, the films were individually immersed in the above sugar-ester solution (concentration of volatile compound was set at 50 ppm) and stored at 20 °C until the sorption equilibrium was established (in this experiment, about 42 days of storage).

**Determination of Volatility from Flavor Solution.** Volatility of volatile compound from each surfactant solution (concentration of volatile compound was set at 100 ppm) was determined by the method described in our previous paper (Matsui et al., 1989a). After 30 min of incubation, helium gas (30 mL/min) was introduced into the headspace of a 300 mL flask to purge the volatile compound to FID. The ratio of GC peak height in surfactant solution to that in water was used as an index of volatility ( $\alpha$ ) of volatile compound from the flavor solution.

**Estimation of Solubility Parameter.** The solubility parameter (SP) values for film ( $\delta_f$ ) and flavor ( $\delta_v$ ) were calculated on the basis of Fedors's parameter concept (Fedors, 1974).

## DERIVATION OF THERMODYNAMIC SORPTION EQUATION FOR AQUEOUS PHASE

According to our proposed sorption concept (Matsui et al., 1994), sorption of solvent (volatile compound) into film was found to obey the equation

$$S = S_0 \exp(-\Delta H_s/RT) \\ = S_0' \exp \gamma [V_v(\delta_v^2 - \delta_c^2)/RT] \quad (1)$$

where  $S_0$  and  $S_0'$  are the frequency factors,  $\Delta H_s$  is the molar heat of sorption,  $V_v$  is the molar volume of volatile compound, and  $\gamma$  is the constant characteristic of polymer property. The proposed concept gave an adequate relationship for vapor phase sorption behavior ( $r = 0.967$ ), whereas for aqueous phase insufficient correlation was observed ( $r = 0.802$ ). This was due to no consideration for interaction between flavor and water or surfactant, which led to a suggestion that the

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<sup>†</sup> This is the third paper on estimating the sorption behavior of flavor into packaging film. The first paper of this series was published in *J. Agric. Food Chem.* (Matsui et al., 1992, 40, 1902-1905).

molar heat of sorption ( $\Delta H_s$ ) in aqueous solution must be estimated accurately.

We have made an assumption for the first step of sorption in aqueous solution—transferring the volatile compound from solution interacting with water to pure liquid state. According to the Hildebrand's concept (Hildebrand et al., 1970), the energy of transferring ( $\Delta E_t$ ) can be defined as

$$\begin{aligned} \Delta E_t &= X_v E_v + X_w E_w - E_m = -\Delta E_m \\ &= -\phi_v \phi_w (X_v V_v + X_w V_w) (\delta_w - \delta_v)^2 \end{aligned} \quad (2)$$

where  $E_v$ ,  $E_w$ , and  $E_m$  are the intermolecular potential energies between volatile compound and water.  $V_w$  is the molar volume, and  $\delta_w$  is the solubility parameter of water (47.9 MPa<sup>1/2</sup>; Burrell, 1975).  $\phi_v$  and  $\phi_w$  are the volume fractions, and  $X_v$  and  $X_w$  are the mole fractions of volatile compound and water, respectively. Taking into consideration that there is no volume change (Hildebrand et al., 1970),  $\Delta E_t$  is equal to the enthalpy of transferring. The partial molar heat of transferring ( $\Delta H_t$ ) a mole of volatile compound from solution to pure liquid is then

$$(\partial \Delta E_t / \partial X_v)_{X_w} = \Delta H_t = -V_v (\delta_w - \delta_v)^2 \quad (\phi_w \approx 1) \quad (3)$$

We defined  $\Delta H_t$  as "driving potential" because the greater was  $V_v (\delta_w - \delta_v)^2 / RT$ , the more sorption was observed (data not shown).

According to Gee's (1947) proposal,  $\Delta H_s$  is the sum of the molar heat of condensation ( $\Delta H_v$ ) of volatile compound and mixing ( $\Delta H_m$ ):

$$\Delta H_s = \Delta H_v + \Delta H_m \quad (4)$$

In our preceding paper (Matsui et al., 1994), we introduced the  $\delta_c$  concept to  $\Delta H_m$ :

$$\Delta H_m = V_v \delta_c^2 \quad (5)$$

Also,  $\Delta H_v$  (driving potential) can be replaced by  $\Delta H_t$ :

$$\Delta H_v = \Delta H_t = -V_v (\delta_w - \delta_v)^2 \quad (6)$$

By introducing eqs 5 and 6 into eq 4,  $\Delta H_s$  for the sorption process in aqueous solution is expressed as follows:

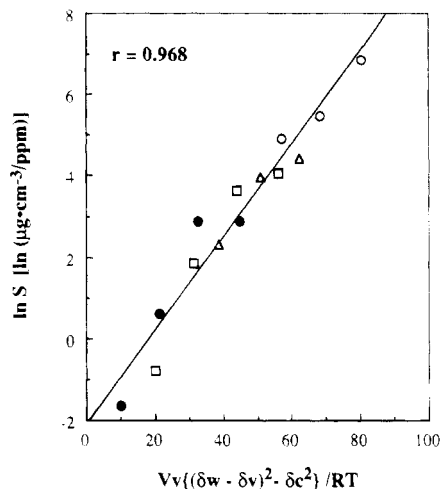
$$\Delta H_s = V_v \delta_c^2 - V_v (\delta_w - \delta_v)^2 \quad (7)$$

Therefore, the following equation is obtained:

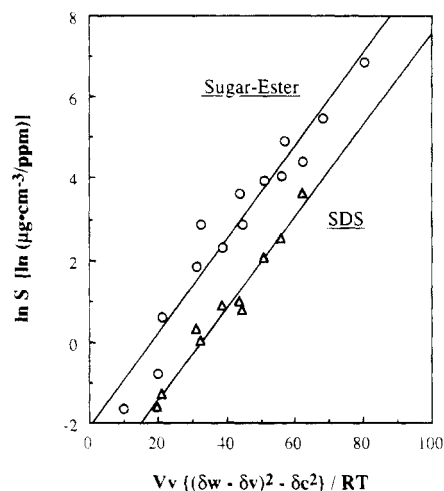
$$\begin{aligned} S &= S_0 \exp(-\Delta H_s / RT) \\ &= S_0 \exp \gamma [V_v [(\delta_w - \delta_v)^2 - \delta_c^2] / RT] \end{aligned} \quad (8)$$

Figure 1 represents the plots of  $\ln S$  into LDPE film against the term of eq 8 for aqueous phase. As a result, more adequate improvement in the correlation was observed ( $r = 0.968$ ) as compared with the plots between  $\ln S$  and the term of eq 1,  $V_v (\delta_w^2 - \delta_c^2) / RT$  ( $r = 0.802$ ) (Matsui et al., 1994). This result supported our concept with respect to the derivation of  $\Delta H_s$  for aqueous phase.

In aqueous system, it is also necessary to consider the solubilization of flavors into surfactant. Figure 2 shows the effect of surfactant on the application of eq 8. The surfactants used were nonionic (sugar-ester) and anionic (SDS) ones, and their concentrations were above the cmc (critical micelle concentration, sugar-ester,



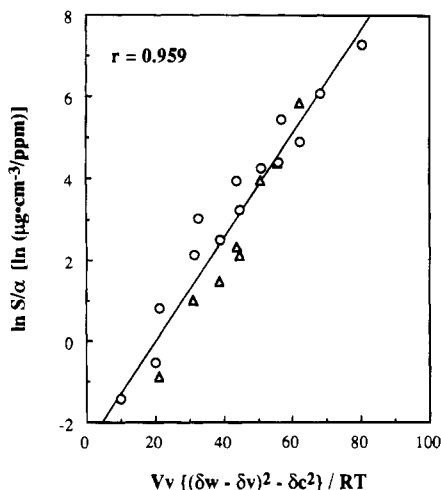
**Figure 1.** Relationship between the term  $V_v [(\delta_w - \delta_v)^2 - \delta_c^2] / RT$  and sorption of volatile compounds into LDPE film at 25 °C for aqueous phase. Volatile compounds: *n*-hydrocarbons (○, 6–10 carbon atoms); ethyl esters (△, 4–10); *n*-aldehydes (□, 4–10); *n*-alcohols (●,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



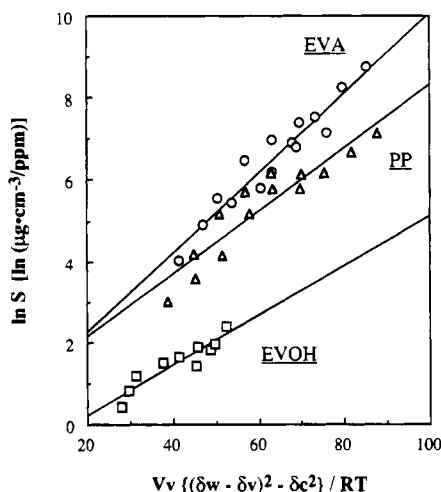
**Figure 2.** Relationship between the term  $V_v [(\delta_w - \delta_v)^2 - \delta_c^2] / RT$  and sorption of volatile compounds into LDPE film at 25 °C in 0.3 w/v % sugar-ester (○) and 1.0 w/v % SDS (△) solutions. Volatile compounds used are the same as in Figure 1.

0.025 wt %, SDS, 0.25 wt %) (Matsui et al., 1989b). As shown in the figure, each plot between  $\ln S$  ( $y$ ) and the term ( $x$ ) of eq 2 gave a linear relationship: for 0.3 w/v % sugar-ester and 1.0 w/v % SDS solutions,  $y = 0.115x - 2.120$  ( $r = 0.968$ ) and  $y = 0.113x - 3.701$  ( $r = 0.983$ ), respectively. Interestingly, both slopes of lines gave a close agreement, revealing that the surfactant did not affect the molar heat of sorption ( $\Delta H_s$ ). On the other hand, for SDS solution having a stronger interaction with volatile compound, the  $y$ -intercept of the line was smaller than that for sugar-ester solution. This implied that surfactant may directly affect the concentration of volatile compounds involved in the sorption process.

Then, taking into account the volatility ( $\alpha$ ) of the volatile compound from solution, which is the index of molecular interaction between surfactant and volatile compound, further improvement of eq 8 was made. The solubility coefficient ( $S$ ) of volatile compound into LDPE film is usually calculated at a concentration of added amount. However, the actual amount of volatile compound involved in the sorption process may decrease with an increase in the molecular interaction. Hence,



**Figure 3.** Relationship between the term  $V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT$  and  $\ln S/\alpha$  into LDPE film at 25 °C in both 0.3 w/v % sugar-ester (O) and 1.0 w/v % SDS ( $\Delta$ ) solutions. Volatile compounds used are the same as in Figure 1.



**Figure 4.** Application of the theoretical sorption eq 10 to various packaging films. Packaging films: PP ( $\Delta$ ); EVA (O); EVOH ( $\square$ ). Volatile compounds: *n*-hydrocarbons (8–11 carbon atoms); ethyl esters (9–11); *n*-aldehydes (8–11); *n*-alcohols (8–11).

the corrected solubility coefficient ( $S_w$ ) may be introduced by a multiplication of a factor of  $1/\alpha$  by  $S$ :

$$S_w = S/\alpha = S_0 \exp \gamma [V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT] \quad (9)$$

Namely

$$S = \alpha S_0 \exp \gamma [V_v[(\delta_w - \delta_v)^2 - \delta_c^2]/RT] \quad (10)$$

Figure 3 represents the plots of  $\ln S/\alpha$  against the term of eq 10 for both sugar-ester and SDS solutions. Surprisingly, a sufficient correlation ( $r = 0.959$ ) was observed. Therefore, the corrected sorption eq 10 may be the most effective in elucidating the sorption behaviors of flavors for aqueous phase.

#### APPLICATION OF THE THERMODYNAMIC SORPTION EQUATION INTO PACKAGING FILMS

A practical approach of the thermodynamic sorption eq 10 for various polymers was performed. Figure 4 shows the relationship between sorptions of volatile

compounds into various polymers and the terms of the equation in 0.3 w/v % sugar-ester solution. Linear relationships existed in each plot in spite of their polarity, and their correlation coefficients were 0.931, 0.963, and 0.932 for PP, EVA, and EVOH, respectively. These sufficient correlations clearly demonstrate that the established concept can be applied to all polymers.

Consequently, the proposed thermodynamic sorption equation led us to make an appropriate prediction for the sorption behaviors of flavors into various packaging films. By applying the equation, it would be possible to develop a lower sorption film or to select more favorable films to pack food.

#### ABBREVIATIONS USED

LDPE, low-density polyethylene; PP, polypropylene; EVA, ethylene-vinyl acetate copolymer; EVOH, ethylene-vinyl alcohol copolymer; SDS, sodium lauryl sulfate; SP, solubility parameter; GC, gas chromatography.

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