

Comparison of Sorption in Orange Flavor Components by Packaging Films Using the Headspace Technique

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Comparisons of equilibrium sorption of orange flavor components (ethyl butyrate, myrcene, and *d*-limonene) were made between LDPE, ionomer, and PET films using the headspace technique. It was possible to measure the sorption of an individual compound in the presence of other compounds using this method at concentration ranges similar to those found in commercial packages. The method of measuring sorption using the headspace technique provided sorption and diffusion coefficient values consistent with those found in the literature. The Fickian behavior of the sorption curves suggests very little interaction between the flavor compounds and the polymers at these low concentration levels. The equilibrium sorption of flavor components by PET film was much lower than that by LDPE and ionomer films. The Hildebrand solubility parameter was used in the explanation of large difference in equilibrium sorption values between polymer films.

INTRODUCTION

The sorption and permeation of aroma compounds from food products by polymeric packaging materials continue to be major concerns in food packaging. The loss of aroma by sorption and permeation through packaging materials was shown by investigators (Durr et al., 1981; Marshall et al., 1985; Mannheim et al., 1987; Kwapong and Hotchkiss, 1987; Hirose et al., 1988; DeLassus et al., 1988; Mohny et al., 1988; Imai et al., 1990). Not much information is available in the literature about the factors determining the equilibrium sorption of flavor compounds between different packaging polymers. Salame (1988) used Permachore values, which are related to cohesive energy density and free volume, to predict flavor loss by permeation. Brant et al. (1991) reported that the equilibrium sorption is not proportional to percent amorphous polymers. The attraction of citrus flavor in an aqueous solution to polymers has been attributed to the difference in cohesive energy density (Halek and Luttmann, 1991).

The traditional gravimetric methods of measuring sorption (Cahn and Schultz, 1963; Casar and Smith, 1986) cannot be used for measuring the sorption of flavors by polymer packaging films. The gravimetric methods will not differentiate sorption of individual flavor compounds when the sorption experiment is performed on flavors composed of many different compounds. Extracting flavor compounds with solvent and then determining the extract concentration by gas chromatography have been used for the quantitative analysis of flavor sorption by packaging materials (Imai et al., 1990). Increasing the extract concentration by distillation or vacuum evaporation has been used to increase the sensitivity of measuring low-magnitude sorption (Kwapong and Hotchkiss, 1987).

This research had two purposes: to apply the more convenient and faster headspace technique in measuring sorption of flavors at lower concentration range and to compare the sorption behavior of major orange aroma components on plastic sealant films using this method.

EXPERIMENTAL PROCEDURES

Materials. The heat-sealable films used in this study were zinc ionomer (Surlyn type 1702), low-density polyethylene (LDPE), and heat-sealable polyester (PET, Melinex 851). The respective thicknesses of the films were 38, 28, and 28 μm . These plastic polymer films were provided by ICI Films (Hopewell, VA). The powdered orange drink mix used in the experiments

was General Foods Kool-Aid brand obtained in local supermarkets. Ethyl butyrate, myrcene, and *d*-limonene were purchased from Aldrich Chemical Co. (Milwaukee, WI).

Flavor Sorption Measurements. The sorption of volatile compounds was carried out in a vacuum glass desiccator at temperatures of 25 ± 1 °C. The powdered orange mixture (1 kg) was placed below the perforated porcelain plate in the desiccator (Figure 1). The desiccator's volume was approximately 3 L. Twenty-milliliter glass vials containing 0.5 g of approximately 1×2 cm plastic film strips were placed on top of the perforated porcelain plate. The headspace concentration of volatile compounds inside the desiccator was monitored by sampling the headspace gas using a gastight syringe. The vacuum port of the desiccator, sealed with cured silicon glue, was used as the sampling port. The sampled gas was analyzed using a gas chromatograph. At selected time intervals, the glass vials containing the polymer films were taken out of the desiccator and capped with Mininert valves (Supelco Inc.), wrapped with Teflon tape, and heated at 60 °C for 70 min. The headspace concentration was determined by GC analysis. The equilibrium amount of volatile compounds sorbed was calculated from the following relationship, which was obtained from material balance

$$C_{pi} = \frac{C_h V_h + C_h K_p m_p}{m_p} = \frac{C_h (V_h + K_p m_p)}{m_p} \quad (1)$$

where C_{pi} is the initial volatile compound concentration in the polymer film before heating ($\mu\text{g}/\text{g}_{\text{polymer}}$), V_h is the volume of headspace inside the glass vial (mL), C_h is the volatile compound concentration in the headspace after heating ($\mu\text{g}/\text{mL}$), K_p is the partition coefficient at heating temperature [C_p/C_h], C_p is the equilibrium concentration of volatile compounds in the polymer film after heating, and m_p is the weight of polymer film inside the glass vial (g).

Sorption Isotherm. The sorption isotherms at 60 °C were determined by injecting known amounts of aroma compounds into the 20-mL sealed glass vials containing 0.5 g of cut polymer films. The vials were placed in a 60 °C oven for 70 min to establish equilibrium. The equilibrium concentrations of the volatile compounds inside the headspace (C_h) were measured by GC, and the equilibrium concentrations of volatile compounds in the polymer films (C_p) were calculated using the relationship

$$m_i = C_h V_h + C_p m_p \quad (2)$$

where m_i is the weight of the volatile compound injected inside the glass vial. Glass vials containing 0.5 g of polymer film sample without volatile compounds were used as the control. The ratio of C_p and C_h at a given concentration was used as the K_p value at 60 °C for determining C_{pi} in eq 1.

Determination of Crystallinity. Differential scanning calorimetry (DSC) was performed using a Du Pont 9900 calo-

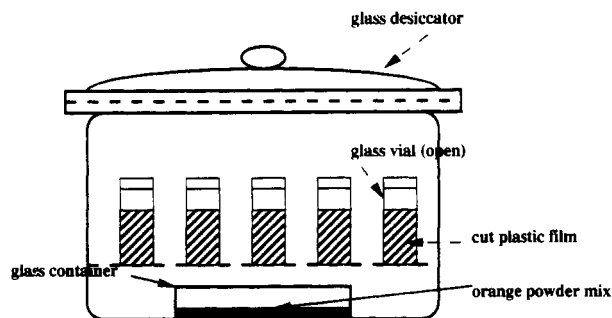


Figure 1. Apparatus used in the sorption of flavor from orange powder mixture.

rimeter. A small quantity of 5–10-mg sample was weighed. The sample and reference (empty pan) were placed in a sample holder and heated at a constant rate of 10 °C/min in an inert atmosphere of nitrogen. The heat of fusion of the polymer sample, $H_{f(\text{obs})}$, was determined by measuring the area of the melting peak below a somewhat arbitrarily interpolated baseline. The mass fractional content of the crystalline regions (crystallinity) was calculated by the equation $X_c = H_{f(\text{obs})}/H_f$, where H_f is the heat of fusion of a perfectly ordered crystalline region.

Gas Chromatography and Mass Spectrometry. A Hewlett-Packard Model 5890 gas chromatograph (GC) equipped with a flame ionization detector and a Hewlett-Packard Model 3396A integrator were used. The column was a Hewlett-Packard HP-5 fused silica nonpolar capillary column with cross-linked 5% phenyl methyl silicone as the stationary phase. The column was 25 m long and had a 0.31 mm inner diameter. The coating thickness of the stationary phase was 1.05 μm . Helium was used as a carrier gas at a flow rate of 2 mL/min. The injection port temperature and the detector temperature were 150 and 200 °C, respectively. The oven temperature was programmed to hold at 50 °C for 3 min initially and then increase at a rate of 6 °C/min until a final temperature of 185 °C was obtained. This temperature was held for 5 min. An injection volume of 500 μL was used for all GC analyses. A methane injection of 10 μL was used as an internal standard.

The same column and procedures as described above were used to identify the peaks with gas chromatography/mass spectrometry (GC/MS). The mass spectrometer detector was Hewlett-Packard Model 5971A.

RESULTS AND DISCUSSION

Four of the major peaks in the gas chromatogram of orange mix were identified by GC/MS as ethyl butyrate, pinene, myrcene, and limonene.

The headspace concentration of flavor compounds was measured as a function of time to determine the time required to establish equilibrium between the polymer film and headspace inside the glass vials at 60 °C. In all cases, equilibrium was achieved in less than 60 min. Therefore, a heating time of 70 min was used to establish equilibrium inside the glass vials to measure sorption. The fact that there was no apparent change in concentration inside the vial headspace after reaching equilibrium indicated negligible flavor loss from the vial during testing. Peaks of flavor compounds were not observed in the controls with only polymer films inside. However, minor peaks with different retention times were observed in negative controls. These peaks may represent monomers, additives, and contaminants that were present in the polymer films before they were exposed to the orange flavor compounds.

The sorption isotherms of flavor compounds and polymer sealant films were determined at 60 °C. The purpose of the measurements was to determine the partition coefficients ($K_p = C_p/C_h$) needed to calculate the amount of flavor sorbed in a polymer. Figure 2 shows an example of sorption isotherms at 60 °C. Units of micrograms per

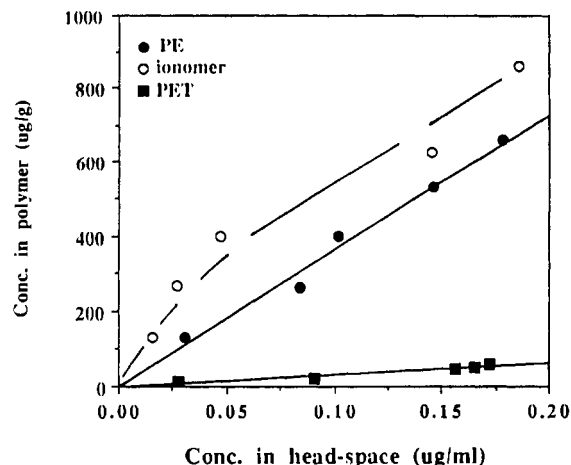


Figure 2. Sorption isotherms of myrcene at 60 °C.

milliliter were used on the X axis of sorption isotherms to obtain K_p values directly from the slope. The sensitivity of the method was not compromised in spite of the higher affinity of flavor compounds to polymeric films than headspace. This is due to the relatively large injection volume of 500 μL that was used to introduce vapor samples into the GC.

Using the headspace technique at 25 °C, sorbed amounts of flavor compounds in sealant films were measured as a function of time. The headspace concentrations inside the desiccator during sorption were 0.23, 0.037, and 0.047 $\mu\text{g}/\text{mL}$ for *d*-limonene, ethyl butyrate, and myrcene, respectively. It was shown that the effect of interactions of sorbing species during the sorption process has to be considered in studying the sorption of such complex mixtures as flavors (Fassler, 1989). With this method, it was possible to determine the sorption of individual compounds in the presence of other compounds without ignoring the interaction between sorbing compounds. Figure 3 shows plots of the square root of time vs micrograms of flavor compounds sorbed per gram of sealant film. The smooth curves have been drawn through the data to represent the continuous weight gain. The drawback of the headspace method is the relatively large variation of data points in comparison to the gravimetric method (Figure 3).

The diffusion constants were calculated from the sorption kinetic curves using Crank's solution (Crank, 1975). For sorption in a plane sheet, it gives the following solution for short times

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2} \quad (3)$$

where M_t is the amount sorbed at time t , M_∞ is the amount sorbed at equilibrium, D is the diffusivity of the vapor in polymer, and l is the half-thickness of the film. The plots of M_t/M_∞ vs $t^{1/2}$ were made, and the slope of the curve represents $2(D/\pi l^2)^{1/2}$. An example of a sorption curve is shown in Figure 4. The shapes of the curves indicated Fickian behavior of sorption for all compounds. This suggests that flavor compounds interact little with a polymer and the polymer does not undergo any swelling or other arrangement at these low concentrations. The slopes of the linear portion of curves were obtained by linear regression, solving for D . The values of diffusion constants obtained by solving for D are in Table I. The diffusion constant values obtained using the headspace techniques were slightly smaller than the values found in the literature (Landois-Garza and Hotchkiss, 1988; DeLassus et al., 1988). However, the values of diffusion constants are within a reasonable range when the differences in

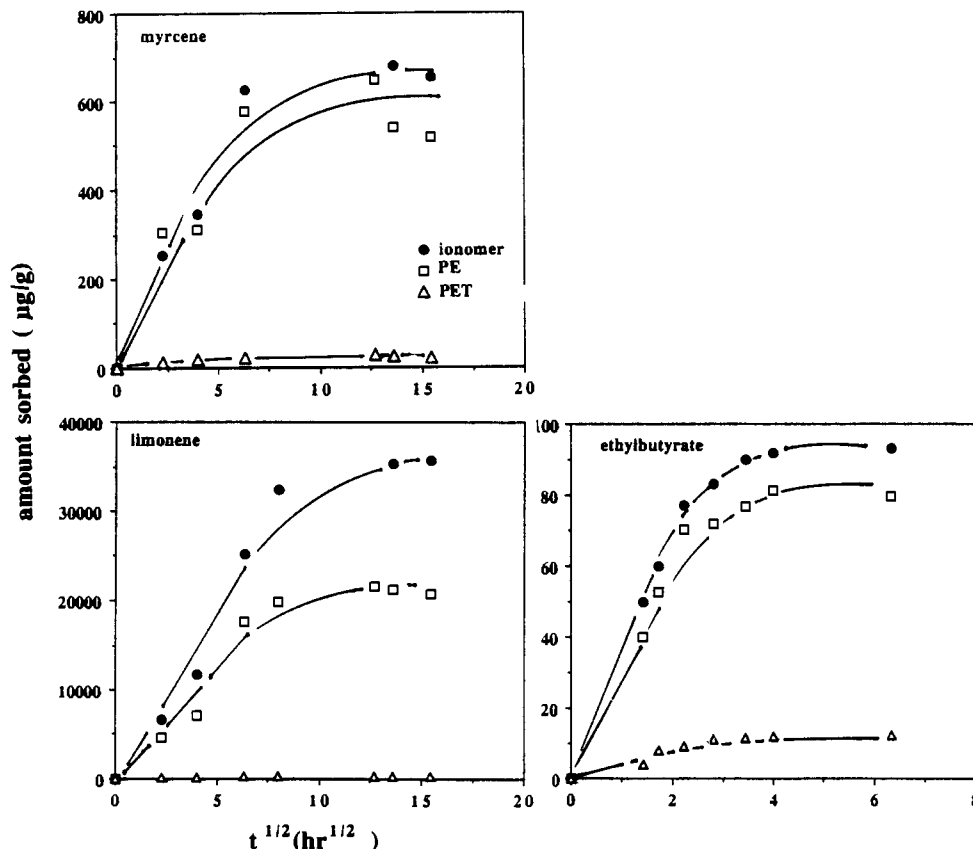


Figure 3. Sorption of flavor components in packaging films at 25 °C.

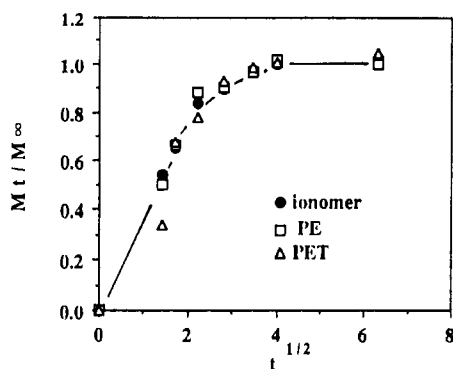


Figure 4. Plot of M_t/M_∞ vs $t^{1/2}$ for ethyl butyrate sorption.

Table I. Comparison of Diffusion Coefficients

	$\times 10^{-12} \text{ cm}^2/\text{s}$				
	LDPE	ionomer	PET	vinylidene chloride copolymer	EVOH PVOH
ethyl butyrate	2.27	14.42	1.97		
myrcene	0.29	5.1	0.42		
limonene	0.13	2.1	0.45		
<i>trans</i> -2-hexenal				0.12 ^a	0.91 ^a
ethyl propionate				192 ^a	
ethyl acetate					1618 ^b
ethyl caproate					313 ^b

^a At 28 °C (DeLassus et al., 1988). ^b At 25 °C (Landois-Garza and Hotchkiss, 1988).

concentrations and the molecular structures are taken into consideration. It is interesting to note that the diffusion coefficient of the ionomer was higher than that of the LDPE. It would seem they would have similar diffusion coefficient values because the ionomer used in this experiment is a copolymer of methacrylic acid and ethylene containing more than 90 mol % ethylene. Ethyl butyrate required a much shorter time, approximately 15 h, to reach

Table II. Solubility (Hildebrand) Parameter and Crystallinity Values

	% crystallinity	Hildebrand's solubility parameter, $\text{Mpa}^{1/2}$
ionomer	29.4	19.2
LDPE	34.5	17.6
PET	45.9	21.6
ethyl butyrate		17.4
myrcene		15.9
<i>d</i> -limonene		15.2

equilibrium in comparison to 50–100 h required for myrcene and *d*-limonene because of higher diffusion coefficients. The higher diffusion coefficient is probably due to the relatively smaller molecular size of ethyl butyrate compared to that of the other compounds tested.

As shown in Figure 3 and Table II, equilibrium sorption values of flavor compounds for PET film were far less than for both the ionomer and LDPE films. The low capacity of PET to sorb organic solvents has been observed by other investigators (Imai et al., 1990; Salame, 1988). The equilibrium sorption values for the ionomer were slightly higher than those for LDPE. A similar ratio between the equilibrium sorption values of polymer films tested is also shown in the sorption isotherms at 60 °C (Figure 2). The crystalline domain of polymers is almost impermeable to penetrants. Therefore, the percent crystallinity of the sealant films was measured to normalize the sorption values for the amorphous regions of polymers. The results presented in Tables II and III show that percent crystallinity is not the reason for the PET film having very little capacity to sorb flavor compounds. This is in agreement with a conclusion made by Brant et al. (1991). It is generally understood that the solution and the swelling of polymers are governed by the thermodynamics of the system (Hildebrand and Scott, 1950; Rogers, 1986). Therefore, the relationship between the magnitude of

Table III. Equilibrium Sorption of Flavors and Solubility Parameter Difference

	sorption at 60 °C and 0.2 µg/mL vapor concn, µg/g of polymer	sorption normalized for % crystallinity, µg/g of amorphous polymer
ionomer-ethyl butyrate	95	145
ionomer-myrcene	900	1374
ionomer-d-limonene	750	1145
LDPE-ethyl butyrate	74	105
LDPE-myrcene	710	1005
LDPE-d-limonene	580	821
PET-ethyl butyrate	9	17
PET-myrcene	60	111
PET-d-limonene	100	185

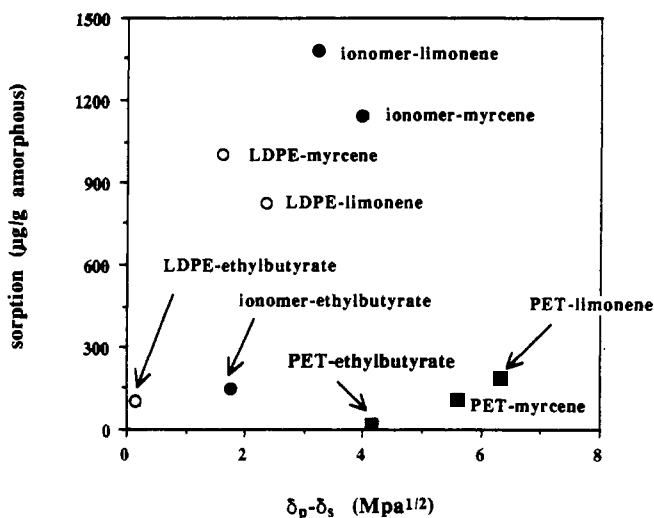


Figure 5. Equilibrium sorption at 60 °C vs the difference in Hildebrand's solubility parameter values of flavor compounds and polymers ($\delta_p - \delta_s$).

equilibrium sorption and Hildebrand's solubility parameter (δ), which is related to the cohesive energy density and enthalpy (ΔH_m) of mixing, was examined. Hildebrand's solubility parameters were calculated using the group contribution method (Barton, 1983). The plot of difference in Hildebrand's solubility parameter values of flavor compounds and polymers ($\delta_p - \delta_s$) vs the equilibrium sorption is presented in Figure 5. The equilibrium sorption values used in Figure 5 were from sorption isotherms at 60 °C and at vapor concentration of 0.2 µg/mL. Since each flavor compound had a different vapor concentration, the sorption data from 25 °C could not be used. PET, which has a greater cohesive energy difference with flavor compounds than both the ionomer and LDPE, sorbed much less flavor compounds than did the ionomer and LDPE films (Figure 5). The reason the cohesive energy difference did not predict sorption of ethyl butyrate is probably due to the relatively higher polarity of ethyl butyrate. Hildebrand's solubility parameter does not predict well the relative solubility of more polar species (Fowkes and Tischler, 1984; Hertz, 1990). At 25 °C, ionomer and LDPE films sorbed flavor compounds at temperatures higher than their respective glass transition temperatures (T_g), and PET sorbed at temperatures lower than its T_g of about 70 °C. Even though the T_g is a function of cohesive energy density, the sorption temperature being lower than the T_g may have contributed to the PET film sorbing very little flavor compounds.

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Registry No. LDPE, 9002-88-4; PET, 25038-59-9; surlyn 1702, 28516-43-0; ethyl butyrate, 105-54-4; myrcene, 123-35-3; d-limonene, 5989-27-5.