

Prediction of Flavor Sorption Using the Flory–Huggins Equation

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Prediction of flavor sorption by packaging polymers was compared between the equation based on the regular solution theory and the Flory–Huggins equation. The Flory–Huggins equation gave much better predictions of flavor sorption than the Scatchard–Hildebrand equation. This indicates the entropic contribution is a significant factor in the flavor sorption by packaging polymers. The difference between the experimental and calculated values from the Flory–Huggins equation was relatively large. It seems the Flory–Huggins equation can provide only a qualitative prediction of flavor sorption, but this is potentially very useful for selection and design of packaging polymers.

Keywords: Prediction; flavor; sorption

INTRODUCTION

The sorption of flavor compounds by packaging material is strongly affected by the type of flavor compounds and polymer materials (Kwapong and Hotchkiss, 1987; Imai et al., 1990; Michials et al., 1968; Brant et al., 1991; Paik and Kail, 1992). Halek and Luttmann (1991) observed the relationship between Hildebrand's solubility parameter and sorption of citrus-flavor compounds in polyethylene and polypropylene. Prediction of flavor sorption is useful not only in packaging material selection and design but also in quantitative identification of important factors governing flavor sorption.

Initial efforts in prediction of flavor sorption were based on modified versions of Hansen's (Hansen, 1967) empirical equation. Hansen's equation was effectively used in the paint and pigment industry in identification of suitable solvents for paint polymers. Empirical refinements were made by Hansen in an attempt to resolve the inconsistencies due to polar interaction (Burrell, 1955; Hansen, 1967). Hansen empirically separated the Hildebrand solubility parameter into three fractions: a dispersive component, a polar component, and a hydrogen bonding component. R. W. Keown (1986, DuPont, Wilmington, DE, unpublished data) used an interaction chart for qualitative prediction of flavor sorption based on Chen's argument that hydrogen bonding components are negligible in most compounds. Matsui et al. (1992) used an empirical method of Chen (1971) which is a modification of Hansen's (Hansen, 1967) empirical equation to correlate sorption data with polymer-flavor compatibility (δ_c). The semilog plot between δ_c and solubility coefficient gave good correlations only for a fixed polymer. Correlation was poor when polymers were not differentiated. However, Chen's method may be useful in practical application in packaging. Paik and Tigani (1993) reported the regular solution theory (Scatchard–Hildebrand equation) is not suitable for quantitative prediction of flavor sorption by polymer materials. The limiting assump-

tions made in the regular solution theory are no volume change ($V^E = 0$) and no entropy change ($S^E = 0$) during mixing at constant temperature. These restrictions seem too severe for an accurate prediction of flavor sorption by polymers with huge molecular weight differences.

Flory and Huggins independently derived equations (Flory, 1953), based on the lattice theory of fluids, to describe the free energy change during mixing of a solvent and amorphous polymer. The first equation was based on athermal behavior (without any energetic effects) of polymer solution. However, modifications were later made for the energetic (enthalpic) effects. The Flory–Huggins equation, which accounts for both entropic and enthalpic components of mixing in polymer solutions, has been used by many investigators to study the behavior of polymer solutions. This equation takes into account the entropic components of mixing due to molecular size differences.

The objective of this study is to determine the entropic contribution in flavor sorption by packaging polymers. This was accomplished by the comparison of the regular solution theory and the Flory–Huggins equation in flavor sorption prediction.

PREDICTIVE EQUATIONS AND ESTIMATION OF SORPTION

Regular Solution Theory. According to the Scatchard–Hildebrand (or regular solution) theory, the activity of a flavor in a packaging polymer can be expressed by the equation

$$RT \ln \gamma_1 = v_1 \phi_2^2 (\delta_1 - \delta_2)^2 \quad (1)$$

where subscript 1 stands for flavor and subscript 2 for polymer, γ is the activity coefficient, ϕ is the volume fraction, v is the molar volume, and δ is the Hildebrand solubility parameter. Equation 1 can be rearranged to

$$\ln a_1 = v_1 \phi_2^2 (\delta_1 - \delta_2)^2 / RT + \ln X_1 \quad (2)$$

Since it is difficult to determine the exact molecular weight of polymers, it is more reasonable to replace the

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mole fraction (X_1) with the volume fraction (ϕ_1).

$$\ln a_1 = v_1 \phi_2^2 (\delta_1 - \delta_2)^2 / RT + \ln \phi_1 \quad (3)$$

From eq 3 the volume fraction of sorbed flavor (ϕ_1) can be estimated if δ and a_1 are known. The activity for an ideal gas is defined as P (partial pressure of a compound)/ P° (partial pressure of pure compound). Activities of flavor compounds in the vapor phase were estimated by determining the partial pressure of flavor compounds using the equation of state ($PV = nRT$), assuming the ideal behavior of the dilute vapors. Experimentally determined Hildebrand solubility parameters were obtained from private correspondence with DuPont CR&D, Weast and Astle (1982), and Michaels et al. (1968).

Flory-Huggins Equation. Flory (1942) and Huggins (1942) have individually derived an equation to describe a free energy change during mixing of a solvent and amorphous polymer. The equation was based on the lattice theory of fluids. The Flory-Huggins equation (Flory, 1953) can be expressed as

$$\ln a_1 = \ln \phi_1 + [1 - (1/m)](1 - \phi_1) + \chi(1 - \phi_1)^2 \quad (4)$$

where subscript 1 represents the solvent, a is the activity, ϕ is the volume fraction, m is the number of segments of the polymer molecule, and χ is the Flory interaction parameter. The Flory interaction parameter (χ) is a function of intermolecular forces. If it is assumed χ is only related to the heat of mixing and the molecular interaction is dispersive in nature, χ can be estimated from solubility parameters as expressed in

$$\chi = (v_1/RT)(\delta_1 - \delta_2)^2 \quad (5)$$

From eq 4 the volume fraction of flavor sorbed by packaging polymer (ϕ_1) can be calculated.

Conversion of Amount Sorbed from Volume Fraction (ϕ_1). Sorption is defined by equation

$$\omega_1 = m_1/(m_1 + m_a) \quad (6)$$

where m is the weight and subscripts 1 and a represent flavor and amorphous polymer fraction, respectively. Masses can be substituted by fraction of amorphous polymer (α_a), density (ρ), and volume fraction (ϕ) as shown in

$$\omega_1 = \rho_1 \alpha_a \phi_1 / [\rho_a (1 - \phi_1)] \quad (7)$$

The chain packing in polymer crystallites is thought to be too dense to sorb even small permanent gas molecules (Michaels and Bixler, 1961). Therefore, it was necessary to use α_a to normalize the sorption value for percent crystallinity.

MATERIALS AND METHODS

Materials. Three packaging polymer materials were used. Low-density polyethylene (LDPE) and ethylene vinyl alcohol (containing 32% moles of ethylene) were obtained from DuPont. Polypropylene (isotactic) was produced by Exxon. All polymer samples were without any additives. Selected physical properties of these polymers are presented in Table 1.

Penetrant compounds representing flavor compounds were selected for this study. *d*-Limonene and linalool with a purity of 97% were obtained from Aldrich Chemical Co. Inc., Milwaukee, WI. Selected properties of these flavor compounds are presented in Table 2.

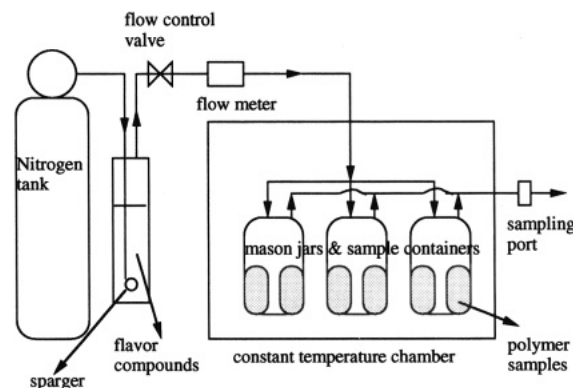


Figure 1. Diagram of apparatus used to generate vapors of flavor compounds.

Table 1. Physical Properties of Packaging Polymers

polymer	density (g/dm ³)	% crystallinity	solubility parameter (MPa ^{1/2})
LDPE	0.923	40.43	17.6
PP	0.905	36.59	17.1
EVOH	1.19	62.69	22.2

Table 2. Physical Properties of Flavor Compounds

penetrant	MW	density (g/cm ³)	solubility parameter (MPa ^{1/2})
<i>d</i> -limonene	136.24	0.840	16.8
linalool	154.25	0.870	18.8

Determination of Flavor Sorption. The schematic diagram of vapor generation and exposure is shown in Figure 1. Nitrogen gas was sparged at a flow rate of 30–40 mL/min through 200–300 mL of pure liquid compound placed inside a 500 mL flask. A bubble flow meter (Supelco) was used to check the nitrogen flow rate. Concentration of vapor was monitored by a Hewlett-Packard 5890A gas chromatograph (GC) with a flame ionization detector. The flow rate of the GC carrier gas was 15 cm³/min. The GC injector and detector temperatures were 100 and 200, respectively. The oven temperature was set at 100 °C, isothermal. Acid washed/silanized 75 μ m diameter glass beads (Supelco) were used as a stationary phase in a 1/8 in. stainless steel column of 1 m in length. The packaging polymers were exposed to nitrogen gas with a known concentration of flavor compounds inside the mason jar. The thickness of polymer samples was approximately 20 μ m. The initial weights of polymer samples were determined prior to sorption experiment and between 20 to 30 mg. These samples were placed inside 0.5 cm³ polypropylene centrifuge tubes with caps open (Fisher Scientific Co.). The capped polypropylene containers were used to prevent loss of flavor during the transfer of samples to the balance. Empty centrifuge tubes exposed to flavors in the same chamber as the samples were used as the negative blanks. The weight of negative blank and the original polymer weight was subtracted from the weight of centrifuge tubes with sorbed samples to obtain the weight gain of sorbed flavor. All samples were prepared in duplicate. The percent errors between duplicates were all within 8% range. Samples were weighed daily until the equilibrium state was attained. Weights were measured by the Cahn 2000 electrobalance.

Crystallinity Determination. Percent crystallinity of polymer samples was determined by a thermal analysis method. The Perkin-Elmer 7 series differential scanning calorimetry (DSC) system was used to determine the heat of crystallization. The samples were heated at a rate of 20 °C/min from 20 to 250 °C scanning range. Approximately 10 mg of the sample was placed in a sample container and sealed. These samples were placed after reaching an apparent equilibrium in sorption. The sample chamber was flushed with nitrogen to prevent oxidation. The percent crystallinity was calculated by dividing the heat of crystallization by specific latent enthalpy of crystallization for a given polymer. Since

Table 3. Comparison of Calculated and Experimental Sorption Values (Grams of Flavor per Gram of Amorphous Polymer) for LDPE

temp (°C)	<i>d</i> -limonene			linalool		
	RS theory	F-H eq	exptl data	RS theory	F-H eq	exp data
25	0.05487 (163%) ^a	0.03594 (73%)	0.0208	0.09450 (3001%)	0.02389 (686%)	0.00304
40	0.02233 (154%)	0.00803 (8.6%)	0.00879	0.03675 (1865%)	0.00844 (351%)	0.00587
55	0.00816 (21%)	0.00302 (54%)	0.0067	0.01803 (1161%)	0.00402 (181%)	0.00243
70	0.00331 (22%)	0.00121 (72%)	0.00426	0.00750 (582%)	0.00180 (64%)	0.0011

^a Percent error = [(calcd value - exptl value)/exptl value] × 100%.

Table 4. Comparison of Calculated and Experimental Sorption Values (Grams of Flavor per Gram of Amorphous Polymer) for PP

temp (°C)	<i>d</i> -limonene			linalool		
	RS theory	F-H eq	exptl data	RS theory	F-H eq	exptl data
25	0.05891 (489%) ^a	0.02438 (143%)	0.01	0.09241 (208%)	0.04465 (49%)	0.03
40	0.02430 (276%)	0.01012 (56%)	0.00646	0.03610 (211%)	0.01550 (34%)	0.0116
55	0.00966 (306%)	0.00359 (51%)	0.00238	0.01837 (502%)	0.00747 (145%)	0.00305
70	0.00383 (307%)	0.00143 (51%)	0.00293	0.00794 (782%)	0.00305 (239%)	0.0009

^a See footnote *a* of Table 3.

Table 5. Comparison of Calculated and Experimental Sorption Values (Grams of Flavor per Gram of Amorphous Polymer) for EVOH

temp (°C)	<i>d</i> -limonene			linalool		
	RS theory	F-H eq	exptl data	RS theory	F-H eq	exptl data
25	0.00437 (424%) ^a	0.00201 (95%)	0.00103	0.02288 (12%)	0.01275 (51%)	0.026
40	0.00160 (291%)	0.00059 (9%)	0.00055	0.00880 (57%)	0.00363 (35%)	0.0056
55	0.00080 (714%)	0.00024 (119%)	0.00011	0.00402 (73%)	0.00155 (25%)	0.00233
70	0.00026 (402%)	0.00010 (67%)	0.000006	0.00156 (217%)	0.00074 (50%)	0.00049

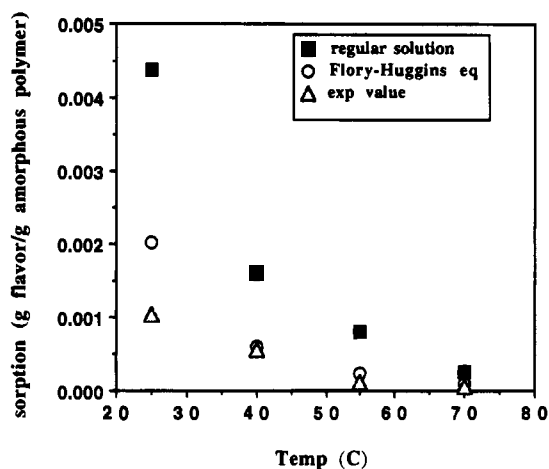
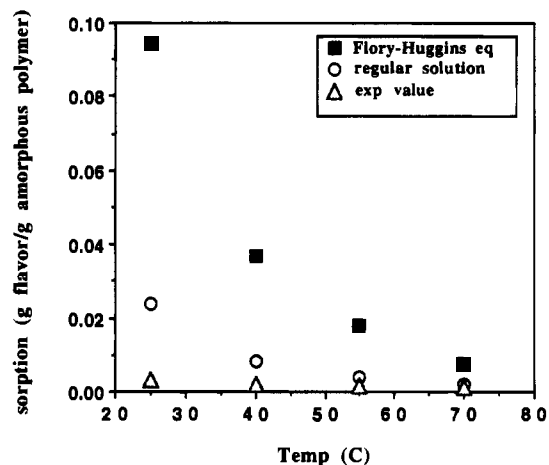
^a See footnote *a* of Table 3.

sorption and desorption of penetrants will affect the crystallinity of sample polymers, the heat of crystallization was measured without desorbing the penetrants. The heat of vaporization of penetrants was subtracted from the total heat under the peak to obtain the true heat of crystallization.

RESULTS AND DISCUSSION

The decrease in sorption with increase in temperature indicates the exothermic nature of the sorption process. The difference between the calculated and experimental sorption values was almost independent of sorption temperature (Tables 3–5).

Representative graphs showing the comparison of calculated and estimated values for linalool and *d*-limonene are shown in Figures 2 and 3. The remainder of the sorption data are presented in Tables 3–5. Results indicate the Flory–Huggins (F–H) equation is able to give a much better prediction of flavor sorption than the equation based on the regular solution (RS) theory. The main difference between the two models

**Figure 2.** Comparison of calculated and experimental sorption values for sorption of *d*-limonene by EVOH.**Figure 3.** Comparison of calculated and experimental sorption values for sorption of linalool by LDPE.

is the consideration of entropic contribution due to the molecular size difference. Therefore, it seems the entropic contribution is an important consideration in the case of flavor sorption by high molecular weight packaging polymers.

Even though the Flory–Huggins equation is more accurate than the equation based on the regular solution theory, it still has relatively large errors in the predictions. The Flory–Huggins equation does not consider the polymer chain conformation, chain stiffness, and free volume which will have an effect on the sorption values. Also, the predictions will be limited to compounds with dispersive interaction when the χ value is calculated using eq 5. In practical applications, χ is used as an empirical parameter. It is necessary to obtain experimental χ values for accurate estimation of flavor sorption using the Flory–Huggins equation. However, the Flory–Huggins equation is very useful in the selection and design of packaging polymers for food. The Hildebrand solubility parameter can be easily calculated from the chemical structure of functional groups of molecules.

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