

# Application of Regular Solution Theory in Predicting Equilibrium Sorption of Flavor Compounds by Packaging Polymers

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Equilibrium sorption values of model flavor compounds and polymers used in packaging were determined by immersing polymer samples in liquid flavor compounds. The equilibrium sorption values were normalized for crystallinity and concentration differences. The plot of  $\ln S$  vs the squared difference between the solubility parameter of polymer and solvents  $(\delta_1 - \delta_2)^2$  resulted in poor correlation. This seems to indicate that modifications are required in applying the Hildebrand-Scatchard concept of solution for the prediction of flavor sorption by polymer packaging materials. Results indicate that the consideration of polymer chain configurations and more reliable  $\delta$  values for polymers may improve the prediction.

## INTRODUCTION

There is a need for understanding of the critical factors affecting flavor sorption by packaging polymers to enable scientists and engineers to predict, select, and design better packaging materials.

On the basis of earlier works, Hildebrand and Scatchard formed the "regular solution theory" based on cohesive energy density (CED). The internal energy, or heat of vaporization ( $\Delta E_v$ ) to molar volume ( $V$ ) ratio, was introduced as the cohesive energy density by Scatchard (1931).

$$\text{CED} = \Delta E_v / V \quad (1)$$

Hildebrand (1936) proposed the square root of CED as a solubility parameter ( $\delta$ ) identifying the solubility characteristics of solutes and solvents.

$$\delta = \text{CED}^{1/2} = \sqrt{\Delta E_v / V} \quad (2)$$

According to Hildebrand, the enthalpy of mixing in a binary system is proportional to  $(\delta_1 - \delta_2)^2$  and is expressed by

$$\Delta H_m = \phi_1 \phi_2 (X_1 V_1 + X_2 V_2) (\delta_1 - \delta_2)^2 \quad (3)$$

where  $X$  is the mole fraction,  $\phi_1$  and  $\phi_2$  are the volume fractions of components 1 and 2, and  $V_1$  and  $V_2$  are the molar volumes of components 1 and 2.  $\phi_1$  and  $\phi_2$  are defined as

$$\phi_1 = X_1 V_1 / (X_1 V_1 + X_2 V_2) \quad (4)$$

$$\phi_2 = X_2 V_2 / (X_1 V_1 + X_2 V_2) \quad (5)$$

Two major assumptions were made in proposing this theory. The change in entropy and volume of mixing were considered to be negligible, and molecular interaction was primarily due to dispersive forces. Solubility predictions of highly polar compounds based on solubility parameter difference were inconsistent due to the second assumption. Refinements were made in an attempt to resolve the inconsistencies and exceptions (Burrell, 1955; Hansen, 1967) for use in practical applications to the paint and coating industry.

Several investigators have shown that 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; Brant et al., 1991; Paik and Kail, 1992). However, only a few studies on the factors affecting the sorption behavior of flavor compounds and polymer packaging materials were found in the literature. Ikagami et al. (1987) observed a semilog relationship between an increase in sorption with an increase in molecular weight in homologous series of penetrant compounds (up to 10 or more carbon atoms). Nielsen et al. (1992) also observed an increase in sorption with increase in molecular weight of sorbing compounds. Halek and Luttmann (1991) and Nielsen et al. (1992) used Hildebrand's solubility parameter concept based on cohesive energy density differences to explain the sorption data of citrus-flavor compounds in polyethylene and polypropylene. Ward and Keown (1989) had some success in using a two-dimensional interaction map in prediction of equilibrium flavor sorption. Keown's map was based on Hansen's (1967) three-dimensional map composed of dispersive, polar, and hydrogen-bonding components of Hildebrand's solubility parameter. However, exceptions were observed with polar and chlorinated compounds in Keown's method. Strandburg et al. (1991) reported a good correlation between the heat of solution ( $\Delta H_s$ ) and the natural log of the solubility coefficient ( $\ln S$ ) for prediction of flavor sorption. The heat of solution was defined as the sum of the heat of condensation and the heat of mixing.

The objective of this study was to examine the application of Hildebrand's regular solution theory in predicting the equilibrium sorption of flavor compounds by polymer packaging materials.

## MATERIALS AND METHODS

**Materials.** The four polymeric resin samples were obtained from Du Pont (Wilmington, DE) and Huntsman Chemical Co. (Woodbury, NJ). The samples included a zinc-type ionomer, Surlyn 1652; an amorphous poly(ethylene terephthalate) (APET), Sellar PT 207; a crystalline poly(ethylene terephthalate) (CPET), Sellar PT 8111; and an isotactic polypropylene (PP). The reagent grade flavor compounds were obtained from Aldrich Chemical Co. (Milwaukee, WI). The compounds used in the model flavor

**Table I. Percent Crystallinity and Density of Packaging Polymers**

polymer	% crystallinity	density, g/cm <sup>3</sup>
polypropylene (PP)	42 <sup>a</sup>	0.904
ionomer (Surlyn)	29 <sup>a</sup>	0.93
APET (Sellar PT)	3 <sup>b</sup>	1.34
CPET (Sellar PT)	48 <sup>b</sup>	1.39

<sup>a</sup> DSC measurements. <sup>b</sup> Density measurements.

**Table II. Equilibrium Sorption Values ( $g_{\text{solv}}/g_{\text{amorphous pol}}$ ) of Model Polymer-Flavor Compound Pairs**

flavor compd	polymers			
	PP	ionomer	APET	CPET
<i>d</i> -limonene	0.217	0.349	0.003	0.004
ethyl acetate	0.089	0.084	0.132	0.006
2,3-butanedione	0.043	0.461	0.190	0.005
acetaldehyde	0.045	0.175	0.117	
cinnamaldehyde	0.003	0.028	0.172	0.0016
acetone	0.034	0.044		0.016
furfural	0.003	0.016	0.023	0.014

system are *d*-limonene, acetone, ethyl acetate, 2,3-butanedione, cinnamaldehyde, acetaldehyde, and furfural.

**Polymeric Sample Preparation.** The polymeric samples were compression-molded 0.25 cm thick on a PHI model press (Pasadena Hydraulics, Inc.) to avoid using films containing additives which may affect the sorption tests. The polymeric samples were placed in a desiccator for 3 weeks to remove as much of the moisture as possible.

**Percent Crystallinity Measurement.** The amount of crystallinity of each polymeric group was measured by either differential scanning calorimetry (DSC) or density measurements. The DSC equipment used was a Du Pont TA Instruments 2100. The machine was calibrated, once a week, with indium. The method involved a first heating at 40 °C for 60 min to evaporate the solvents. A sample of approximately 10 mg of the film was weighed. The sample was then placed in a small metallic container and was sealed shut. The container with a sample of polymer film was then placed with a reference (empty container) in a Du Pont Instruments 910 differential scanning calorimeter chamber. The tests were conducted in a controlled atmosphere of nitrogen. The initiation temperature of the tests was 40 °C. From this temperature, the sample was heated to 220 °C, at a constant rate of 10 °C/min. The calculation for the percent crystallinity ( $x$ ) was

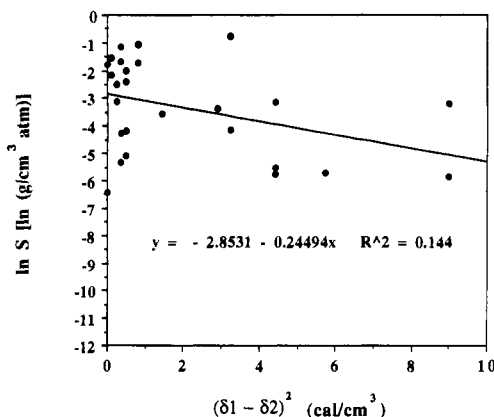
$$x = (\Delta H / \Delta H_c) \times 100\% \quad (6)$$

where  $\Delta H$  denotes the heat of fusion of the unknown sample and  $\Delta H_c$  denotes the heat of fusion of a 100% crystalline material. Density, which was correlated with percent crystallinity, was used to measure the PET crystallinity. The results of percent crystallinity measurements and densities are shown in Table I.

**Sorption Measurement.** The sample holder consisted of a 0.64-cm thick aluminum base with a 7.3 cm o.d. A stainless steel wire shaped into a ring held the samples. Five replicate samples were tested for each polymer. The sample holder was placed in a wide mouth, quart-size Mason jar filled with pure flavorant at 23 °C and 50% relative humidity. Every 3 days, the samples were blotted dry and weighed on a Mettler analytical balance until equilibrium was reached.

## RESULTS AND DISCUSSION

The equilibrium sorption values ( $g/g_{\text{amorphous polymer}}$ ) summarized in Table II were normalized to account for the crystalline fraction of polymers. The chain packing in polymer crystallites is thought to be too dense to sorb even small permanent gas molecules (Michaels and Bixler, 1961). In this study, the percent crystallinity of polymers was measured after equilibrium sorption was reached. It is important to use the crystallinity values after equilibrium is reached for normalizing sorption values because crystallinity values for polymers can change during sorption



**Figure 1.** Plot of squared difference between the solubility parameter of polymer and solvents  $(\delta_1 - \delta_2)^2$  vs natural log of normalized equilibrium sorption value ( $S$ ).

process. The equilibrium sorption values normalized for crystallinity were converted to solubility coefficient ( $S$ ) with the units of " $g_{\text{flav}}/cm^3_{\text{amorph}} \text{ atm}$ ".

The sorption in a rubbery amorphous polymer is assumed to be similar to solubility in organic liquid (Rogers, 1965). Accordingly, it should be possible to predict sorption in the amorphous fraction of a semicrystalline polymer using the solubility concept. The  $\phi_1\phi_2 (X_1V_1 + X_2V_2)$  term in eq 3 was assumed to be constant for all flavor-polymer pairs because of the very large molar volume of polymers which gives similar values for this term. Hence,  $(\delta_1 - \delta_2)^2$  was used in place of  $\Delta H_m$  to correlate with equilibrium sorption values. The energy of sorption can be expressed by an Arrhenius-type relationship (Rogers, 1965; Gee, 1947)

$$S = S_0 \exp(-\Delta H_s / RT) \quad \text{or} \quad \ln S = -\Delta H_s / RT + \ln S_0 \quad (7)$$

where  $S_0$  is the frequency factor. Gee (1947) proposed the energy of sorption ( $\Delta H_s$ ) or heat of solution is the sum of the heat of condensation ( $\Delta H_v$ ) and mixing ( $\Delta H_m$ ) for sorption of vapors by a polymer. According to Gee's proposal,  $\Delta H_v$  is equal to zero and  $\Delta H_s$  should equal to  $\Delta H_m$  since the sorption tests in this experiment were performed using liquid penetrants. Therefore,  $(\delta_1 - \delta_2)^2$  vs  $\ln S$  should result in a linear relationship. However, very little correlation can be observed in Figure 1. This is especially surprising because of the smooth curves obtained in swelling vs  $\delta$  of solvents for determining the  $\delta$  value for polymers (Michaels et al., 1968; Takahashi, 1983). The energy of sorption ( $\Delta H_s$ ) may not equal  $\Delta H_m$  as Gee (1974) proposed, and perhaps the energy needed to rearrange the configuration of polymer chains may have to be taken into consideration.

The application of Hildebrand's regular solution theory in the paint industry met with inconsistencies in predicting the solubility of polar compounds. The inability to predict the solubilities of polar compounds is the result of using London's formula in Hildebrand's derivation by assuming that the molecular interaction is primarily due to dispersive interaction. Therefore, the  $\ln S$  values of only the nonpolar compounds were plotted against  $(\delta_1 - \delta_2)^2$  to examine if our correlation can be improved by excluding polar compounds. As shown in Figure 2, no apparent improvement was observed in the correlation without the  $\ln S$  values of the polar compounds: cinnamaldehyde, acetone, and furfural. Thus, it can be concluded that factors other than polar interaction may have contributed more to the poor correlation. As a matter of fact, using Hansen's (1967) predictive methods did not improve the correlation.

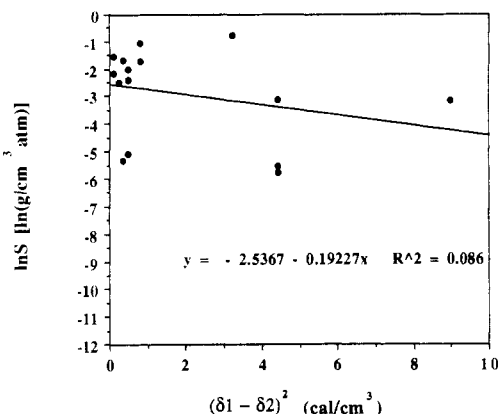


Figure 2. Plot of  $(\delta_1 - \delta_2)^2$  vs  $\ln S$  for nonpolar compounds.

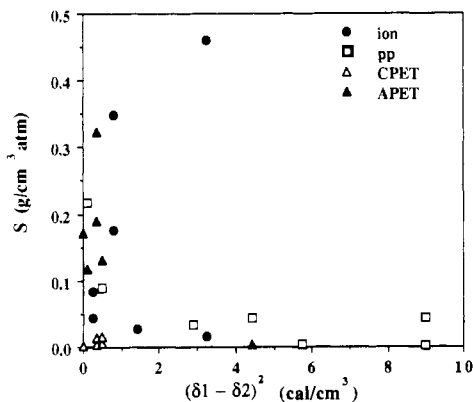


Figure 3. Plot of  $(\delta_1 - \delta_2)^2$  vs normalized equilibrium sorption value ( $S$ ).

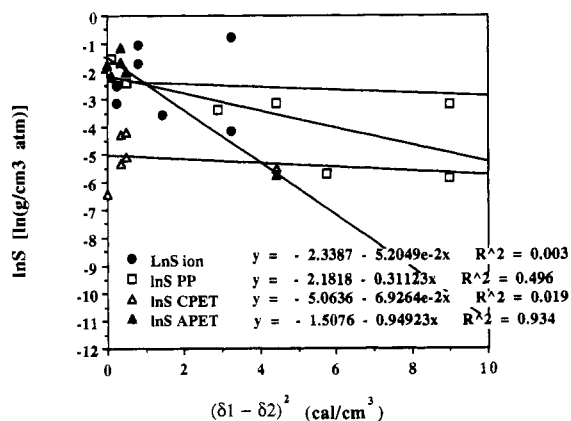


Figure 4. Plot of  $(\delta_1 - \delta_2)^2$  vs  $\ln S$  for separate packaging polymers.

Since the relationship between  $S$  and  $\Delta H_m$  is logarithmic, a small error in  $\delta$  at the lower range of  $(\delta_1 - \delta_2)^2$  can result in an order of magnitude error for  $S$  values (Figure 3). This may also have contributed to the poor correlation.

Another possible cause of the poor correlation may be due to the difference in chain configuration between polymers. If it is assumed that the values of  $\Delta H_m$  are correct, then the  $T\Delta S_m$  term in eq 8 will determine the

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (8)$$

correlation in the plot of  $\ln S$  vs  $(\delta_1 - \delta_2)^2$  since it is the  $\Delta G_m$  which ultimately determines the equilibrium sorption. Thus, clustering of data for the solubility coefficient ( $S$ ) values of different polymers (Figure 3 and Table II)

and the significant improvement in the separate correlation of  $\ln S$  vs  $(\delta_1 - \delta_2)$  for PP and APET (Figure 4) suggest chain configuration and entropy of mixing may not be negligible in polymer-flavor sorption. In conclusion, polymers may deviate too much from Hildebrand's regular solution to apply the regular solution theory without considering chain configuration and  $\Delta S_m$ . We are presently in the process of measuring the thermodynamic parameters of mixing ( $\Delta G_m$ ,  $\Delta H_m$ ) by an inverse gas chromatography method to determine the contribution of  $\Delta S_m$  in polymer-flavor sorption.

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