Infusion of Volatile Flavor Compounds into Low-Density Polyethylene

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Supercritical fluids can extract components from some matrixes (e.g., fat and flavors from food) as well as infusing additives into synthetic polymer matrixes. To study the feasibility of infusing flavors into matrixes as a potential flavoring mechanism, a wide range of volatile flavor compounds was infused into a well-defined synthetic polymer (low-density polyethylene) using supercritical carbon dioxide. The polymer was then extracted, and the amount of infused compound was determined. The effects of time, temperature, pressure, rate of depressurization, volatile concentration, and volatile properties on the degree of infusion were studied. Infusion with supercritical carbon dioxide achieved much higher loadings of the polymer (0.01 to 6.87 mg/g LDPE, depending on the volatile molecule being infused) compared to those achieved by static diffusion. Forty-five volatiles were infused, from which a model was developed to predict infusion as a function of certain physicochemical properties.

Keywords: *Supercritical fluid; carbon dioxide; SCF; modeling; QSPR*

INTRODUCTION

Supercritical fluid infusion (SFI) has been used in polymer research to modify polymer properties by the infusion of nonvolatile chemicals (*1*). For instance, plastics can be impregnated with pesticides, and wood can be infused with preservatives and fire retardant chemicals (*1*). Most infusion processes involve one chemical compound or a few closely related compounds. However, there are around 2500 compounds that possess flavor properties (*2*) with a wide range of chemical and physical properties. The feasibility of infusing such a mixture into typical food matrixes using supercritical carbon dioxide needs to be established. Some of the potential problems have been identified in reports of supercritical fluid extraction (SFE) of flavor compounds from starch-based foods (*3* and *4*). To achieve quantitative extraction of all compounds, it was necessary to treat low-water food matrixes with water and to modify the supercritical carbon dioxide with organic modifiers. Pretreatment with water is thought to open up the starch matrix, allowing the supercritical fluid better access to flavor molecules entrapped in the starch matrix. Organic modifiers are required to increase the polarity of the supercritical fluid (SCF) to ensure complete extraction of more polar compounds. Thus, although starch matrixes are common in foods, it was decided to use a simpler, synthetic polymer matrix for a preliminary study of flavor infusion.

Nielsen et al. (*5*) observed that a range of volatile compounds were absorbed by low-density polyethylene (LDPE) films immersed in solutions of volatile compounds. To analyze the volatiles in the LDPE samples, extraction with supercritical fluid carbon dioxide proved successful. It seemed reasonable to assume that the extraction conditions used by Nielsen et al. (*5*) should be equally effective in transporting volatiles into the matrix if the concentration gradient was reversed.

The interest in infusing flavors into foods is based mainly on the difficulties of flavoring foods that are manufactured through the extrusion cooking process (e.g., snack foods based on extruded starch matrixes). Addition of flavor prior to extrusion leads to unacceptable losses when the product expands and the flavor compounds are effectively steam-distilled into the atmosphere (*6*). There can also be undesirable changes in the flavor as a result of thermal degradation, oxidation, and polymerization (*7*). The current solution is to flavor the puffed product by surface dusting with an oil-based flavor mixture (*8*). However, this procedure is not entirely satisfactory. Adding flavor only to the outside of the product can give satisfactory initial flavor release and perception, but the flavor can fade too rapidly leaving an unflavored bolus in the mouth. This might be overcome if flavor could be distributed throughout the matrix. Supercritical CO_2 has the potential for flavor infusion, which could be achieved post-extrusion at a relatively low temperature, thus avoiding thermally induced changes or flavor flash-off. There are other advantages, such as minimizing autoxidation (*9*) due to the exclusion of oxygen during infusion, and avoiding the need for oil to carry the flavor, therefore reducing the fat content of the product as well as the possibility of rancidity.

The theoretical mechanisms by which small-molecular-weight molecules are infused into a polymeric matrix by supercritical fluids are well-established. The diffusion coefficients of the solutes in the SCF are approximately an order of magnitude greater than those encountered in conventional liquids (*10* and *11*). This, combined with the near-zero surface tension (*12*), allows easy entry of the SCF into the polymer matrix. In some cases, this causes a reduction in the glass transition temperature

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(Tg) (*12* and *13*) through plasticization of the polymer. Following plasticization, further entry of carbon dioxide into the polymer is facilitated, causing it to swell (*14*), increasing the free volume of the polymer. Solute molecules can then be transported more freely into the polymer. When the system is depressurized, the SCF leaves the matrix almost instantaneously as it returns to its gaseous state and the matrix returns to its original state. The solute molecules are not soluble in gaseous CO_2 and can only be desorbed from the polymer at a rate determined by their diffusivity in the polymer (*13*); thus, they are retained in the polymer matrix.

The partitioning of molecules between phases is a common phenomenon and there are two approaches to describing the relationship. The first, mechanistic, approach requires a detailed knowledge of the process by which molecules are transported and partitioned between the phases under the specific operating conditions. The second, empirical, approach builds a model based on experimental data. This latter approach has been widely used to model partition of drugs and environmental pollutants in biological systems by a process known as quantitative structure property relationship (QSPR) (*15*−*17*). Several hundred physicochemical and topological parameters for each chemical compound can be generated through a software program, and those playing a significant role in describing the relationship with the observed behavior of the molecules can be identified and built into a model (*18*). The model can then be further refined and validated by predicting the behavior of additional compounds and comparing these predictions with their observed behavior.

This paper investigates the use of LDPE as a model system for the infusion of flavor molecules using supercritical carbon dioxide. From the data obtained, a QSPR model is proposed to predict infusion of any molecule (within the limits of the experiment) into LDPE. This information should provide a stepping stone toward SCF-infusion of flavor molecules into more complex biopolymer matrixes and ultimately into food products themselves.

MATERIALS AND METHODS

Supercritical Fluid Infusion. The infusion of ethyl butyrate, ethyl-2-methyl butyrate, hexanol, hexanal, anethole, menthone (Firmenich SA, Geneva, Switzerland), *trans*-2-hexenal, hexyl acetate, furan, methyl acetate, methyl furan, hexanone, ethyl methyl furan, cymene, nonanone, benzaldehyde, methyl salicylate, 2-methyl butanol, linalool, acetylthiophene, 2-isobutyl-3-methoxy pyrazine, menthyl acetate, ethyl undecanoate, *trans*-ethyl-cinnamate, pyrazine, 1,2-propandiol, ethyl lactate, heptanone, octanone, 3-ethyl-2-methyl pyrazine, octanol, eugenol, α-damascone, propan-2-ol, dimethyl sulfide, 3-methyl butanal, octane, dimethylpyrazine, menthofuran, guaiacol, 2,6-dimethyl cyclohexanone, 2,3-diethylpyrazine, decanal, menthol (Aldrich, Dorset, UK), and limonene (ACROS Organics, Loughborough, UK), was achieved using the Suprex Autoprep 44 supercritical fluid extraction system (Anachem Limited, Luton, UK). The Autoprep was operated in "static" mode (in which the extraction cell was pressurized and then sealed) rather than the more commonly used "dynamic" mode (in which SCF flows through the cell during the extraction period). Approximately 1 g of ground, low-density polyethylene (particle size about 1 mm diameter, MW 35 000, density 0.906, crystallinity 17.4%; Aldrich, Dorset, UK), was placed in a 3-mL extraction cell with 10 μL of each of the initial seven volatiles (hexanal, trans-2-hexenal, ethyl butyrate, ethyl methyl butyrate, hexanol, hexyl acetate, and D-limonene). The cell was then filled with SFE-grade CO_2 (BOC, Leeds, UK), pressurized, and sealed. For the initial infusion experiment, the pressure of CO_2 within the cell was 120 atm, the temperature was 45 °C, and the infusion time was 30 min. Operating conditions were varied to optimize the infusion process (Table 1).

Table 1. Factors and the Range of Conditions Used to Optimize the Infusion Process

factor	range
duration of infusion	2−90 min
infusion temperature	40−100 °C
infusion pressure	100−400 atm
rate of depressurization	15−45 atm/min
quantity of volatile/g polymer	1−100 μL
quantity of limonene/g polymer[a]	0−20 μL

[a] Limonene was included as an independent variable in case it interacted with the other volatiles.

After the infusion was completed, the infused polymer was washed three times with hexane (Fischer Scientific, Loughborough, UK) to remove surface-coated volatiles. The washed polymer was then stored at room temperature until ready for extraction and analysis of the infused volatiles. A control and a blank sample were also produced to determine the extent of uptake through diffusion processes in the absence of supercritical carbon dioxide or absorption from the laboratory atmosphere. For the control sample, the cell was loaded with the same quantity of LDPE and volatiles, sealed in air at atmospheric pressure and held at 45 °C for 30 min. The blank sample was treated in a manner similar to the control, except that no volatiles were added to the vessel. The control and the blank samples were washed using the same procedure described above.

Infusion Optimization. The infusion parameters were optimized via a series of full factorial designed experiments (Design-expert 5, Minneapolis, MN). This approach was adopted to reveal any significant effects of individual factors and any interactions between factors. The factors and the range of conditions used in these experiments are given in Table 1. A temperature of 40 °C was chosen to ensure that the carbon dioxide was supercritical at the lowest pressure used (100 atm), and 100 °C represented the upper limit to avoid melting of the LDPE and potential thermal degradation of the flavor compounds. Although a range of pressures from 100 to 400 atm was tested, increasing pressure reduced volatile uptake such that 100 and 200 atm were the effective limits of operation. Using the optimum infusion conditions established with the initial seven volatiles, 40 more volatiles were infused in batches of five compounds (20 μL of each) to avoid changing the properties of the supercritical CO_2.

Volatile Extraction and Analysis. Extraction of the volatiles from 200 mg of infused polymer was achieved by adding 500 μL of methanol (containing 100 μg/mL of ethyl hexanoate internal standard). The samples were sealed and left to extract overnight at room temperature.

Aliquots of the supernatant (1 μL) were analyzed by GC−EIMS (Fisons GC8000−MD800) fitted with a splitless injector at 240 °C. The GC conditions were DB5 Column (J & W Scientific, Folsom, CA), 30 m × 0.25 mm i.d. and 1.0 μm film thickness; carrier gas He (25 kPa); temperature gradient, 40 °C for 2 min, then 40 °C to 160 °C at 8 °C/min. Quantification was achieved by comparing the peak areas for compounds in the sample chromatogram with those of authentic standards, taking into account variation in the peak area of the internal standard.

Model Development. The model was generated by calculating 76 physicochemical and topological parameters (Cache 3.2, Oxford Molecular, Oxford, UK) from the structures of the 45 volatiles studied. Multiple linear regression (Guideline+ V7.05, Camo ASA, Oslo, Norway) was used to compare the infusion behavior of the volatiles (amount infused) with the calculated parameters. From this regression analysis, several parameters were identified as being significant, and these were then built into an initial model to predict the amounts of compound infused using a D-optimal design (Design-expert 5,

Table 2. Concentration of Volatiles (mg/g) Extracted from Infused, Control, and Blank LDPE Samples

volatile	infused	SD	control	SD	blank
hexanal	0.82	± 0.03	0.08	± 0.03	nd
ethyl butyrate	0.36	± 0.00	0.06	± 0.02	nd
ethyl methyl butyrate	0.54	± 0.03	0.05	± 0.01	nd
trans-2-hexenal	0.46	± 0.01	0.03	± 0.01	nd
hexanol	0.49	± 0.04	0.01	± 0.00	nd
hexyl acetate	0.71	± 0.05	0.01	± 0.00	nd
limonene	1.45	± 0.15	0.02	± 0.00	nd

[a] Infusion was carried out in supercritical carbon dioxide at 120 atm and 45 °C for 30 min. Values are the mean of 3 replicate analyses. SD, standard deviation; nd, not detected.

Minneapolis, MN). The model was refined and validated as described in the Results section so that it was capable of predicting the extent of infusion of unknown molecules into LDPE.

RESULTS AND DISCUSSION

Initial Experiments. The volatiles studied were the six used by Nielsen et al. (*5*) (hexanal, *trans*-2-hexenal, ethyl butyrate, ethyl methyl butyrate, hexanol, and hexyl acetate) plus limonene, which was included because terpenoid compounds are known to diffuse readily into LDPE packaging from food matrixes (*19*). Besides the infused samples, control and blank samples were prepared to measure uptake by diffusion/partition in the absence of SCF and to ensure no carry-over of volatile compounds in the infusion apparatus, respectively. Extraction of the infused and control LDPE samples showed that both samples contained all seven test volatiles (Table 2). The concentration of the volatiles in the SCF infused samples were much higher than those in the control samples (about 6 to 70 times more), demonstrating the effectiveness of SFI for incorporating volatile compounds into the LDPE matrix. No trace of volatile could be found in the blank samples, demonstrating that pick-up of volatiles from the Autoprep equipment was not significant. Because of the low concentrations found in the control samples, the GC analysis was operating close to its limits of detection, and the relative errors associated with these replicates was greater than those of the infused replicates (Table 2).

Infusion Optimization. The optimization process was carried out using six of the seven volatile compounds from the initial experiments: hexanal was excluded, as the background amounts hindered accurate quantification. Five infusion parameters were studied: four were related to the properties of the SCF (temperature, pressure, time, and depressurization mode), and the other was the concentration of volatiles in the SCF (quantity of volatile added to the infusion cell). The upper and lower limits used in these experiments are given in Table 1.

Temperature, Pressure, and Amount of Volatile Added. These three factors were studied in a full factorial design and the data were analyzed in two ways: first, to give the overall contribution of each factor to volatile infusion (Table 3) and second, to show the effect of varying each factor within the design space (Table 4). In Table 3, the relative contributions of each factor are expressed on a relative, dimensionless scale where a higher value indicates a greater contribution. From the data in Table 3, it is clear that increasing the amount of volatile had the greatest effect on volatile compound infusion. Temperature was the next most important factor, with pressure being the least important. It therefore appears that, within the conditions used here, the state of the SCF is not a significant factor (although it can be optimized) in determining the amount of compound infused; instead, the concentration of the volatile is the major driving force.

Table 3. Relative Contribution of Temperature, Pressure, and the Amount of Volatile Added to the Amount of Volatile Compound Infused into LDPE

volatile	temperature	pressure	volatile added
ethyl butyrate	10.3	6.4	77.5
trans-2-hexenal	9.4	5.3	77.9
ethyl methyl butyrate	13.2	5.5	77.2
hexanol	10.4	6.4	79.0
hexyl acetate	14.8	5.8	74.9
limonene	2.2	0.4*	91.5

[a] Values are for comparison where the greater the value, the greater the effect on the amount infused. *Denotes a non significant effect $P > 0.05$

Table 4. Effect of Time, Temperature, and Pressure on the Amount of Volatile Infused (mg/g)

	temp. (°C)		time (min)		pressure (atm)	
volatile	40	100	2	30	100	200
ethyl butyrate	0.01	0.03	0.05	0.09	0.02	0.01
trans-2-hexenal	0.01	0.03	0.39	0.72	0.02	0.01
ethyl methyl butyrate	0.02	0.05	0.46	1.08	0.04	0.02
hexanol	0.02	0.06	0.00	0.00	0.05	0.02
hexyl acetate	0.02	0.07	0.72	1.19	0.06	0.03

[a] A zero value indicates no significant effect $P > 0.05$

In Table 4, the values for each SCF factor were extracted from all the factorial experiments giving a hypothetical parameter which assumes that an experiment was carried out using one of the factors (e.g., temperature) alone. Because of the way in which the values were extracted, variation is expressed as the root-mean-square value over the whole data set.

From Table 4, an increase in temperature increased the amount infused, presumably by increasing the rate of diffusion of the CO_2 (and the solutes) into the polymer matrix. Similarly, temperature reduced the density of the CO_2, thereby encouraging the partitioning of the volatiles into the polymer matrix (*11*) and altering the mobility of the chains of the matrix itself (*20*), all factors which assist the volatile compounds in accessing the polymer matrix. It is likely that a combination of these factors resulted in an increase in the amount of volatile infused.

Pressure had a statistically significant effect on the amount of volatile infused ($P < 0.0001$). The effect of decreasing pressure from 200 to 100 atm was that the amount of volatile infused was increased (Table 4). Pressure is one of the main factors that affects the density of the CO_2 and ultimately the degree of solvation of the volatiles in the SCF.

The amount of volatile added to the cell linearly correlated with the amount of volatile infused (Figure 1); this affect was statistically significant ($P < 0.0001$). This linear relationship suggested a simple partitioning processes between the SCF and polymer phases. If the infusion process were more complex and dependent on certain sites which favored incorporation of volatiles, then a nonlinear function would be expected.

During the infusion optimization, it was found that the infusion of limonene was dependent only on the amount of volatile added to the infusion cell; pressure and temperature had no effect on the amount of li-

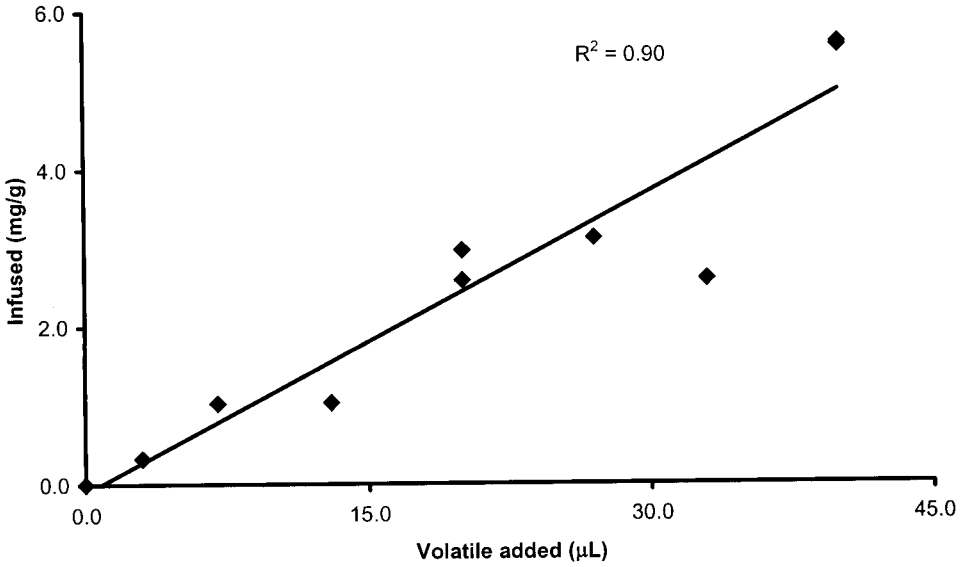

Figure 1. Effect of initial amount of compound (ethyl methyl butyrate) added to infusion cell on amount infused into LDPE.

monene infused. Therefore, the infusion of limonene might be achieved via a mechanism different from that of the other volatiles. Because of this anomalous behavior, the amount of limonene added to the LDPE was varied independently of the amounts of the other volatiles; however, altering the amount of limonene added to the infusion cell had no significant effect on the infusion of the other volatiles (data not shown).

Depressurization and Time of Infusion. Controlling depressurization of the system was a potential method for increasing the amount of volatile infused. The rationale was that as the system was depressurized slowly, the volatiles contained within the SCF became less soluble because of a reduction in the number of the solute−solvent interactions, as a consequence of the reduced density of the SCF. The volatiles should therefore partition more readily to the LDPE matrix (*1* and *11*). Although fast and slow depressurization were attempted, the Suprex Autoprep 44 apparatus did not allow for precise control of depressurization, and no differences in volatile uptake were observed. A more precise method of controlling depressurization is needed to ascertain whether this factor does affect volatile uptake.

Time of infusion was studied at 2, 16, 30, 60, and 90 min. There was no difference between the amounts infused for 30 min and those infused for 90 min. However, for all compounds except hexanol, twice as much volatile was infused after a 30 min infusion compared to that infused for 2 min (Table 4). However, an infusion time of 2 min was adopted, because the increase in time was disproportionate to the increase in the amount infused (i.e., for a 14-fold increase in time, only a 2-fold increase in the amount infused was observed).

The amounts of compounds infused under the "optimized conditions" (optimum temperature and pressure) are shown in Table 5, along with the percentage infused (amount in LDPE × 100/initial amount in the infusion cell). The amounts infused were of the order of 0.5 to 1.7 mg/g polymer, and between 2.6 and 8.5% of the initial compound was infused into the polymer. An additional 40 compounds were infused under the optimal conditions (Table 6) and the amounts found in LDPE ranged from 0.01 mg/g (furan) to 6.87 mg/g (*trans*-ethyl-cinnamate).

Table 5. Amount of Volatile Infused into LDPE (mg/g) under Optimum Conditions (% infused refers to the amount of volatile infused relative to the amount of volatile added)

volatile	infused	% infused
ethyl butyrate	0.52	2.6
ethyl methyl butyrate	1.39	7.0
trans-2-hexenal	0.66	3.3
hexyl acetate	1.5	7.5
hexanol	1.5	7.5
limonene	1.7	8.5

Modeling of Infusion. The experiments described above show the key experimental parameters affecting infusion of the test compounds. Closer inspection of the infusion results indicated a crude relationship between molecular weight and the extent of infusion. Further studies were carried out to determine the basis of this relationship so that a predictive model could be formulated. An initial QSPR model for 24 volatiles was created using the Cache software to calculate physicochemical and topological parameters for each compound. These were correlated with the amounts of each volatile infused to identify the parameters involved and to develop an initial model linking the parameters and the amount infused. This initial model was extended using a wider range of compounds, and the model was improved by incorporating a nitrogen atom count function. A further set of compounds was selected, and the actual and predicted values were determined. An equation was obtained (eq 1) containing the physicochemical descriptors dipole moment (DM), nitrogen group count (NGC), polarizability (P), Lumo energy (LE) and gradient normalization (GN):

$$\text{Amount infused} = (-38 + 8.1\text{DM} + 12\text{NGC} + 8.4\text{P} + 8.2\text{LE} - 2.9\text{GN})^2 \quad (1)$$

The equation was used to predict the amounts infused for all of the 45 volatiles, and a plot of predicted amount against the actual amounts infused is shown in Figure 2. There was a good correlation between the two sets of values, producing an overall correlation coefficient of 0.82 and a predicted *r*-squared of 0.76.

From the modeling procedure, it was found that the most significant factor was polarizability. In most cases,

Table 6. Concentrations of Compounds Infused into LDPE at 100 atm, 100 °C, and 30 min Infusion Conditions[a]

volatile	amount infused, mg/g	volatile	amount infused, mg/g
furan	0.01	pyrazine	0.60
methyl acetate	0.02	1,2-propane diol	0.74
2-methyl furan	0.03	ethyl lactate	1.06
isoamyl acetate	0.12	limonene	1.71
2-hexanone	0.48	heptanone	1.87
2-ethyl-5-methyl furan	0.84	octanone	2.02
ρ-cymene	1.41	3-ethyl-2-methylpyrazine	2.70
2-nonanone	1.50	octanol	5.22
menthone	1.51	eugenol	6.19
benzaldehyde	1.90	α damascone	6.51
methyl salicylate	1.94	propan-2-ol	0.03
2-methyl-1-butanol	2.24	dimethyl sulfide	0.04
linalool	2.25	3-methylbutanal	0.51
2- acetylthiophene	2.93	octane	1.2
2-isobutyl-3-methoxy pyrazine	3.79	dimethyl pyrazine	1.81
anethole	4.07	menthofuran	2.26
menthyl acetate	5.11	guaiacol	3.50
ethyl undecanoate	5.92	2,6-dimethylcyclohexanone	3.62
trans-ethyl-cinnamate	6.87	2,3-diethylpyrazine	3.96
menthol	5.60	decanal	5.43

[a] Each value is the average of two determinations with a pooled variation of 20%.

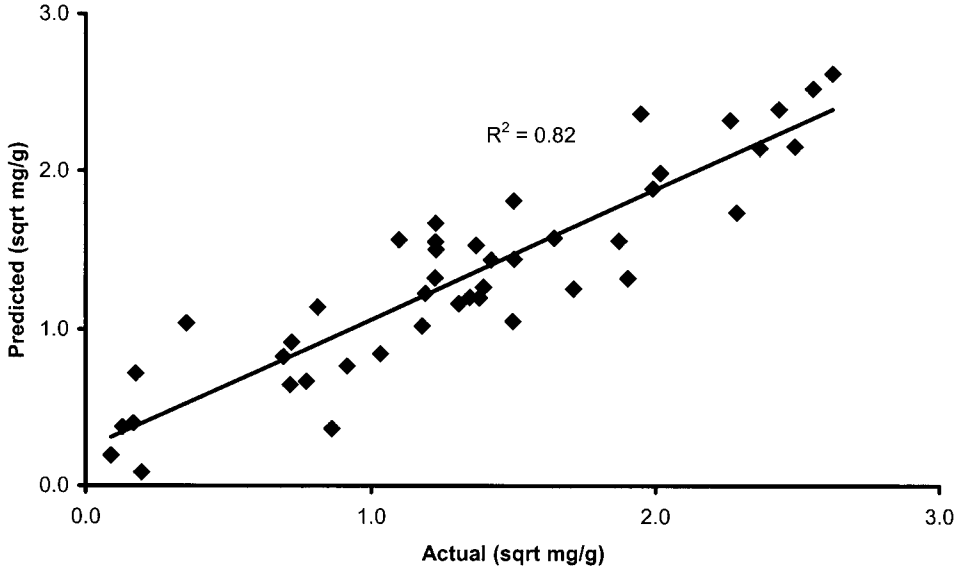

Figure 2. Model of 45 volatiles showing correlation between the actual amount infused (experimental) and predicted values (generated by the model.)

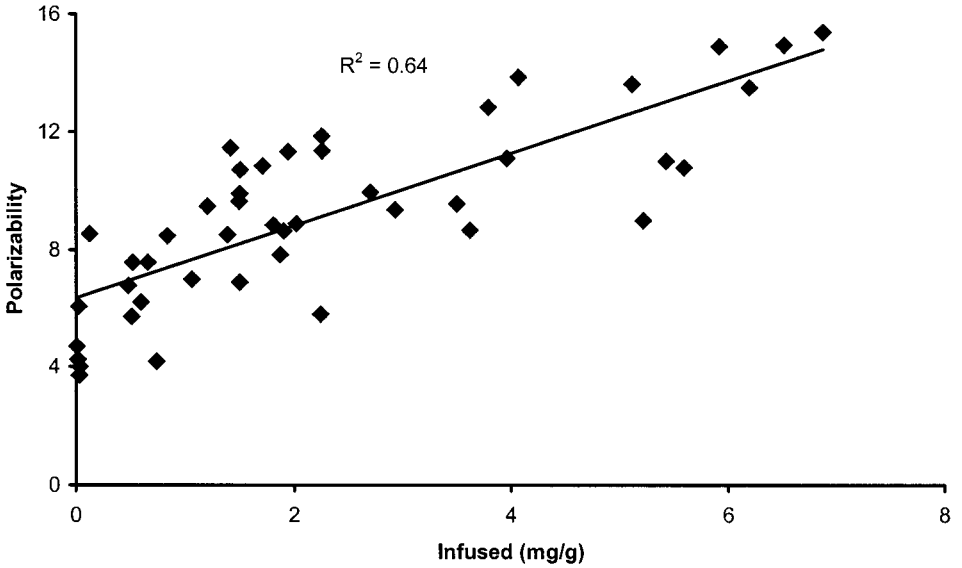

Figure 3. Relationship between polarizability of compound and amount infused (mg/g).

this particular parameter accounted for most of the correlation (R^2 of 0.7) with the other physicochemical parameters accounting for small differences between the different compounds infused. Polarizability is a measure of the strength of the dipole induced in a molecule in the presence of an electrical field (*21*). From the infusion data there is a general trend of increasing polarizability with the amount infused (Figure 3). Polarizability is related to the linear solvation energy relationships (LSER) used in partition processes (*22*) along with cohesive energy, i.e., the internal energy of vaporization per unit volume (*23*) between the two phases (LDPE and SCF). However, as all the intermolecular forces have been overcome in a SCF the cohesive energy of the SCF is zero, whereas the cohesive energy of the polymer is 9.3 kJ/mol (Cache, Oxford Molecular, Oxford, UK). Therefore volatiles can easily move in to and out of the SCF but not the LDPE, as the cohesive energy is inversely related to the diffusion permeability and solubility (*24*). However, as the LDPE has a greater polarizability than that of the SCF, the volatiles should be attracted toward the LDPE in relation to their increasing polarizabilites.

The data above show that infusion of volatile flavor compounds into a simple, well-defined synthetic polymer is possible and that the QSPR technique provides a suitable model for predicting the infusion of any other volatile flavor compound under the conditions used. The initial concentration of volatile and the polarizability of the compound are the key factors determining the amount infused. The feasibility of applying this technique to naturally occurring biopolymers such as starch (with very different physical properties than LDPE) is currently being investigated.

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