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VANILLIN AND ORTH-VANILLIN BETWEEN CORRUGATED-BOARD
AND HEADSPACE; AND BETWEEN LOW DENSITY POLYETHYLENE
AND AN AQUEOUS PHASE

presented by

LEI PEI

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING

Major professor

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DETERMINATION OF THE PARTITION DISTRIBUTION OF VANILLIN AND ORTHO-VANILLIN BETWEEN CORRUGATED-BOARD AND HEADSPACE; AND BETWEEN LOW DENSITY POLYETHYLENE AND AN AQUEOUS PHASE

By

Lei Pei

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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ABSTRACT

DETERMINATION OF THE PARTITION DISTRIBUTION OF VANILLIN AND ORTHO-VANILLIN BETWEEN CORRUGATED-BOARD AND HEADSPACE; AND BETWEEN LOW DENSITY POLYETHYLENE AND AN AQUEOUS PHASE

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Gas chromatograph, high performance liquid chromatograph, and thermal stripper/thermal desorption procedures were employed to determine the partition coefficient, (K) values, of vanillin and ortho-vanillin between corrugated board and headspace, and between low density polyethylene (LDPE) and an aqueous phase. The derived coefficient values were as follows:

1) The partition coefficients, $K_{B/H}$ values for vanillin between corrugated board and headspace, were 179 at 23°C, 98 at 38°C, and 48 at 50°C, respectively. The $K_{B/H}$ values for ortho-vanillin were 663 at 23°C, 353 at 38°C, and 223 at 50°C, respectively.

2) For the aqueous phase/LDPE/ system, the partition coefficient, $K_{P/A}$ were 32.7 at 23°C and 18.7 at 32°C for vanillin and 48.5 at 23°C as compared with 28.7 at 32°C for ortho-vanillin.

3) The diffusion coefficients (D) for vanillin and ortho-vanillin through LDPE were determined according to Crank's method (1976) and were 2.0×10^{-13} cm^2/sec at 23°C and 3.9×10^{-13} cm^2/sec at 32°C for vanillin; and 6.0×10^{-14} cm^2/sec at 23°C and 1.5×10^{-13} cm^2/sec at 32°C for ortho-vanillin at 90% of equilibrium state.

To my parents

ACKNOWLEDGMENTS

I would like to express my sincere appreciation and thanks to my advisor, Dr. Jack R. Giacin, School of Packaging, Michigan State University, for his advice, kindness, patience, encouragement, and positive guidance.

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INTRODUCTION

The transfer of volatile, low molecular weight organic compounds, between product and package is always a concern with polymeric package systems (Mohney, 1988). This can lead either to a direct loss of product quality or to damage of the package, which indirectly might affect the product negatively (Nielsen, 1992). The phenomenon of transport involves sorption which refers to the uptake by the packaging material of sorbate initially contained by the product, and migration which is the reverse process by which compounds originally contained in the package are transferred to the packaged product. The sorption process is of paramount importance in avoiding the effect of "flavor scalping" (Mohney, 1988), while migration is important with regard to food safety issues (Foulke, 1991).

The diffusion coefficient, D, is used to provide information related to the time required to attain a constant rate of sorption or migration, since both processes tend to reach equilibrium to equate their chemical potential values (Gavara, 1992). The amount of a specific volatile substance sorbed by a packaging material can be described by the partition coefficient, value K, which is defined as the concentration of the sorbate in the polymer phase divided by the concentration of the sorbate in the contact phase (Nielsen, 1992). In a two-phase food/polymer system, the transfer of a component (sorbate) from one phase to the other, proceeds until the system attains thermodynamic equilibrium. The equilibrium concentration value of the sorbate in each phase is a function of the initial concentration,sorbate solubility in both contact and polymer phases, and temperature (Gavara, 1992).

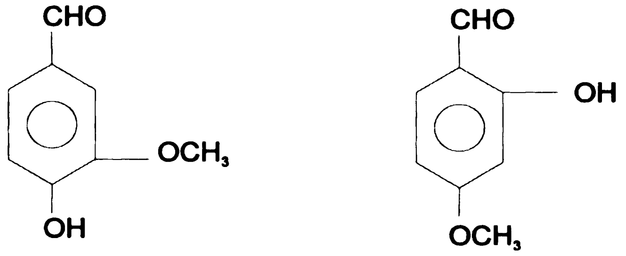
In this regard, corrugated board or paperboard is another packaging concern, especially for recycled paper products, if they contact food directly, such as the food contained by corrugated boxes during transportation. Paper is recycled at a fairly low temperature, and contaminants could remain. Some recycled products could be made of newspaper, which may contain dioxins and furans, and a complex mixture of related compounds that are formed in trace amounts when chlorine or chlorine derivatives are used as the primary bleaching agents in making white paper products. The most toxic dioxin is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD), which has been shown to cause cancer in laboratory test animals (Foulke, 1991).

In the present study, two equilibrium partition systems were considered, namely, (I) corrugated board/vanillin or ortho-vanillin/headspace; and (ii) low density polyethylene-vanillin or ortho-vanillin-aqueous phase. These served as a model system to address the problem, where volatilization of organic moieties from corrugated board and their subsequent permeation through a primary package, which is a polymeric structure, can result in contamination of the contained product. The partition coefficients (K) of vanillin and ortho-vanillin between corrugated board and headspace; and LDPE and an aqueous phase were determined by a series of analytical methods, including gas chromatography, high performance liquid chromatography, and a thermal stripper / thermal desorption (TS/TD) procedure. Statistical analysis of the partition coefficient (K) data, the vanillin and ortho-vanillin diffusion coefficient values, and their solubility in LDPE were also performed.

LITERATURE REVIEW

4.1 Vanillin and Ortho-vanillin

Vanillin, the common name for 3-methoxy-4-hydroxy-benzaldehyde, occurs in nature as a glucoside which hydrolyzes to vanillin and sugar. Ortho-vanillin is a byproduct from the manufacture of vanillin from guaiacol which is present in wood tars (Van Ness, 1983). Their chemical structures are shown in Figure 1.



Vanillin **Ortho-vanillin**

Figure 1: Chemical structure of vanillin and ortho-vanillin

The aroma and taste of vanillin have been recognized because of its wide use in food as a flavoring. The use of vanillin as a flavor can be traced back to about 1520 when Cortez, the Spanish conqueror of Mexico, was served a chocolate drink flavored with vanilla, which contains vanillin, by the Aztec Indians. Cortez took the flavor back to Europe which started its spread around the world (Van Ness, 1983). The major quantity of vanillin used today comes mainly from lignin, which is a waste product from the manufacture of paper pulp. A smaller amount is made synthetically from guaiacol (2-

methoxyphenol) (Van Ness, 1983). Besides being a very popular flavor, vanillin is also used in the synthesis of drugs. The largest single use for vanillin as a starting material for the manufacture of the antihypertensive drug called Aldomet, which is manufactured by Merck. Aldomet is l-3-(3,4-dihydroxy phenyl)-2-methylalanine. L-dopa is another drug made from vanilla and is used for the treatment of Parkinson's disease (Ainscough and Brodie, 1990).

A liquid chromatographic method for determination of vanillin, vanillic acid, etc. was described by Didney (1989). The liquid chromatograph was

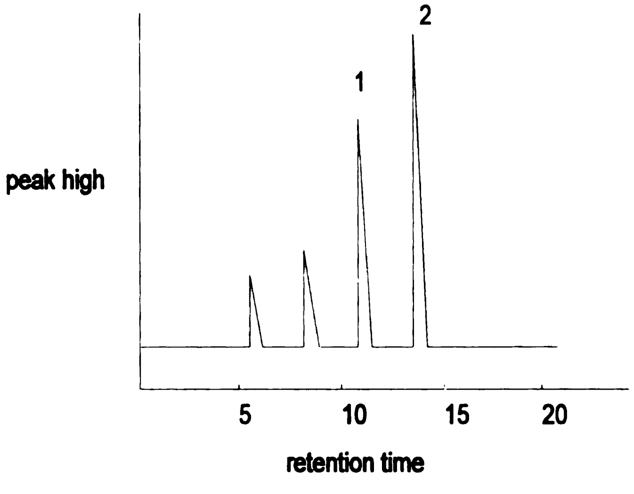


Figure 2: Typical chromatogram of standard solution of vanillin and vanillic acid.

operated at flow rate of 2.5 ml/min, with UV detection at 254 nm. The column was stainless steel, 25 cm x 4.6 mm id, packed with C18 on 10 µm totally porous irregular particles, LiChrosorb or equivalent. Mobile phase was 10% (v/v) methanol and 90% (v/v) LC grade water. A typical chromatogram of a standard solution of vanillin and vanillic acid is shown in Figure 2. Peak 1 is vanillin with a retention time of 11 min and peak 2 is vanillic acid with a retention time of 13 min.

4.2 Corrugated Board in Packaging

By virtue of its remarkable utility, exceptional strength characteristics, light weight, and low cost, corrugated and fiberboard packaging materials are extensively used in a variety of industrial packaging functions. About 67 million tons of paper are produced annually in the United States, and this tonnage is about equally divided between paper (0.012 in thick or less) and paperboard (over 0.012 in) (Handbook of Packaging Engineering, 1992).

4.2.1 Construction of Corrugated Board

Two categories of packaging paperboard are used today: one used for cartons and the other used for corrugated board. The corrugated fiberboard is produced basically for the construction of single-faced corrugated fiberboard, single-wall corrugated fiberboard, double-wall corrugated fiberboard, and triple-wall corrugated fiberboard, as shown in Figure 3. Single-faced corrugated fiberboard is used principally for wrapping, and for interior packing. Single-wall corrugated fiberboard, is made by gluing flat facings to each side of the corrugated member. It is manufactured in various kinds and grades of paperboard and in varying thickness. The archetype construction, which gives strength and rigidity to the fiberboard, also provides cushioning and insulation characteristics. Double-wall corrugated fiberboard consists of three flat facings and two corrugated members. Like single-wall board, it is manufactured in various types and grades of materials and in varying

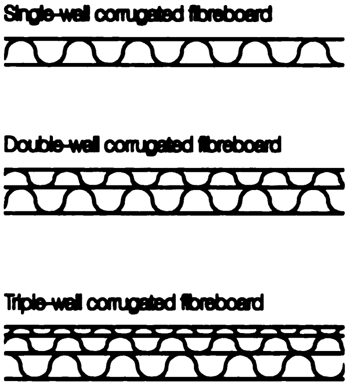


Figure 3: Basic construction of corrugated fiberboard

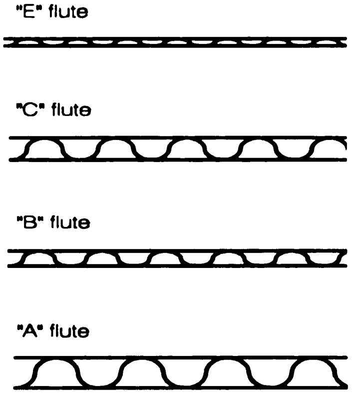


Figure 4: The flutes of corrugated fiberboard

thicknesses, but it offers greater strength or cushioning than that provided by the single-wall structure. The triple-wall corrugated fiberboard consists of four flat facings and three corrugated members and is most applicable for packages requiring exceptional rigidity and high puncture resistance.

The flutes or arches of corrugated board are specified by size A, B, C, or E, as shown in Figure 4 (Friedman, 1977). A is the largest. C is next followed by B. The "E" flute has the smallest flute (Friedman, 1977). Listed below are the dimensions for each flute.

A Flute	36 ± 3 flutes per lineal foot	1/4" in thickness
B Flute	50 ± 3 flutes per lineal foot	1/8" in thickness
C Flute	42 ± 3 flutes per lineal foot	3/16" in thickness
E Flute	94 ± 3 flutes per lineal foot	3/64" in thickness

For double-wall and triple-wall board, the flute sizes for each sheet of corrugated material are usually different (Fibre Box Association, 1992). This technique combines their advantages, and prevents any weakness that might result if the flutes were perfectly aligned. For instance, the B and E flute have better printing character, and A and C flute have relatively better cushioning ability. The CB flute double wall board will give the user better cushion and compression ability, at the same it will have better printing quality.

4.2.2 Method of Corrugated board Making

The facings of corrugated board are usually made from spruce or pine chips digested by an "incomplete cook" process which preserves the long fibers of the original wood cellulose. This process results in a high yield and a product of exceptional tearing strength (Friedman, 1977). "Softwood" is the term used in the paper industry for coniferous or needle-bearing trees, whose fibers will run up to 1/4 inch in length, as compared to less than 1/10 inch for that of “Hardwood” fibers. A fiber in cross section looks somewhat like a hollow tube of irregular wall made up of a lamellae of fibrils, as shown in Figure 5. These fibrils are made up of microfibrils that are composed of chains of cellulose molecules, about 3 million in each microfibril, along with short-chain hemicellulose molecules and other polymeric residues (see figure 6) (Handbook of Packaging Engineering, 1992). In papermaking, the wood is cooked with chemicals to remove the lignin and carbohydrates that enclose the lamellae of fibrils. The kraft process, also known as the sulfate process, is used on soft-woods to produce the strongest pulp product which is called natural kraft paper. Wood that has been converted into small chips is cooked for several hours in digester, which is followed by washing and bleaching. The slurry for making paper is then put into beaters, where the bundles of fiber are broken up and hydration of the fibrils takes place; that is , the fibrils combine chemically and physically with water to become thoroughly “wetted” so that they swell. From there the mixture of pulp is ready to go through the papermaking machine. Two basic machines are used today: the fourdrinier machine and the cylinder machine. (Handbook of Packaging Engineering, 1992). The paperboard above 12 points can be made on either type of machine.

Corrugating medium is made by a semi-chemical process in which virgin hardwoods and recycled corrugated containers are used as the raw materials. A soaking in caustic soda or neutral sodium sulfite, to soften the lignin and carbohydrates that bind the fibers together, is followed by grinding

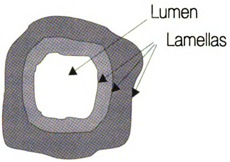


Figure 5: Cross section of fibers

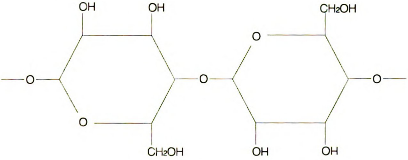


Figure 6: Cellulose Molecule

Length of chain is from 100 to 3,000 units in a diskrefiner (Handbook of Packaging Engineering, 1992). This method results in a low-cost pulp because of the raw materials and process, but it is hard to bleach. The common basis weights of corrugating medium are 26 and 33 lb./msf (Fibre Box Association, 1992).

Paper is a kind of material that can be recycled. There is a growing industry, government and consumer interest in recycling materials in the United States. However, paper is recycled at relatively low temperature, and contaminants could remain. Some recycled products are made of newspaper which may contain dioxins and furans, and a complex mixture of related compounds that are formed in trace amounts when chlorine or chlorine derivatives are used as the primary bleaching agents in making white paper products. The most toxic dioxin is 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD), which has been shown to cause cancer in laboratory test animals (Foulke, 1991).

4.3 Plastics in Packaging

Plastics are now one of the fastest growing materials in the packaging industry. The principal resins used in packaging are polyethylene, polypropylene, polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamides, and ethylene vinyl alcohol copolymer (Bonis, 1994). Among them, polyethylene, particularly low-density polyethylene (LDPE), is widely used throughout the packaging industry.

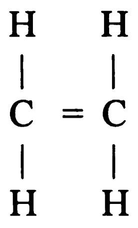
The choice of a plastic for use in a particular application will be governed by a number of considerations. There are first, the environmental conditions of packing, shipment, and storage; second, physical characteristics of the packaging materials; and third, chemical characteristics including the compatibility between packed product and packaging. The following listing presents several important properties of plastics that are related to the packaging industry. The numbers in parenthesis are the ASTM standards describing the method for their evaluation.

Chemical	Chemical composition and microstructure
	Molecular weight and molecular weight distribution
	Morphology and crystallinity
Physical	Density (ASTM D-1505)
	Coefficient of linear thermal expansion, Length/Length (ASTM D-696)
	Deflection temperature (ASTM D-648)
	Thermal conductivity, cal-cm/sec. sq cm °C (ASTM C-177)
	Melting temperature Tm
	Glass transition temperature Tg
	Melt Flow Index (ASTM D-1238)
Mechanical	Tensile strength, psi (ASTM D-638)
	Elongation, length/length (ASTM D-638)
	Bursting strength (ASTM D-774)
	Impact strength (ASTM D-3420)
	Tear strength (ASTM D-1004)
	Coefficient of friction (ASTM D-1894)
	Heat sealability
	Gloss (ASTM 2457)

The International Union of Pure and Applied Chemistry (IUPAC) defined a polymer as a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units (also called a macromolecule). Polymers include wood, protein, and plastic. The molecular weight range of a synthetic polymer is between 10,000 and 10 million. It has been found that in many cases the polymer molecules have the form of linear or slightly branched chains (Mark, Atlas, 1995). For synthetic polymers or plastics, the chemical composition and microstructure, molecular weight distribution, and the morphology and crystallinity properties are important, since they affect many of the characteristic physical and mechanical properties of a polymer (Billmeyer, 1972).

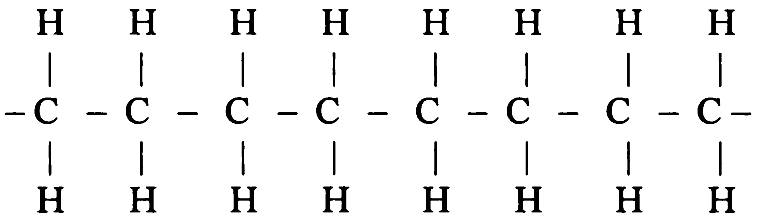
4.3.1 Polyethylene

Ethylene is the simplest of all monomers, as far as chemical structure is concerned. Through a chemical reaction, the double bond can be opened and two ethylene molecules combined into a dimer. Further addition of many repeating units yields the polymer, polyethylene (Giacin, 1994).



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Polyethylene is a family of addition polymers based on ethylene , which is essentially a straight-chain compound:



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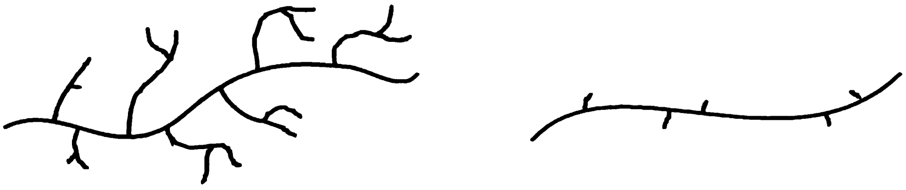
- & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - \\
 & | & & | & & | & & | & & | & & | & & | & & | & \\
 & H & & H & & H & & H & & H & & H & & H & & H &
\end{array}$$

with hundreds, and sometimes thousands of carbon atoms in each chain. Polyethylene can be linear or branched, a homopolymer or copolymer. A segment of a chain branching interferes with the close packing of the molecules and results in a soft and lower density material. Less branching, on the other hand, allows the molecules to pack together and makes the polymer tend to crystallize because of the structural regularity, which produces a stiffer, more dense, and less permeable material (Hernandez, 1994). The glass transition temperature (Tg) is about -125 °C , and Tm is 135 °C for high density and 110 °C for low density, respectively (Mark and Atlas, 1995).

There are basically two variants of polyethylene, differing in structure and properties as well as in the manufacturing process. High density polyethylene (HDPE), whose density is between 0.95 and 0.970 gram/cc, has a percentage of crystallinity from 70 to 90%. Low density polyethylene (LDPE) with density from 0.910 to 0.950 gram/cc, typically has a crystallinity ranging between 40 to 60% (Hernandez, 1994) .

The process for making high density polyethylene was developed by Prof. Karl Ziegler of Germany and several others by using a catalyst of titanium tetrachloride and triethyl aluminum in the middle 1950s', notably

Phillips Petroleum Company (Handbook of Packaging Engineering, 1992). This process works at normal atmospheric pressure and room temperature, so it is sometimes called low-pressure polyethylene. The molecular structure of high density polyethylene is essentially linear with relatively few side branches as compared to LDPE. This is shown in Figure 7. Thus, the molecules are permitted to line up nearly parallel and close together to crystallize and provide a hard, stiff, impermeable material for injection-molding containers.



Low-density polyethylene High-density polyethylene

Figure 7: Molecular structures of polyethylene

Long-chain branched low-density polyethylene is normally produced by high-pressure processes, in autoclave or tubular reactors by means of a free-radical polymerization procedure (Manders, 1994) which is carried out at approximately 50,000 psi and temperatures of about 300 °F (Handbook of Packaging Engineering, 1992). This process produces ramifications in the main backbone chain resulting in a branched polymer that is actually a mixture of large molecules with different backbone lengths, various side chain lengths and with various degree of side-chain branching. The applications of LDPE can be as both film and sheet, injection molding, coating, and blow molding because of their flexibility, moisture protection, and light weight. In the United States, about 55% of the total LDPE is made into films with thickness as less than 12 mils (300 microns) (Handbook of Packaging Engineering, 1992).

Currently, Polyethylene continues to experience significant technological developments (Manders, 1994). Over the years, production of polyethylene has developed a high degree of control over such polymer properties as molecular-weight distribution and degrees of short- and long-chain branching. Molecular weight can be controlled by chain-termination agents and reactor conditions, such as with linear low density polyethylene (LLDPE).

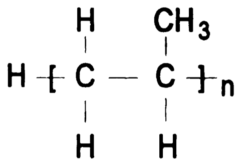
LLDPE is characterized by a narrow distribution of MW and a linear structure with very short branches, due to the presence of butene, hexene or octene as a comonomer (Hernandez, 1994).

Butene	$HC = CH_1CH_2CH_3$
Hexene	$HC = CH(CH_2)_3CH_3$
Octene	$HC = CH(CH_2)_5CH_3$

LLDPE has a higher degree of crystallinity and is stiffer than LDPE because of the linearity of its molecules, and it has higher tensile strength, puncture resistance, tear properties and elongation than LDPE.

4.3.2 Polypropylene

Polypropylene (PP) is a group of thermoplastic polymers based on the polymerization of propylene monomer, $CH_2=CH-CH_3$. It is produced under controlled conditions of heat and pressure in the presence of Ziegler Natta catalysts (Bailey and Brauer, 1994).



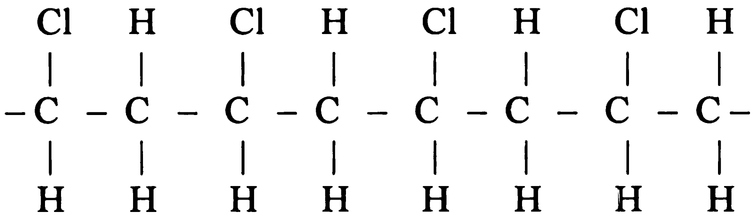
$$H\left[\begin{array}{c}H\\|\\C\\|\\H\end{array}-\begin{array}{c}CH_3\\|\\C\\|\\H\end{array}\right]_n$$

There are three basic types of polypropylene: isotactic, atactic, and syndiotactic (Giacin, 1994). Isotactic polypropylene is the most common commercial polypropylene, whose molecular structure allows it to assume a helical and crystalline configuration, which offers a enough material stiff enough for a wide range of commercial applications. It has a density of 0.90-0.91 gram/cc, and a melting point of 165 °C. The melt-flow index for this material ranges from under 0.3 gram/10 min. for extruded sheets to greater than 800 gram/10 min. for some fiber grades (Bailey and Brauer, 1994). Other advantages of the resin include resistance to most organic solvents, with the exception of very strong oxidizing agents such as fuming nitric acid or sulfuric acid. Atactic polypropylene, which has a random molecular pattern, is commonly used as an adhesive, or mixed with other materials, such as asphalt, for roofing applications. Syndiotactic polypropylene offers a lower melting point, better impact resistance and more clarity than isotactic homopolymer polypropylene (Hernandez, 1994).

Random copolymers of polypropylene typically contain several percent of ethylene as comonomer (Hernandez, 1994). The copolymers with a melt flow index of 35 gram/ 10 min. or above find applications in thin-wall parts, recently used for injection-molded food packaging (Bailey and Brauer, 1994).

4.3.3 Polyvinyl chloride (PVC)

PVC is a homopolymer of vinyl chloride, $CH_2{=}CHCl$. The vinyl chloride is produced by the thermal dehydrochlorination of ethylene dichloride, which in turn is manufactured by either the direct chlorinating of ethylene, or the oxy-chlorination of ethylene with hydrochloric acid and oxygen (Hernandez, 1994).



$$-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

Vinyl chloride is converted to PVC via a free-radical addition polymerization, using one of four basic processes: Suspension, emulsion, bulk or solution (Maresca, 1994). Approximately 90% of the world production of PVC is produced by the suspension polymerization method and initiated by peroxide free-radical catalysts. In this process, the microscopic droplets of vinyl chloride are suspended in water by vigorous agitation. After polymerization, the residual vinyl chloride monomer is removed by heating the resin under vacuum. PVC is then centrifuged and dried to remove the water. The molecular weight of PVC is controlled largely by the polymerization temperature, and to a much lesser extent by the initiator concentration. Higher reaction temperatures generally produce lower-molecular-weight resins.

PVC has a wide range of properties depending on the manufacturing process used. In addition to good physical properties, the polymer has excellent transparency, chemical resistance, long-term stability, flammability resistance, weatherability, flow and electrical properties. The versatility of PVC is a direct result of its blending compatibility with a wide variety of plasticizer, fillers, pigments, and other additives. The PVC resin can be processed by all the standard thermoplastic fabrication techniques including: (1) extrusion, (2) calendering, (3) injection molding, (4) blow molding, (5) powder molding, (6) blown film, and (7) coating (Maresca, 1994).

4.3.4 Polyethylene Terephthalate (PET)

PET resins are produced by the reaction of purified terephthalic acid (PTA) and ethylene glycol as shown in figure 8. It is a condensation, linear, semicrystalline, thermoplastic homopolymer that has found great acceptance as carbonated beverage packaging material due to its properties of toughness, clarity, recyclable, and the development of high speed bottle processing technology. PET has a Tg of approximately 69 °C and Tm of 265 °C. (Mark, 1995)

Although the vast majority of PET resin ends up in blow-molded containers (Mitchell, 1994), PET based glass coated films have been used

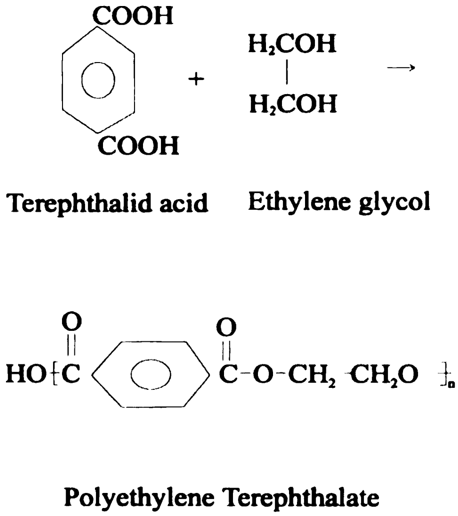


Figure 8: PET is condensed from terephthalic acid (PTA) and ethylene glycol

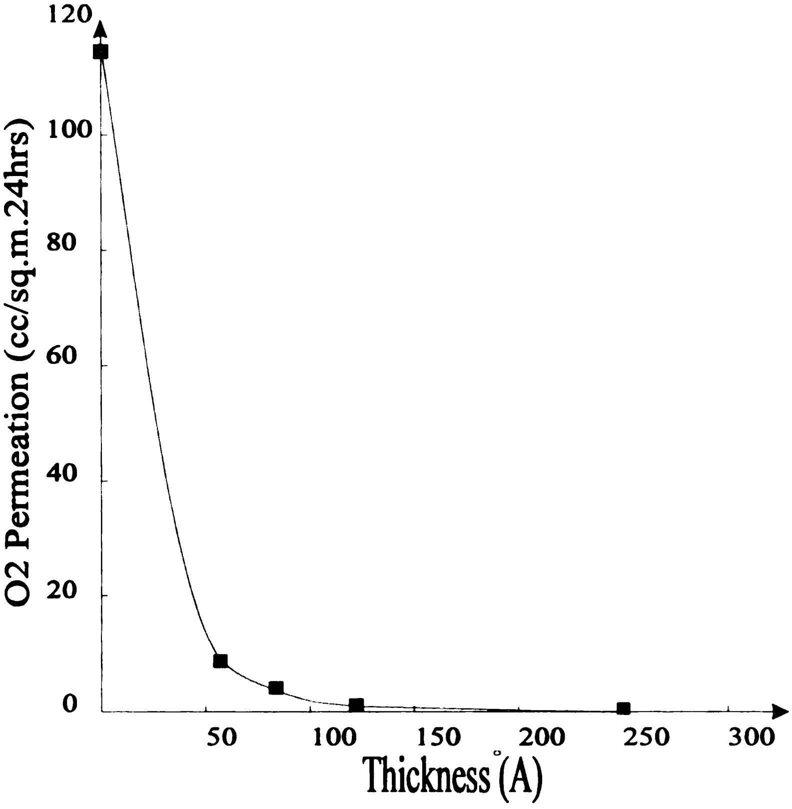
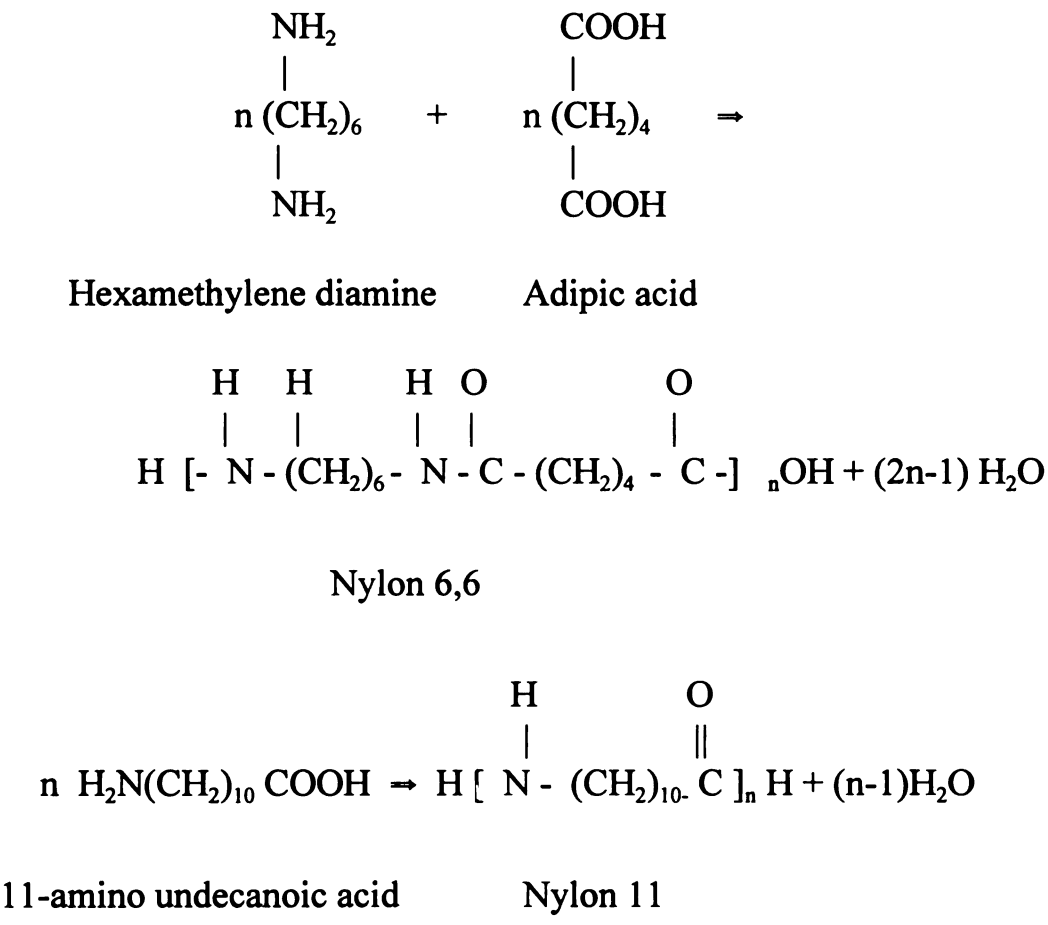


Figure 9: Oxygen transmission of Clearcoat on 0.5 mil PET vs. coating thickness

Source: Mastat Izu, High Performance Ovonic Clearcoat Barrier Film Technology, 1993 commercially and have been available at development pricing since mid-1993, for incorporation into packaging systems on an everyday basis for high barrier to permit microwaveability in food packaging (Brody, 1993). The chemical composition of the coating ranged from SiO to SiO_2 (Silicon dioxide). The coating has been given the designation SiO_X rather than silica's SiO_2 because the coating is a mixture of SiO + SiO_2 to achieve barrier coatings. Glass coated packaging materials usually have significantly higher oxygen barrier properties than their base plastic substrate films, due to the properties imparted by the coating. Figure 9 shows a plot of the oxygen transmission rate vs. coating thickness data for 0.5 mil PET films coated with Ovonic Clearcoat, which is a technology developed by Energy Conversion Devices, Inc.(Izu, 1993). The figure illustrates that a coating of approximately 120 Å is sufficiently thick to maximize oxygen barrier properties. To date, deposition of SiO_X coatings has been mainly onto PET substrates. Since the bulk of the work has been on PET, the lowest transmission rates have been achieved on it.(Felts, 1993)

4.3.5 Polyamides

Polyamides or Nylons, are condensation, linear, thermoplastic polymers that contain the amide group as a recurring part of the chain. At low humidity, polyamide exhibit strong inter and intramolecular force of atraction, due to the presence of H-bonding between the HN- group and the polar carbonyl group -C=O. The molecular structure thus gives Nylons the properties of toughness, good puncture resistance, impact strength and temperature stability. For instant, Nylon-6,6 has the melt point of 269 °C. Polyamides also typically exhibit good chemical resistant and are a good barrier to gas, oil, and aromas. It is, however, moisture sensitive, due to H-bonding disruption of the polymers



$$\begin{array}{c} NH_2 \\ | \\ n\,(CH_2)_6 \\ | \\ NH_2 \end{array} \quad + \quad \begin{array}{c} COOH \\ | \\ n\,(CH_2)_4 \\ | \\ COOH \end{array} \quad \Rightarrow$$

$$H\,[-\,\overset{\overset{H}{|}}{N} - (CH_2)_6 - \overset{\overset{H}{|}}{N} - \overset{\overset{O}{|}}{C} - (CH_2)_4 - \overset{\overset{O}{|}}{C}\,-]\;{}_nOH + (2n-1)\,H_2O$$

$$n\;H_2N(CH_2)_{10}\,COOH \rightarrow H\,[\,\overset{\overset{H}{|}}{N} - (CH_2)_{10} - \overset{\overset{O}{\|}}{C}\,]_n\,H + (n-1)H_2O$$

Figure 10: Chemical structure of selected commercial nylons

naturaly which results in oxygen permeability increasing with moisture content (Hernandez, 1994). Nylon can be made by the condensation of diamines and dibasic acids or the condensation of amino-acids (See figure 10).

A diverse degree of crystallinity is obtained depending on the temperature and quenching rate (Hernandez, 1994). When the cooling rate is increased, a less crystalline nylon is obtained, since the polymer was not given sufficient time to form crystallites. For most packaging applications, nylons are used in film form. It can be combined with other materials that add moisture barrier and heat sealability such as LDPE, ionomer, or EVA. The degrees of crystallinity can be controlled during the film production.

A new polymer was developed by Toyobo Co., Ltd. that is called MXD-6 Nylon (Watanabe, 1987). The MXD-6 nylon is a polycondensation of meta-xylene diamine (MXDA) and adipic acid as shown in Figure 11.

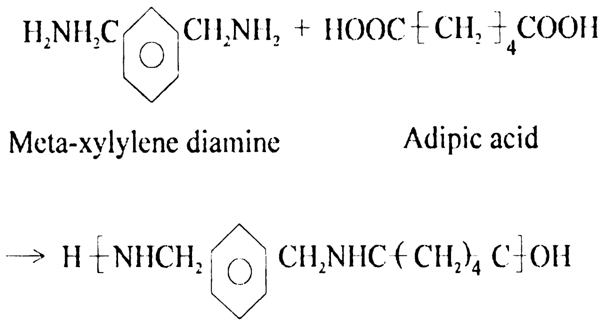


Figure 11: Chemical structure of MXD-6 Nylon.

MXD-6 Nylon provides a good barrier not only to gases but to moisture as well. The gas barrier properties are better than Nylon-6 and PET at all humilities, and better than ethylene / vinyl alcohol copolymer (EVOH) at 100% RH, due to the existence of the benzene ring in the MXD-6 polymer chain(Watanabe, 1987). The benzene ring in the MXD-6 polymer chain results in its having a higher tensile modulus than Nylon-6; and the MXD-6 Nylon film has good dimensional stability at the high temperatures and tensions found in printing and laminating processes. (Watanabe, 1987)

4.3.6 Ethylene Vinyl Alcohol (EVOH)

Ethylene / vinyl alcohol copolymer are produced by a controlled hydrolysis of ethylene / vinyl acetate copolymer. The presence of OH functional groups on the backbone chain has a dramatic effect on the polymers properties. If the percent of vinyl alcohol in the ethylene / vinyl alcohol copolymer is in the range of 20% to 50%, the copolymers obtained combine the processability and water resistance of polyethylene and the gas and odors barrier characteristics of polyvinyl alcohol. The most important characteristic of EVOH is the outstanding oxygen and odor barrier properties (Hernandez, 1994). EVOH also provides a very high resistance to oils and organic vapors. For packaging applications, EVOH can be used in a flexible film structure or fabricated into a rigid container. It can also be coextruded in combination with PE or PP, and laminated or coated to various substrates including PET, PE, and Nylons, etc. (Hernandez, 1994).

4.3.7 Morphology of Packaging Polymers

The increasing use of plastics, which contain traces of solvent residues from processing, in food packaging has led to the need for more information about interactions between plastic packaging materials and foods (Halek and Chan, 1994). At the same time, sorption is also one of the major problems of concern with the packaging of foodstuffs (Hotchkiss J. H., 1988). In general, these are related to the morphology within the polymer, such as structural regularity of the chains, free vibrational and rotational motion of chain segments, so that different conformations can be assumed, presence of specific groups which produce strong lateral intermolecular bonds, and the absence of bulky side groups, which can inhibit the vibrational and rotational mobility of an intrinsically flexible chain (Mark 1995).

The polymer molecule experiences torsional oscillation and / or rotation around covalent single bonds, which is called micro-brownian motion. The size and frequency of "hole" formation between the molecules are quiet important to the diffusion, solubility, and permeability of permeant molecules. Temperature is another factor that can influence the mass transfer process. Above the glass transition temperature (Tg), the polymer chains experience segmental mobility, and as the temperature is increased, the size and frequency of 'hole' formation increases, as a result of increased segmental mobility. Thus, creating a more accessible pathway for permeant molecules to diffuse through the polymer bulk phase.

4.4 Mass Transport phenomena

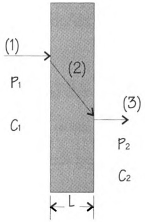
4.4.1 Permeation

The major advantages of plastics films are flexibility, the indeep draw capability, heat sealability, and the fact that they can be either translucent or opaque, as required. Their barrier properties vary and are dependent on the individual polymers chemical and physical properties. No polymer is an absolute barrier. However, recent developments have made available high barrier plastics packaging materials, particularly in the form of multi-layer structures and with the use of coatings. These developments led to the necessity to investigate the specific permeability of plastic films to various gases, vapors and liquids. The transfer of gases, vapors and liquids through films is considered under the title of permeation.

The permeation mechanism actually involves three steps: (1) absorption and dissolution of the penetrant into the polymer surface exposed to the high penetrant concentration; (2) diffusion of the penetrant through the polymer; and (3) desorption and evaporation of the penetrant from the low concentration surface of the polymer, as shown in figure 12.

Presented in Figure 12 is a generalized permeation model. If it is assumed that (1) the concentration gradient of the permeant gas within the polymer film or slab (dc/dl=constant) is constant at steady-state; and (2) there is no interaction of penetrant with the polymer, the permeability constant P can be related to the diffusion coefficient D and the solubility coefficient S of the penetrant in the polymer by the following equation (Mohney, 1988):

$$P = D\,S \qquad (1)$$



Where: P1 and P2 = Partial pressure of permeant gas at the two surfaces of the film or slab.

C1 and C2 = Concentration of permeant gas at the two surfaces of the film or slab.

L = Film or slab thickness

Figure 12: The permeation mechanism

In this case, the permeability constant P is a function of both the diffusion and solubility coefficients. The diffusion process can be described by the Fick's first and second laws of diffusion (Crank, 1975)

$$F = -D\,(dc/dx) \qquad (2)$$

$$dc/dt = d[\,D\,(dc/dx)]/dx \qquad (3)$$

Where,

F : The flux or the rate of transfer of penetrant per unit area, expressed as mass of diffusant per unit area per time.

c: the concentration of the penetrant in the film, expressed in the same units of mass of diffusant per unit of volume or mass of the polymer.

D: the mutual diffusion coefficient, in $(\text{length})^2/\text{time}$.

t: time

x the length in the direction in which transport of the penetrant molecules occurs.

To obtain the flux (F) or the diffusion coefficient (D) from equations (1) and (2), the initial and boundary conditions associated with the experimental method are needed, and the expressions solved to give the desired values (Hernandez, 1986).

Only approximated values will be obtained when the diffusion coefficient is calculated using these equations. If permeation involves interacting organic vapors, the relationship between P, D, and S is more complex than that indicated by equation (1). For such cases, diffusion processes may be concentration as well as time dependent that results in swelling of the polymer matrix and a non-ideal Henry's Law relationship (Crank, 1975).

4.4.2 Solubility

Sorption is a phenomena describing the dissolution or transfer of a substance from the contacting phase to a polymeric packaging materials. The solubility of essential flavors in polymer structures is of paramount importance in avoiding the effect of "flavor scalping" or loss due to sorption. The solubility coefficient can be calculated from sorption experiments by substitution into the expression (Hernandez, 1986):

$$S = \frac{M_\infty}{w \cdot b} \qquad (4)$$

Where: S: solubility coefficient

M_∞: total amount of mass absorbed

w: weight of the polymer tested

b: driving force (concentration or pressure)

The solubility coefficient is expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force concentration or penetrant partial pressure. The amount of penetrant (Mt) sorbed by the film during time t is given by following expressions (Crank, J, 1975).

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-(2n+1)^2\pi^2 Dt}{\ell^2}\right] \qquad (5)$$

Where, M_∞: the amount of penetrant sorbed by the film at equilibrium.

M_t: the amount of penetrant sorbed by the film during time t.

ℓ: the thickness of the film.

If the time to reach $M_t/M_\infty = 0.5$ is $t_{1/2}$, which means the time required to reach a sorption level equal to half the equilibrium value, M_∞, the diffusion coefficient (D) can be determined from equation (5) as follows:

$$D = \frac{0.049\,\ell^2}{t_{1/2}} \qquad (6)$$

For film samples, the diffusion coefficient (D) is determined by substitution into equation (6) for sorption studies carried out until equilibrium is reached (Mohney, 1988).

The solubility and diffusivity of liquids and gases in polymers is dependent upon chemical composition, polymer molecular structure, and polymer morphology. For sorption, if the polymer and sorbate have equivalent solubility parameters, they should be mutually soluble or, substances with similar chemical structures should be quite likely to dissolve in each other (Hoftyzer and Krevelen, 1976). The solubility parameter, δ, for a particular polymer or sorbate can be obtained from the respective cohesive energy E_{coh}, which is defined as the increase in internal energy U per mole of substance, if all the intermolecular forces are eliminated in a condensed state (Hoftyzer and Krevelen, 1976).

$$\delta = \left(\frac{E_{coh}}{V}\right)^{1/2} \tag{7}$$

Where, E_{coh}: The cohesive energy
δ : solubility parameter
V: Molar Volume

Formally, the cohesive energy may be divided into three compoments, corresponding to the following three types of interaction forces, dispersion forces, polar forces, and the contribution of hydrogen bonding. The solubility parameter components may be predicted from these group contributions, using the following equations (Hoftyzer, P. J. and Van Krevelen, 1976):

$$\delta_d = \frac{\Sigma F_{di}}{V} \tag{8}$$

$$\delta_p = \frac{\Sigma F_{di}}{V} \tag{9}$$

$$\delta_h = \frac{\Sigma F_{di}}{V} \qquad (10)$$

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2} \qquad (11)$$

Solubility is dependent upon the chemical composition of both the packaging materials and penetrant, polymer molecular structure, and polymer morphology. The storage temperature also affects the sorption significantly (Nielsen, 1992). In general, with an increase in temperature there is a decrease in solubility. The temperature dependence of the solubility coefficients can also be described by an Arrhenius type equation (Maekawa, 1994):

$$S = S_0 \exp -(H_s / RT) \qquad (12)$$

Where, S: solubility coefficient

S_0: pre-exponential constant

H_s: the heat of condensation

The heat of condensation, H_s, can be positive or negative. For the condensable vapors such as an organic compound, it is negative due to the relatively large heat of condensation. Therefore, the solubility coefficient of a vapor decreases with increasing temperature.

4.4.3 Migration

Migration is the passage of molecules originally contained by the package itself into the product. In food packaging regulations, the term migration is used to describe the transfer of substances from the package to the foodstuff. A distinction is usually made between Global and Specific migration. Global migration refers to the total transfer or migration of all migrating species, whether they are toxic or not, from the packaging system into the packaged food, whereas specific migration relates to one or more identifiable substances that is a constituent of the packaging material. In principle, the measurement of total or Global migration from a packaging materials is quite simple. It consists of placing a sample of the material of known surface area in contact with an appropriate food simulant or solvent under defined time-temperature conditions (FDA Guidelines for Chemistry and Technology Requirements of Indirect food Additive Petitions, 1976) and determining total transfer. With respect to specific migration, limits are designed to restrict the transfer into food of those compounds (i.e. monomer) known or deemed potentially hazardous to human health, but do not take into account the total quantity of other migrants transferring into the contact phase (Giacin, 1994).

Both sorption and migration involve the partitioning of low molecular weight organic species between the polymeric packaging material and the contact phase, quantitatively described by the partition coefficient (K)

$$K = \frac{[\, C_p \,]}{[\, C_c \,]} \qquad (13)$$

Where, C_p: substance concentration in polymer

C_c: substance concentration in contacting phase

The partition coefficient K is defined as the ratio of the equilibrium concentration of a component in the contacting polymeric material over the equilibrium concentration of the component in a fluid phase. Hence, a large partition coefficient means that the substance has a higher affinity for the plastic than for the contacting phase, and larger amounts are absorbed by the packaging material.

4.5 Modeling the equilibrium distribution of vanillin between the paperboard shipper and a LDPE primary packaging system

A model of equilibrium distribution of vanillin between the paperboard shipper and a LDPE primary packaging system was described by Maekawa (1994). Vanillin and ortho-vanillin were proposed as model compounds for this study. A schematic diagram of the mechanism of vanillin and ortho-vanillin volatilization or permeation and associated equilibria is as follows:

$$\begin{array}{c}\text{Corrugated board}\\ \text{shipping container}\end{array} \rightleftharpoons \begin{array}{c}\text{Container}\\ \text{headspace}\end{array} \rightleftharpoons \begin{array}{c}\text{Polyethylene}\\ \text{(LDPE)}\end{array} \rightleftharpoons \begin{array}{c}\text{Aqueous}\\ \text{phase}\end{array}$$

Gas chromatographic analysis processes, High performance liquid chromatographic analysis processes, and electrobalance analysis were involved in Maekawa's study to determine the partition coefficient of vanillin or ortho-vanillin between paperboard and headspace, LDPE film and the aqueous phase.

All the studies were carried out at 23°C. The average partition coefficient values for vanillin and ortho-vanillin between paperboard and headspace were 21.6 and 77.5, respectively at 23°C. The average partition coefficient values for vanillin and ortho-vanillin between LDPE film and an aqueous phase were 3.8 and 574, respectively.

Migration of volatiles such as vanillin and ortho-vanillin from a corrugated paperboard shipper was considered a mass transfer process under defined test conditions to include:

I. Time
II. temperature
III. the nature and volume of the respective phases associated with the system equilibrium

The driving force for migration is the concentration gradient, where the volatile species of interest transfer from a region of higher concentration (i.e. corrugated paperboard) to the region of lower concentration. The results from this study show that the times to reach equilibrium in the corrugated container/headspace/LDPE packaging system are on the order of 10^3 days for a 20 mil wall thickness LDPE ampule (Maekawa, 1994).

MATERIALS AND METHODS

5.1 Materials

The following items and equipment were used in this study:

1: Packaging material:

- Kraft corrugated board. D/F 200 lb specification, C-flute, (Midwest Papermart, Lansing MI)
- Low density polyethylene, (Dey Laboratories, Inc. Napa, CA).

2: Volatile sorbates:

- 99% purity vanillin and ortho-vanillin (Aldrich Chemical Co. Milwaukee, WI).

3: Solvent:

- Chromatography grade acetonitrile (Aldrich Chemical Co. Inc. Milwaukee, WI).
- HPLC grade water (Aldrich Chemical Co. Inc. Milwaukee, WI).

4: Vials and Cans:

- 40 ml screw cap amber glass vials with Teflon coated silicone septa (Supelco Inc., Bellefonte, PA).
- Uncoated two-piece steel cans (American National Can, La Porte, IN)

5: Gas Chromatography:

  Type: HP 5890A (Hewlett Packard, Avondale, PA)

  Column: Fused silica capillary column (30m x 0.32mm ID) intermediate polarity stationary phase SPB-5 (Supelco Co., Bellefonte, PA)

6: Dynamic Thermal Stripper System, Model 1000 (Dynatherm Analytical Instruments Inc., Kelton, PA)

Thermal Desorption System, Model 890 (Dynatherm Analytical Instruments Inc., Kelton, PA)

7: High Performance Liquid Chromatography, Model 150-C ALC/GPC with Waters 486 tunable absorbance detector

8: Thermal ovens

9: Analytical balance

10: Vacuum filter system

5.2 Methods

There are three principal experimental phases in this study which are described in detail below:

5.2.1 Part 1: Determination of equilibrium partition distribution of vanillin and ortho-vanillin between corrugated board and its headspace

5.2.1.1 Construction of Calibration Curve

Gas chromatography analysis required construction of two (2) calibration curves, based on sample handling. A standard calibration curve was developed by direct injection of vanillin and ortho-vanillin standard solutions of known concentration into the gas chromatograph. Calibration curves for both vanillin and ortho-vanillin, based on the thermal stripper / thermal desorption (TS/TD) procedure, were also constructed. The procedure for developing the TS/TD calibration curve involved injecting a predetermined quantity of vanillin or ortho-vanillin standard solution directly onto the carbotrap 300 sorption tube, and then desorbing the vanillin and ortho-vanillin through the Dynatherm thermal desorption system (model 890) to the gas chromatograph for quantification.

Test conditions for gas chromatography analysis:

Type: HP 5890A, Hewlett Packard, Avondale, PA.
Column: Fused silica capillary column (30m x 0.32 mm ID) intermediate polarity stationary phase SPB-5 (Supelco Co., Bellefronte, PA)
Injector: 5 µl liquid syringe, 500 µl gas tight syringe (Hamilton)

Flow rate:	Helium	7.0	ml/min.
	Air	400	ml/min.
	Hydrogen	40	ml/min.
	Nitrogen	30	ml/min.
Temp:	Initial	60	°C
	Final	200	°C
	Rate	7.5	°C/min.

The conditions of DT/ST system:

Type: Model 1000, Dynatherm Analytical Instruments Inc., Kelton, PA.

Dynamic thermal stripper:

Temperature:	oven	80	°C
	block	105	°C
	sorption tubes	50	°C
Purging time:		46	min

Thermal desorption unit:

Temperature:	transfer line	230	°C
	desorber	340	°C
	valve	230	°C
Desorption time:		8	min

Peak areas and retention time were recorded by the use of a computer integrator (HP3395, Hewlett-Packard, Farmington, MI). The retention times of vanillin and ortho-vanillin observed in the determination of the calibration factor, by direct on column injection, were 14.73 and 12.88 minutes, respectively. Retention times for both vanillin and ortho-vanillin, based on the thermal stripper / thermal desorption (TS/TD) procedure, were 15.3 and 13.2 minutes, respectively. The data is shown in appendix A. Calibration factors (C.F.) were determined from the slope of the linear calibration curve.The calibration curves are shown in Figure 19, 20, 21, and 22.

5.2.1.2 Initial vanillin and ortho-vanillin levels in corrugated board

The initial levels of vanillin and ortho-vanillin in corrugated board were determined by the thermal stripper / thermal desorption method. In this procedure, two small pieces of paperboard, about 3 x 60 mm in dimension, for a total surface area of 3.6 cm^2 were placed into the sparging tube (Supelco Co., Bellefonte, PA) of the thermal stripper instrument (Model 1000, Dynatherm Analytical Instrument, Inc. Kelton, PA). The sparging tubes were then mounted in the oven of the thermal stripper instrument (Model 890, Dynatherm Analytical Instruments, Inc., Kelton, PA) and connected to the sorption tubes positioned outside the oven. The sorption tubes, containing Carbotrap 300 multi-bed materials (Supelco Co., Bellefonte, PA), were covered with sleeve heaters. After sample preparation, the carbotrap sorption tubes containing the trapped volatiles were transferred to the tube chamber of the thermal desorption unit (Model 890, Dynatherm Analytical Instrument, Inc. Kelton, PA). The sorbed volatiles were then desorbed by heating for 6 minutes at 340 °C with the valve and transfer line heated to 230 °C, so as to maintain the desorbed compounds in the vapor phase and allow their transfer to the gas chromatograph. The operating conditions for the TS/TD procedure are the same as the conditions described above for construction of the required calibration curve.

5.2.1.3 Equilibrium partition between corrugated board and headspace

Two different techniques were employed to provide corrugated board samples of known migrant concentration levels. For the ortho-vanillin studies, samples were prepared with an ortho-vanillin generation system as shown in Figure 13. Here, an aliquot of 500 μl was withdrawn from the headspace of the

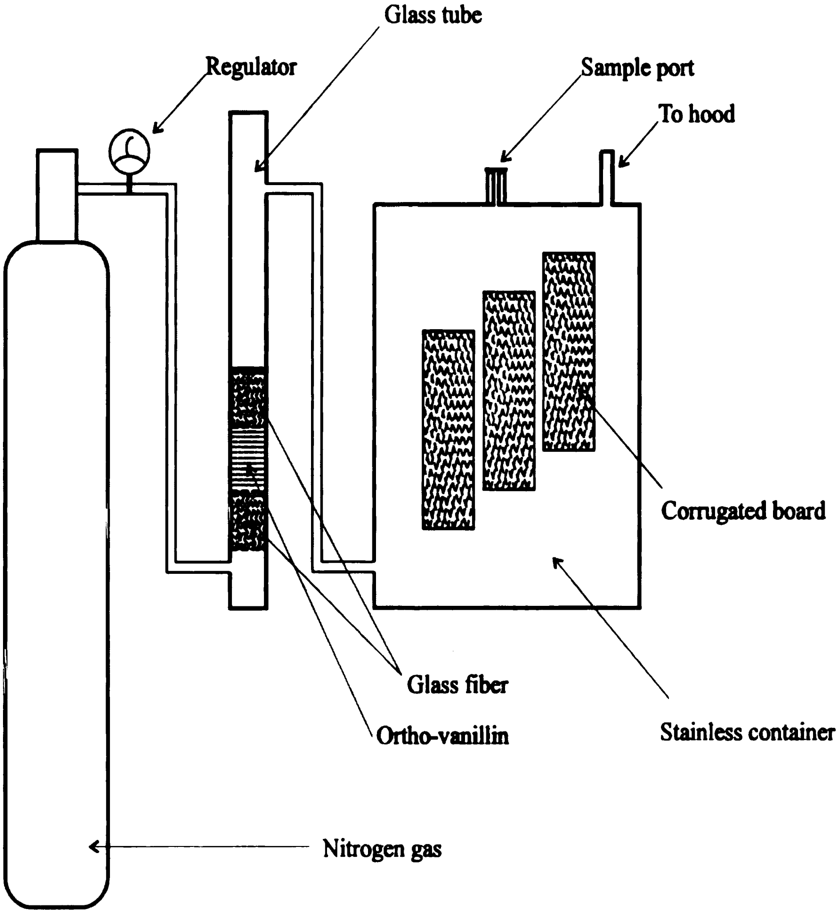


Figure 13: Ortho-vanillin generation system for preparation of paperboard samples of known o-vanillin concentration

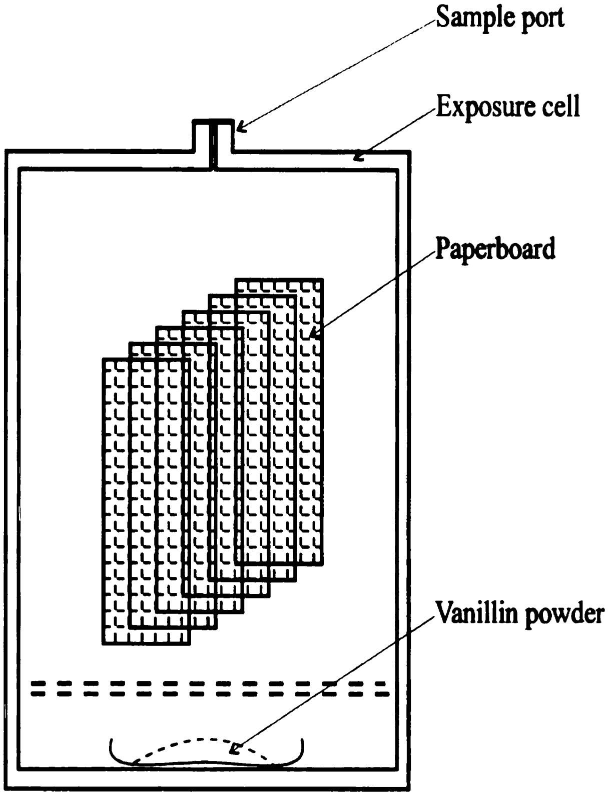


Figure 14: Direct exposure method for preparation of paperboard samples of known vanillin concentration

stainless steel cell and injected directly into the gas chromatograph to determine the ortho-vanillin vapor pressure, which was controlled through the adjustment of the nitrogen gas flow rate. Corrugated board samples were analyzed at predetermined time intervals by the thermal stripper-thermal desorption method to provide corrugated board samples of known ortho-vanilllin concentration levels. For vanillin migration studies, samples were prepared by a direct exposure technique, as shown in Figure 14.

The procedure employed to determine the partition coefficient for the corrugated board / headspace / vanillin and ortho-vanillin is as follows:

42 strips of paperboard samples, 1 x 6.5 cm in dimension, for a total surface area of 273.0 cm^2 , were cut from paperboard which had been exposed to vanillin or ortho-vanillin vapor, to provide corrugated board samples of known vanillin and ortho-vanillin concentration levels. The strips of paperboard were placed into uncoated two-piece steel cans, 300 x 406 mm in diameter and height, respectively (American National Can, La Porte, IN). Prior to sealing, a small hole (1 mm, diameter) was punched in the can lid to provide a sampling port, which was covered (interior surface) with Teflon pressure sensitive tape (Supelco Co., Bellefronte, PA). A self sealing silicone rubber septum was also affixed to the outer surface of the sampling port (Mocon, Minneapolis, MN). The cans were seamed with a hand seamer (Model 23 H, Dixie Canner Equipment Company, Athens, GA).

The sorption cells were then stored at 23, 38 and 50 °C respectively for 7 days to allow system equilibration and then sampled (Maekawa, 1994). The equilibrium concentration of vanillin and ortho-vanillin in the headspace was determined by removing a 500 μl sample from the headspace with a gas-tight syringe (Hamilton Co.) through the sampling port and analyzing for vanillin and o-vanillin levels by gas chromatography. The vanillin and ortho-vanillin levels in the paperboard were determined by taking paperboard samples of approximately 0.3 gram and analyzing for sorbate concentration levels by the thermal stripper-thermal desorption method.

5.2.2 **Part 2:** Determination of the stability of vanillin and ortho-vanillin in aqueous solutions

5.2.2.1 Determining calibration factors for the HPLC procedure

Approximately one gram of vanillin or ortho-vanillin was weighed, transferred to a 100 ml volumetric flask and diluted to volume with acetonitrile. Both vanillin and ortho-vanillin solutions were then diluted by a serial dilution technique, to give standard solutions of 0.5, 1.0, and 2.0 ppm (wt/volume), respectively. The standard solutions were filtered with a Micromate syringe (Popper & Sons, Inc. New Hyed Park, NY) with a Millipore Millex filter HV4, 0.45 μm (Waters Chromatography Division, Marlborough, MA), then transferred to 4 ml screw cap clean glass vials with a hole cap (Supelco, Inc, Bellefonte, PA) and a PFTE septum for the HPLC automatic sampling injection system. The standard solutions were analyzed by the HPLC analysis procedure. The mobile phase was prepared by a filter-degas system as shown in Figure 15. The filter was an organic replacement filter, 0.5 μm, from Waters Chromatography Division. The mobile phase was 40% methanol with 60% HPLC grade water (v/v percent).

The calibration curves were plotted as an average area respond for each standard concentration vs. the quantity of vanillin or ortho-vanillin injected. The calibration factors were then determined based on the slope of the curves. The conditions for HPLC analysis was as follows:

Model: Waters™ 150-C ALC/GPC
Detector: Waters™ Turnable Absorbance Detector
Wavelength 275 μm
Column: Delta-Pak™, C^{18} 300Å, 3.9 x 150 mm
Mobile phase: 40% Methanol & 60% HPLC grade water (v/v %)
Temperature: 23 °C
Flow rate: 1 ml/min.
Inj. Vol.: 10 μl

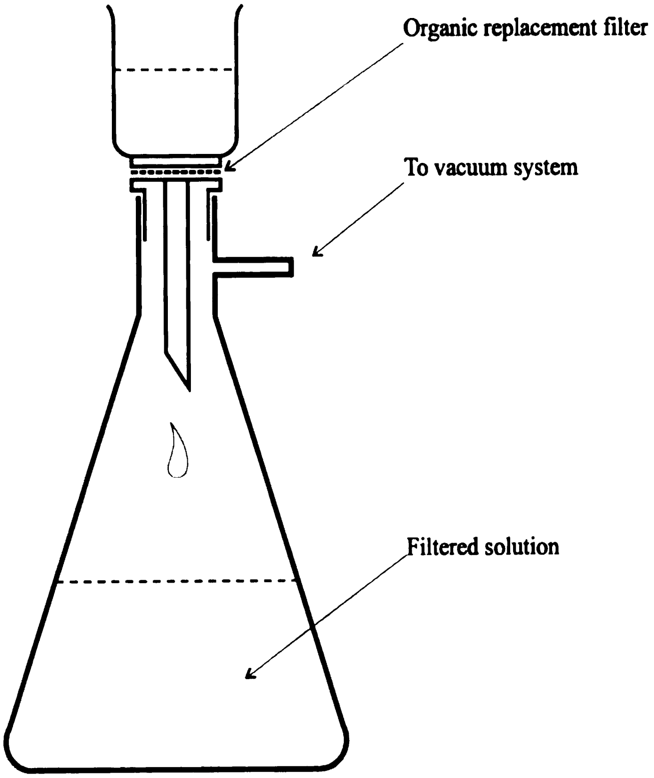


Figure 15: Vacuum filter system

5.2.2.2 Determining the stability of vanillin and ortho-vanillin solutions

Two sample solutions were evaluated in this study. For the first sample, approximately 0.001 gram of vanillin was weighed, transferred to a 1000 ml volumetric flask and brought to volume with fresh HPLC grade water. An accurate initial concentration was determined by the HPLC analysis procedure. A 35 ml sample of the standard solution was then added to 40 ml screw cap amber glass vials with teflon coated silicone septa (Supelco, Bellefonte, PA) and the sample stored at ambient conditions (23 °C, 50% RH).

For the second solution, 0.001 gram of vanillin was weighed, transferred to a 1000 ml volumetric flask and brought to volume with HPLC grade water which was degassed. A vacuum degass system, Figure 16, was designed to outgas the aqueous phase solution. Degassing was carried out for about 30 minutes. The solution was degassed again for about 20 minutes, and then 35 ml sample solution was transferred to 40 ml screw cap amber glass vials with teflon coated silicone septa (Supelco, Bellefonte, PA).

The headspace of the vials were flushed with pure N_2 gas to displace the headspace air and the vials capped. All the glassware used in this process was covered by aluminum film to protect vanillin from light because of its light sensitive property. The vials containing sample solutions were stored in an environmental chamber, Figure 17 (page 54), while pure N_2 gas continuously flowed through the chamber to maintain the samples under a nitrogen atmosphere, and effectively excluded oxygen. The storage temperature was 23 °C. At predetermined time intervals, the sample vials stored at both ambient condition and in the environmental chamber were assayed for vanillin levels.

Ortho-vanillin sample solutions of known concentration were also prepared as described above, degassed and stored in the environmental chamber, and assayed at predetermined time intervals as well.

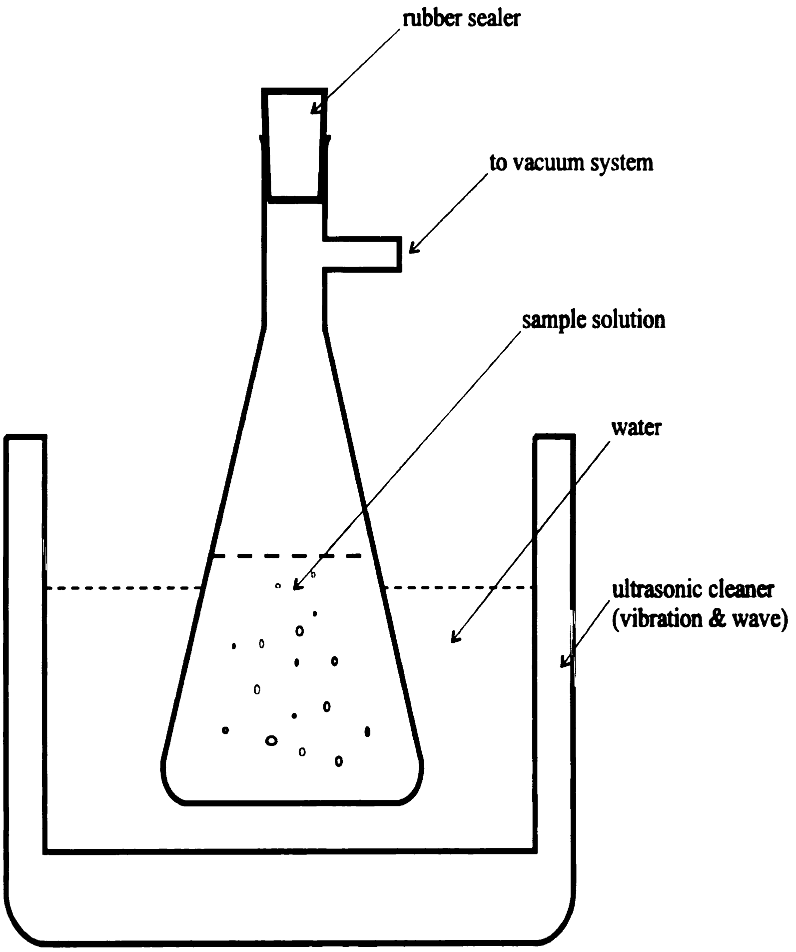


Figure 16: Vacuum degas system

5.2.3 Part 3: Equilibrium partition distribution of vanillin and o-vanillin between low density polyethylene and an aqueous contact phase.

The procedure was designed to determine sorbate uptake by the LDPE, as a function of storage time, to provide equilibrium as well as non-steady state uptake values for both vanillin and o-vanillin. The level of uptake by the LDPE was determined by the difference method (Kashtock, Giacin, and Gilbert, 1980)

14 Round polymer disks, 23 mm diameter, for a total surface area of approximately 8.3 cm^2 were cut from LDPE film with a punch. The surface to volume ratio is the same as found with a designed LDPE form-fill seal ampoule. The films of approximately 5 mils thickness were made from the LDPE ampoule resin by a compression molding procedure. The polymer disks were weighted and threaded onto a stainless steel wire frame with 2 mm high and 4 mm diameter glass rings used to separate the polymer disks. The wire frames, with the mounted disks, were then placed into 40 ml screw cap amber glass vials (28 mm diameter, 98 mm high) with teflon coated silicone septa (Supelco, Bellefonte, PA) and 35 ml of the respective sorbate solutions that had been degassed were added to the vials. A schematic design of the test system is shown in Figure 18. Concentrations of 0.520 ppm (wt/volume) for the aqueous solutions of ortho-vanillin, and 0.434 ppm (wt/volume) aqueous solutions of vanillin were evaluated in the sorption studies. The sorbate solutions were prepared by dissolution of the individual sorbates in HPLC grade water that had been degassed.

The sorption vials were stored in the environmental chamber shown in Figure 17 at temperatures of 23 and 32 °C, respectively, and sampled every two days until equilibrium sorption conditions had been obtained. Aliquots of the aqueous solution were removed from the sorption vials and the concentration of vanillin and ortho-vanillin determined by HPLC analysis.

Control samples were also prepared and stored under the same conditions. The control samples consisted of degassed vanillin or ortho-vanillin standard solutions, stored in the 40 ml screw cap amber glass vials in the absence of polymer disks. These solutions were assayed at predetermined time intervals to insure that there was no degradation or concentration change in the sample solutions that was not attributed to sorbate uptake by the LDPE film samples.

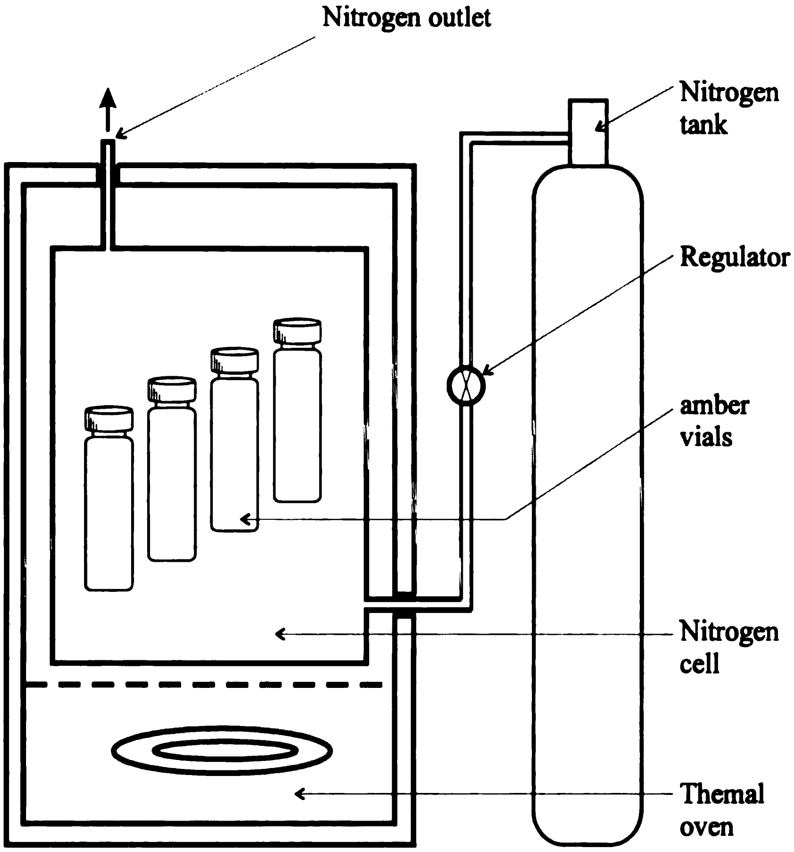


Figure 17: Enviromental controlled sample storage chamber

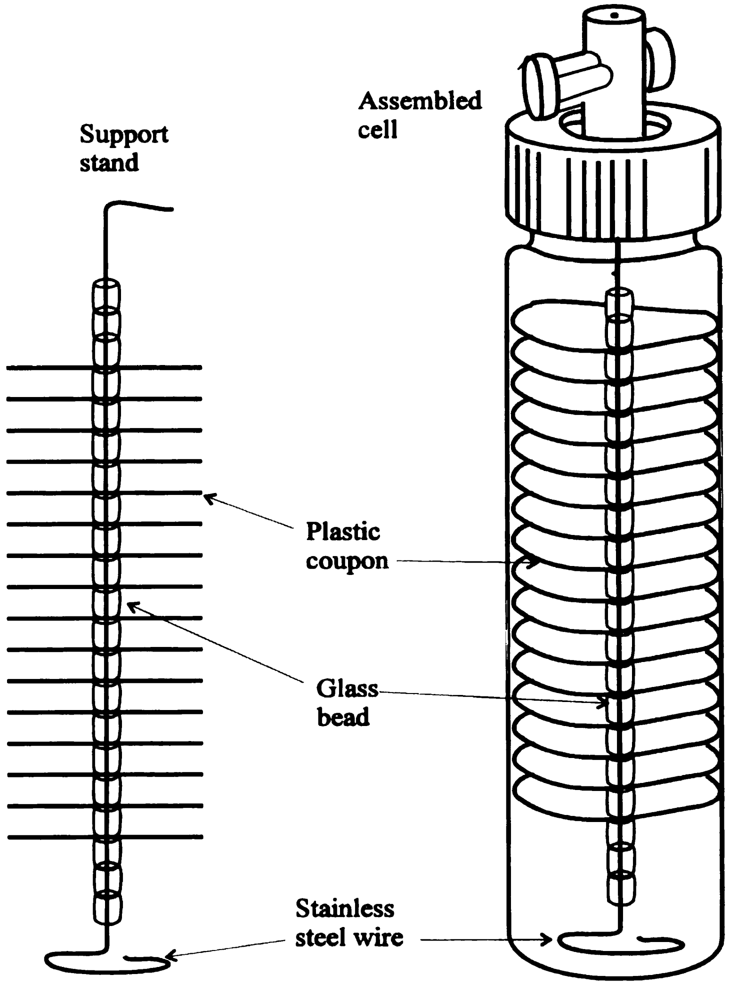


Figure 18: Sorption liquid test cell

RESULT AND DISCUSSIONS

6.1 The results of equilibrium partition distribution of vanillin and ortho-vanillin between corrugated board and its headspace

6.1.1 Initial vanillin and ortho-vanillin levels in corrugated board

The measurement of vanillin and ortho-vanillin levels in corrugated board was carried out by the thermal stripper/thermal desorption technique. A series of preliminary analyses with corrugated board samples were carried out to determine the optimum temperature and purge time needed for the quantitative desorption of residual vanillin and ortho-vanillin. Based on the results of preliminary studies, an oven temperature of 80 °C and a purge time of 30 minutes afforded conditions which allowed for the desorption of over 90% of the initial residual vanillin and ortho-vanillin in the paperboard. The initial vanillin and ortho-vanillin concentrations (weight/weight) are summarized in Table 1. The following equation is used to calculate the concentration:

$$[C] = \frac{\text{A.U. x C.F.}}{\text{W}} \qquad (14)$$

Where: A.U.: area response from chromatograph (A.U.)

C.F.: calibration factor (g/A.U.)

W: sample weight (g)

Table 1: Initial concentration of vanillin and ortho-vanillin in corrugated board

sample	o-vanillin (sample from stack center) ppm (wt/wt)	vanillin (sample from stack center) ppm (wt/wt)	vanillin (sample from stack top) ppm (wt/wt)
1	0.3000	1.0594	0.2838
2	0.1923	0.8587	0.1891
3	0.3131	0.7928	0.3101
4	0.3255	1.1376	0.2348
average	0.2829	0.9591	0.2545
std.dev	±0.061	±0.163	±0.054

Measurements were carried out on four (4) replicate samples. The initial concentration levels of vanillin and ortho-vanillin in the paperboard, which was located in the middle of the board stack, were 0.96 ppm with a standard deviation of ±0.163 and 0.2829 ppm with a standard deviation of ±0.061, respectively. The vanillin concentration for the board at the stack top had a lower value, which was 0.25 ppm with ±0.054 as the standard deviation. The reason for this finding may be that the vanillin molecules, which were in the paperboard placed on the top of the stack, were volatilized into the surrounding air during shipping and storage after production.

6.1.2 Vanillin and ortho-vanillin equilibrium partition distribution between corrugated board and headspace

The partition coefficient $K_{B/H}$ is defined here as the equilibrium concentration of vanillin or ortho-vanillin in the paperboard divided by the equilibrium concentration in the headspace. Partition equilibrium experiments were carried out at three temperatures, namely 23, 38, and 50 °C, to determine the influence of storage temperature on $K_{B/H}$ values.

To determine the time needed to attain a steady state concentration level in the sorption cells, a 500 μl aliquot was withdrawn from the headspace of the sorption cell following 2 days storage, and the sample injected directly into gas chromatograph for quantitation. This process was repeated every two days until the headspace concentration of vanillin and o-vanillin reached a steady state level. A different sorption cell was sampled for both vanillin and ortho-vanillin analysis. The results showed that the system had equilibrated within 7 days period (See Appendix C). To get a material balance, the levels of vanillin and o-vanillin retained by the corrugated board were determined by the thermal stripper/thermal desorption method. All analyses were carried out in duplicate. The partition coefficient ($K_{B/H}$) values were calculated by substitute into Equation (15), and the results are summarized in Table 2. The test conditions for the headspace studies for both vanillin and ortho-vanillin are listed below.

The test conditions for the headspace studies of ortho-vanillin:

Initial ortho-vanillin concentration: 3.4 ppm (wt/wt)
The weight of paperboard which was sealed in every sorption cell: 16.6 grams
The surface area of paperboard sealed in every sorption cell: 270 cm^2
Initial ortho-vanillin content in paperboard: 56.44 μg
Time of storage: 7 days

The test conditions for headspace studies of vanillin:

Initial vanillin concentration:	3.17 ppm (wt/wt)
The weight of paperboard which was sealed in every sorption:	16.6 grams
The surface area of paperboard sealed in every sorption cell:	273 cm^2
Initial vanillin content in paperboard:	53 μg
Time of storage:	7 days

A series of sorption cells were prepared to follow the equilibrium partition distribution, with each cell being sampled only one time. This was done to insure no losses of volatiles through the sampling system. The relationship between the partition coefficient $K_{B/H}$ and temperature is illustrated graphically in Figures 19 and 20. As shown, the equilibrium partition coefficient $K_{B/H}$ decreased with an increase in storage temperature. This is not unexpected, as the solubility of vanillin and o-vanillin in the paperboard was found to decrease with an increase in temperature.

$$K_{B/H} = \frac{[C_B]}{[C_H]} \qquad (15)$$

Where: $[C_B]$: vanillin or o-vanillin concentration in corrugated board at equilibrium (μg/g).

$[C_H]$: vanillin or o-vanillin concentration in headspace at equilibrium (μg/g).

The partition coefficients ($K_{B/H}$) determined for vanillin and ortho-vanillin were 179 and 663 for the corrugated board and headspace, respectively, at 23 °C. The $K_{B/H}$ values were reduced to 48 and 223 for vanillin and ortho-vanillin respectively, when the storage temperature was 50 °C. Thus, at the higher storage temperature, higher levels of volatile are lost from the paperboard. The storage temperature thus affected the partition coefficient significantly in this study.

Table 2: Partition coefficient $K_{B/H}$ between headspace and paperboard for vanillin and ortho-vanillin as a function of temperature.

Vanillin							
	Vanillin in headspace			Vanillin in paperboard			
Temp. °C	conc. ppm (wt/v) (μg/cc) x10^{-3}	content μg	conc. avg & std. x10^{-3}	conc. ppm (wt/wt) (μg/g)	content μg	conc. avg & std.	$K_{H/B}$
23	16.22 17.16	7.18 7.60	16.69 std.0.67	3.10 2.88	51.70 48.03	2.99 std.0.16	179
38	25.79 22.83	11.42 10.12	24.31 std.2.09	2.56 2.22	42.75 37.07	2.39 std.0.24	98
50	42.46 35.34	18.81 15.66	38.90 std.5.04	1.77 1.95	29.59 32.57	1.86 std.0.13	48
ortho-vanillin							
	O-vanillin in headspace			O-vanillin in paperboard			
Temp. °C	conc. (wt/v) (μg/cc) ppm x10^{-3}	content μg	conc. avg & std. x10^{-3}	conc. ppm (wt/wt) (μg/g)	content μg	conc. avg & std.	$K_{H/B}$
23	4.62 6.39	2.05 2.83	5.01 std.1.25	3.23 3.41	53.58 56.64	3.32 std.0.13	663
38	7.89 9.88	3.50 4.37	8.88 std.1.39	2.90 3.38	48.14 56.06	3.14 std.0.337	353
50	14.86 10.24	6.58 4.54	12.55 std.3.27	2.83 2.78	46.91 46.21	2.81 std.0.03	223

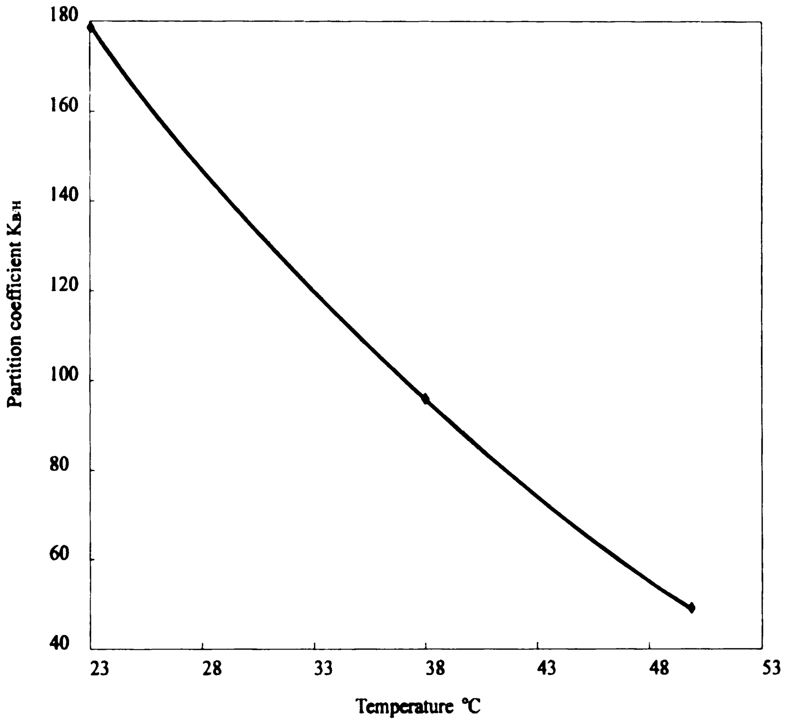


Figure 19: Vanillin partition coefficient $K_{B/H}$ between headspace and paperboard as a function of temperature.

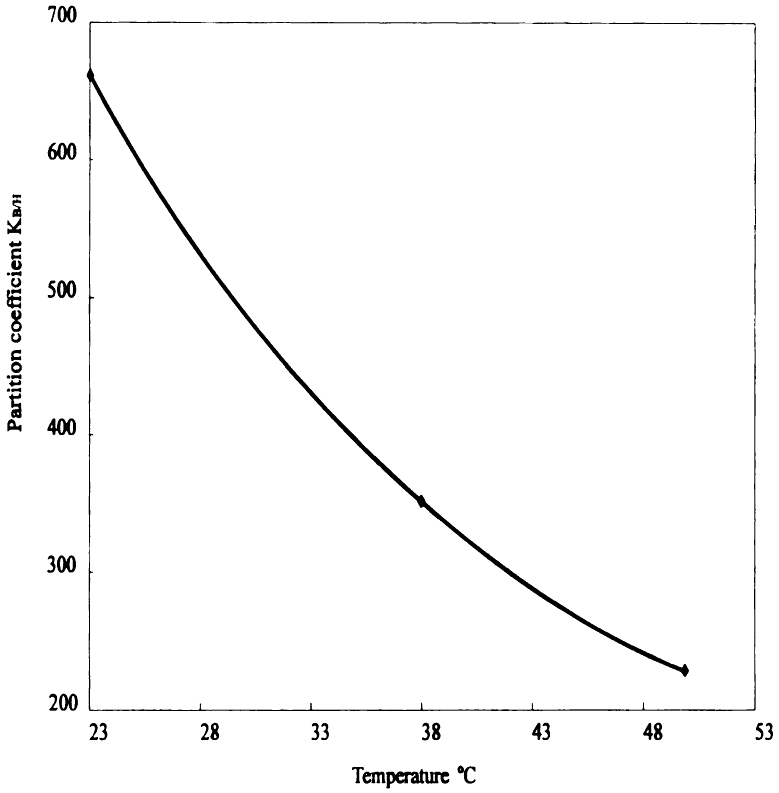


Figure 20: Ortho-vanillin partition coefficient $K_{B/H}$ between headspace and paperboard as a function of temperature

6.2 Stability of vanillin and ortho-vanillin in an aqueous phase

To determine the stability of vanillin and ortho-vanillin in an aqueous phase, standard solutions of known concentration were prepared and transferred into 40 ml screw cap amber glass vials. One set of samples had been degassed prior to filling the test solution and was stored in a nitrogen flushed chamber maintained at ambient temperature (See Figure 17). The other set of samples was simply prepared with non-degassed HPLC grade water and stored at ambient conditions. The aqueous samples were analyzed every 3 days by the HPLC process described in the previous section. A standard solution made of vanillin in acetonitrile was used to monitor the stability of the HPLC procedure. The data for this study is summarized in Table 3, and presented graphically in Figure 21, where the concentration of vanillin and o-vanillin in the respective solutions is plotted as a function of storage time.

As shown in Table 3, the concentration of vanillin in the samples simply prepared with non-degassed HPLC grade water and stored at ambient condition degraded significantly over time and after 9 days storage, the concentration of vanillin tended to zero. This concentration change was found to be the result of vanillin oxidation to yield a more polar product, as evidenced by the detection of an additional peak in the chromatograph prior to the retention time of vanillin.

Table 3: Storage stability of vanillin and ortho-vanillin in aqueous solutions (23 °C)

vanillin concentration change (ppm wt/v)					
storage time	0 days	3 days	6 days	9 days	12 days
non-degassed	1.01	0.95	0.42	0.00	0.00
degassed	1.07	1.07	1.09	--	1.08

ortho-vanillin concentration change (ppm wt/v)			
storage time	0 days	5 days	10 days
degassed	0.46	0.46	0.46

Figure 22 shows that vanillin has a retention time of about 2.46 minutes under the assay conditions employed. Further, the peak at 2.46 minutes decreased gradually as a function of storage time, while at the same time a new peak (retention time of 1.00 min.) appeared in the chromatograph following 3 days storage and this peak at 1 minute continued to increase as a function of storage time. Comparing the retention time of the newly developing peak with that of vanillic acid, showed similar retention time values, indicating that the vanillin was undergoing oxidation under the storage condition selected. Perestelo (1989) reported that vanillin undergoes oxidation to vanillic acid. Therefore, the newly developing peak was assumed to be vanillic acid, the oxidation product of vanillin, (See Figure 23).

From the ortho-vanillin storage stability studies, a comparison of the respective chromatograms showed similar results, as evidenced by the development of a new peak in the chromatograph at a retention time of 0.86 minutes, as compared to a retention time of 3 minutes for the ortho-vanillin sample. This is illustrated in Figure 24, where the chromatograms obtained at time equal 0 and 9 days storage are presented.

For both vanillin and ortho-vanillin solutions prepared by the degassing procedure and stored in the nitrogen environmental chamber, no evidence of oxidation was observed over a 12 day storage period. This indicated that if properly degassed of oxygen, solutions of vanillin and o-vanillin were quite stable. Therefore, all sorption studies carried out to determine the partition distribution of vanillin and o-vanillin between an aqueous phase and LDPE, the solutions were degassed, as described in the Materials and Methods Section, to insure that measured changes in sorbate concentration were due to their uptake by the polymer phase, and not the result of oxidation.

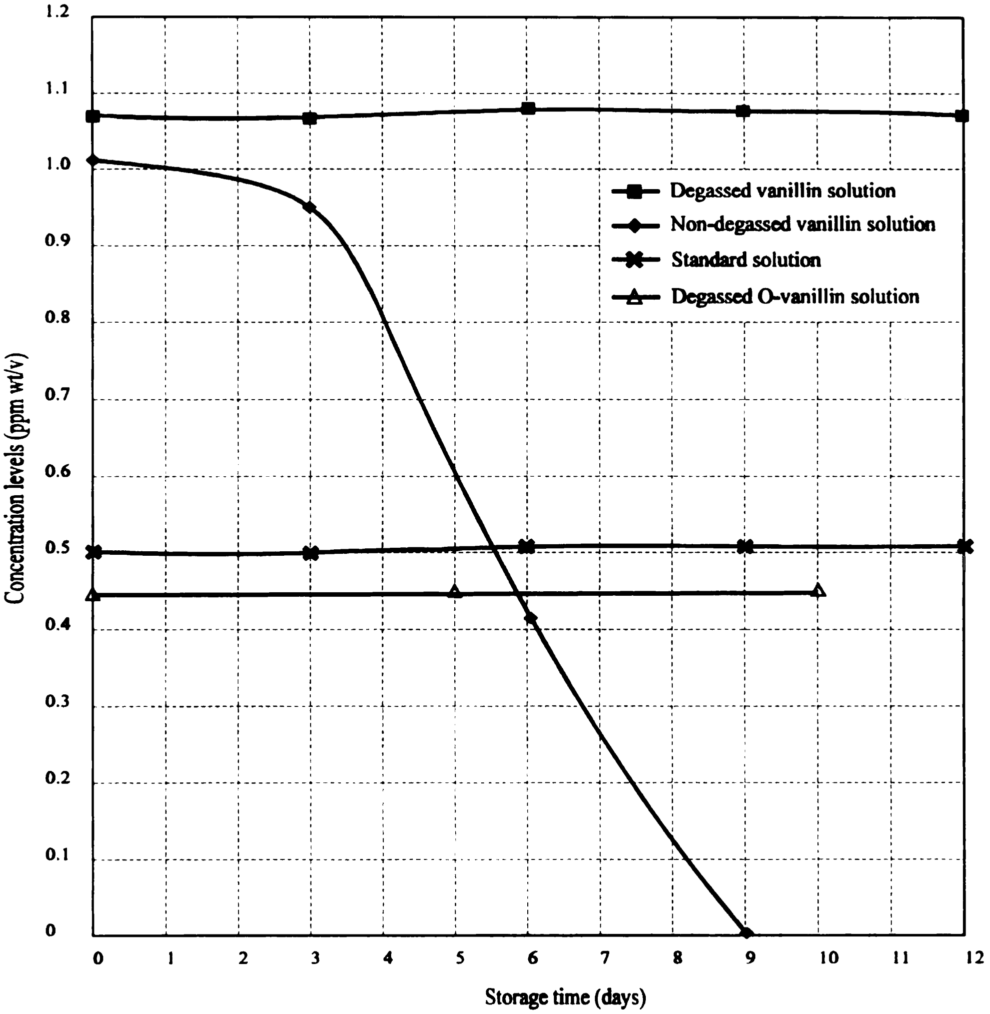


Figure 21: Storage stability of vanillin and ortho-vanillin in aqueous phase (23 °C)

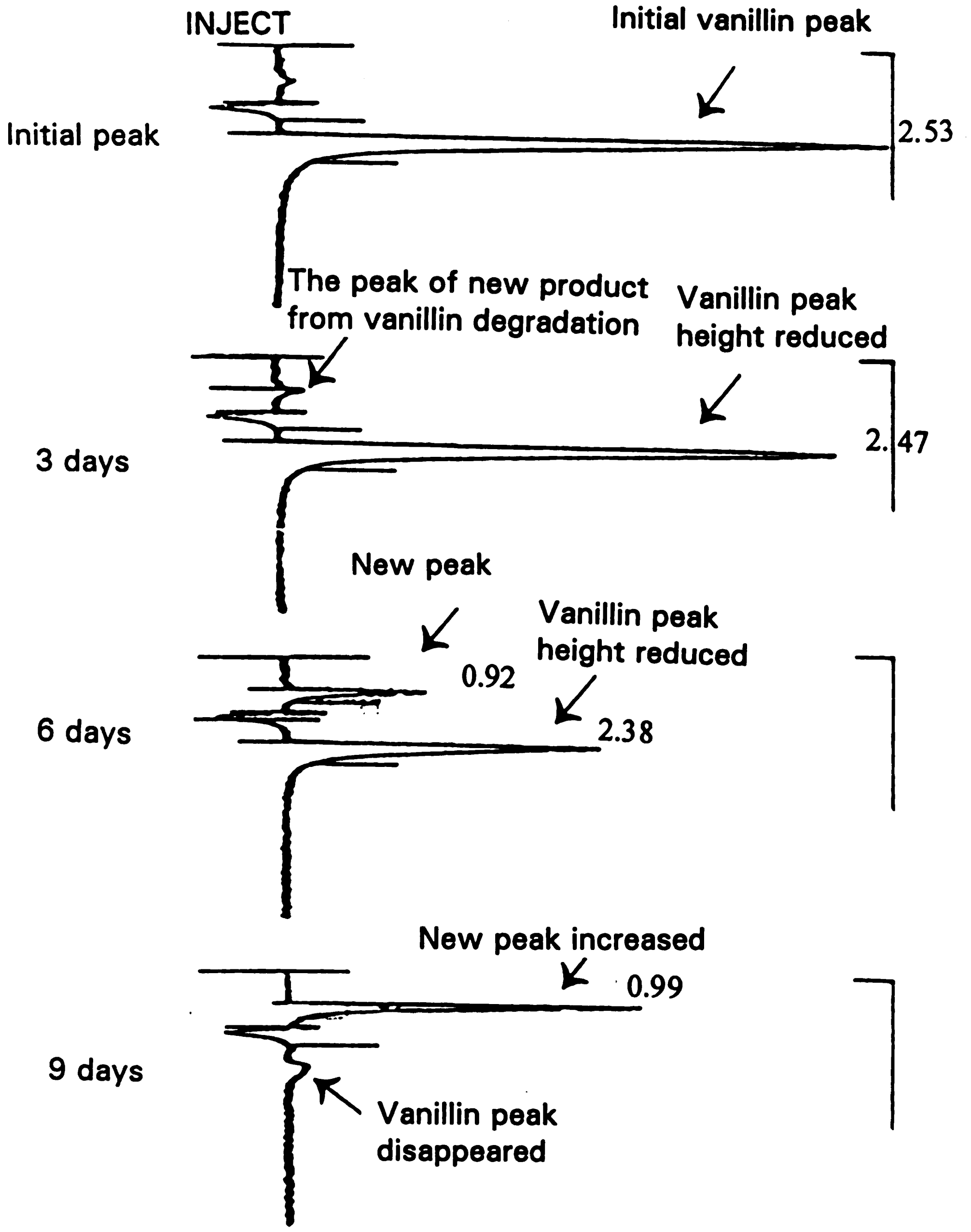


Figure 22

Process of vanillin degradition shown by the chromatography peak change

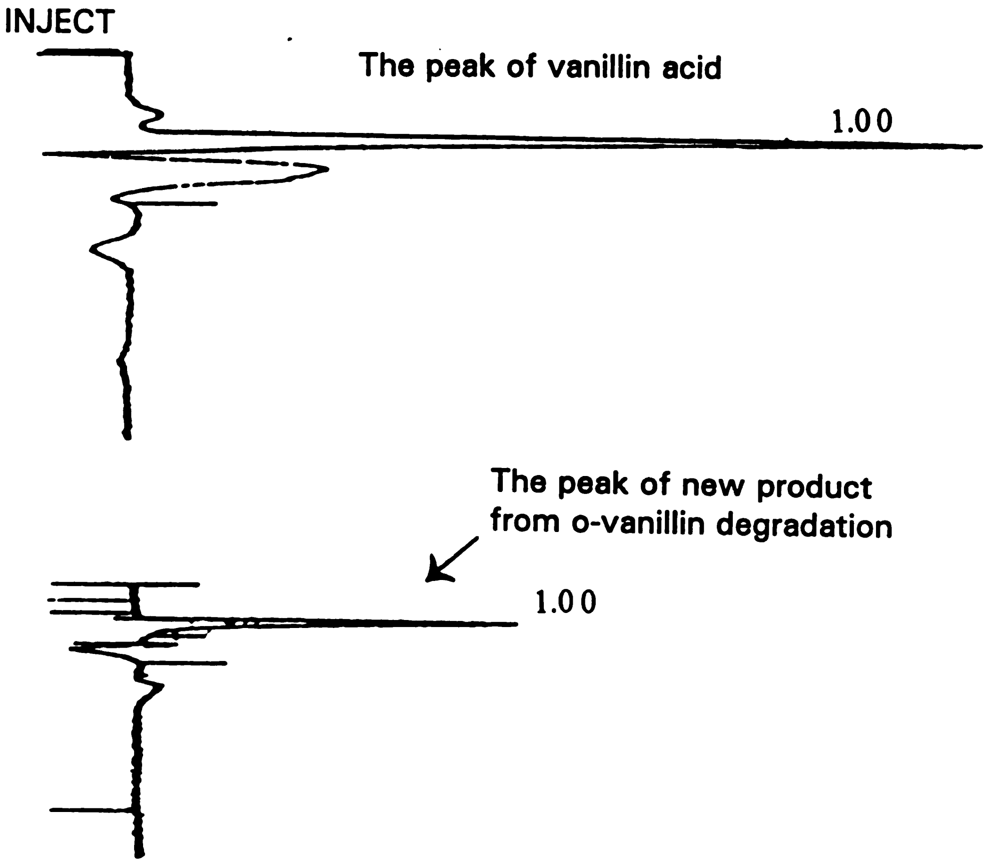


Figure 23 Both vanillin acid peak and the peak from vanillin degradition have the similar retention time.

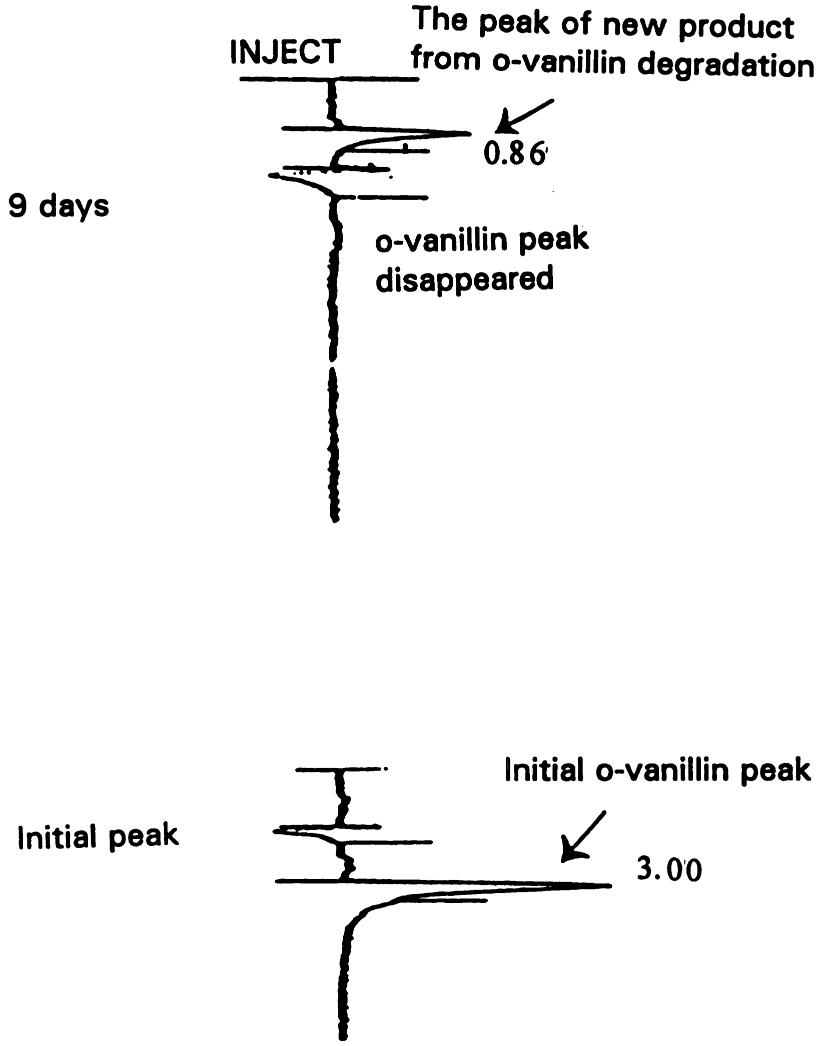


Figure 24 The oxidition of ortho-vanillin yielded a more polar product which has the retention time of 0.86 minute

6.3 The uptake of sorbates by the LDPE as a function of storage time

6.3.1 Determination of partition coefficient values ($K_{P/A}$) and data analysis

In these studies, the uptake of vanillin and o-vanillin from an aqueous phase was determined as a function of storage time to provide equilibrium as well as non-steady state uptake values for both vanillin and ortho-vanillin. Partition distribution studies were carried out at 23 and 32 °C, respectively. There were two replicate samples in these studies and every sample was assayed three times by the HPLC procedure. The samples were analyzed every two days over a 14 days period to determine the non-steady state uptake values, as well as the equilibrium state values. Individual vials were sampled just one time. For one concentration of vanillin or o-vanillin at one storage condition, 42 data points were available for their analysis.

The results of the partition distribution studies for vanillin and ortho-vanillin at 23°C and 32 °C are summarized in Tables 4, 5, 6, and 7, respectively. For better illustration, the results are also presented graphically in Figure 25, 26, 27, and 28, where the sample concentration change in both polymer and aqueous phases are plotted as a function of storage time. The results of the control samples and the vanillin- and o-vanillin solutions (acetonitrile standards) were also plotted as a reference to monitor the stability of the aqueous solutions of vanillin and o-vanillin as a function of time and temperature, and the consistory of the HPLC procedure. Here, the partition coefficient values ($K_{P/A}$) are defined as the concentration of vanillin or ortho-vanillin in the LDPE phase divided by their aqueous phase concentration levels (equation 12).

The results of the sorption studies are presented graphically in Figure 29, where the concentration ratio for both vanillin and ortho-vanillin at the two temperatures of test (i.e. 23°C and 32 °C) were plotted as a function of storage time to equilibrium. The initial concentrations of vanillin and ortho-vanillin in the aqueous phases, which were 0.434 ppm (wt/wt) and 0.520 ppm (wt/wt) respectively, decreased while their concentration in the polymer phase increased until equilibrium concentration levels were attained. These equilibrium concentration levels were then used to determine the respective $K_{P/A}$ values.. The storage times needed to reach steady state levels for vanillin in this polymer / aqueous phase system was four (4) days at 32°C and six (6) days at 23°C. For ortho-vanillin, the system attained equilibrium after six (6) days storage at 23°C and eight (8) days storage at 32°C.

Table 4: The data of partition distribution studies of vanillin at 23°C

storage time (days)	weight of polymer (gram)	avg. conc. in aqueous (ppm w/w)	avg. conc. in polymer (ppm w/w)	$R_{P/A}$*	avg. $R_{P/A}$ and std.
2	0.73	0.42	0.93	2.24	2.8
	0.68	0.41	1.34	3.27	std. 0.5
4	0.73	0.29	6.80	23.23	23.9
	0.59	0.31	7.55	24.63	std. 0.7
6	0.71	0.26	8.17	33.78	34.6
	0.58	0.27	9.68	34.47	std. 0.8
8	0.64	0.26	9.70	37.65	35.0
	0.63	0.27	8.87	32.35	std. 2.7
10	0.66	0.28	8.15	29.07	31.0
	0.60	0.28	9.16	33.00	std. 2.0
12	0.56	0.28	9.80	35.41	32.7
	0.63	0.28	8.43	29.90	std. 2.8
14	0.65	0.27	8.17	31.94	30.3
	0.69	0.28	7.94	28.60	std. 1.7

$R_{P/A}$: Concentration Ratio, defined as sorbate concentration in the polymer phase divided by the aqueous phase concentration at time t.

Table 5: The data of partition distribution studies of vanillin at 32°C

storage time (days)	weight of polymer (gram)	avg. conc. in aqueous (ppm w/w)	avg. conc. in polymer (ppm w/w)	$R_{P/A}$*	avg. $R_{P/A}$ and std.
2	0.54	0.42	0.94	2.24	2.9
	0.63	0.41	1.46	3.58	std. 0.7
4	0.64	0.33	5.74	17.37	16.8
	0.66	0.33	5.37	16.13	std. 0.6
6	0.67	0.32	5.76	17.80	17.8
	0.69	0.32	5.72	17.78	std. 0.0
8	0.66	0.31	6.46	20.62	19.4
	0.65	0.32	5.92	18.20	std. 1.2
10	0.64	0.32	5.98	18.42	17.9
	0.70	0.32	5.61	17.41	std. 0.5
12	0.68	0.32	5.97	18.71	20.0
	0.60	0.32	6.78	21.30	std. 1.3
14	0.67	0.33	5.70	17.50	18.43
	0.64	0.32	6.22	19.35	std. 0.9

$R_{P/A}$: Concentration Ratio, defined as sorbate concentration in the polymer phase divided by the aqueous phase concentration at time t.

Table 6: The data of partition distribution studies of ortho-vanillin at 23°C

storage time (days)	weight of polymer (gram)	avg. conc. in aqueous (ppm w/w)	avg. conc. in polymer (ppm w/w)	$R_{P/A}$*	avg. $R_{P/A}$ and std.
2	0.75	0.47	2.48	5.30	4.8
	0.70	0.48	2.09	4.36	std. 0.5
4	0.66	0.39	7.18	18.63	19.2
	0.58	0.39	7.76	19.77	std. 0.6
6	0.67	0.35	8.76	24.83	25.1
	0.67	0.35	8.88	25.37	std. 0.3
8	0.61	0.28	13.55	47.89	47.1
	0.58	0.29	13.59	46.21	std. 0.8
10	0.74	0.25	13.03	52.83	51.1
	0.61	0.28	13.86	49.30	std. 2.0
12	0.64	0.27	14.00	52.69	50.1
	0.56	0.30	13.99	47.43	std. 2.7
14	0.61	0.28	13.53	47.60	45.8
	0.63	0.29	12.73	43.91	std. 1.8

$R_{P/A}$: Concentration Ratio, defined as sorbate concentration in the polymer phase divided by the aqueous phase concentration at time t.

Table 7: The data of partition distribution studies of ortho-vanillin at 32°C

storage time (days)	weight of polymer (gram)	avg. conc. in aqueous (ppm w/w)	avg. conc. in polymer (ppm w/w)	$R_{P/A}$*	avg. $R_{P/A}$ and std.
2	0.67	0.49	1.55	3.15	3.1
	0.62	0.49	1.51	3.07	std. 0.1
4	0.67	0.42	5.44	13.03	11.1
	0.58	0.45	4.15	9.20	std. 0.7
6	0.62	0.36	9.30	26.06	26.3
	0.56	0.37	9.72	26.55	std. 0.3
8	0.60	0.35	9.79	27.68	26.0
	0.69	0.35	8.56	24.30	std. 1.7
10	0.60	0.35	9.68	27.35	26.7
	0.68	0.35	8.93	25.82	std. 0.8
12	0.70	0.33	9.55	29.05	31.8
	0.59	0.33	11.40	34.62	std. 2.8
14	0.60	0.34	10.38	30.27	29.0
	0.62	0.35	9.70	27.76	std. 1.3

$R_{P/A}$: Concentration Ratio, defined as sorbate concentration in the polymer phase divided by the aqueous phase concentration at time t.

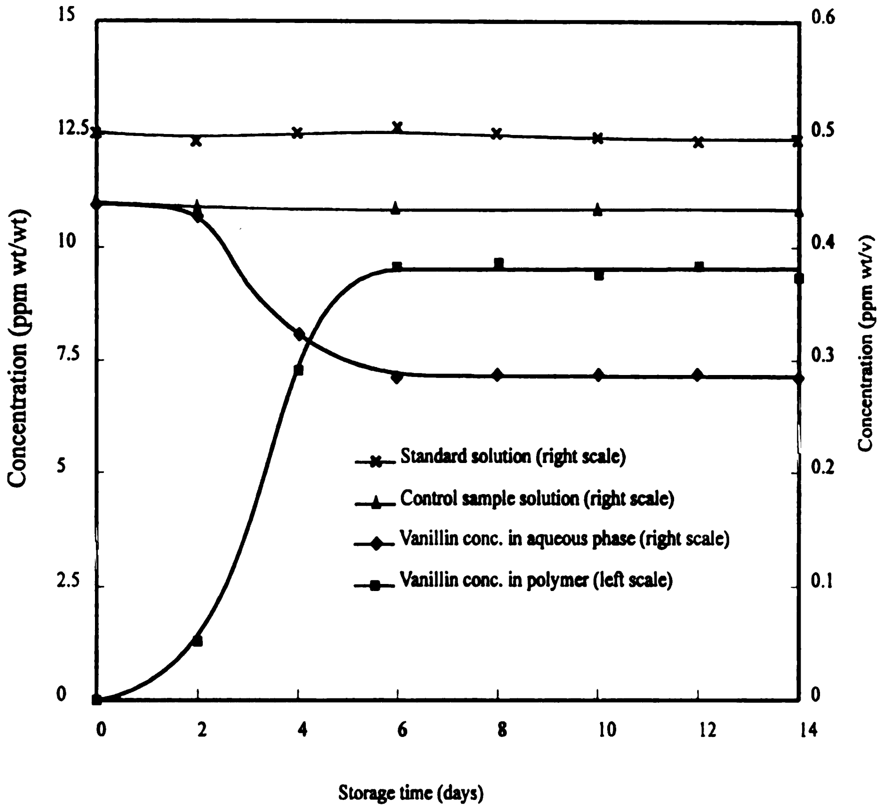


Figure 25: The sample concentration change in both polymer and aqueous phase as a function of time, including control sample and standard solution.

vanillin at 23°C

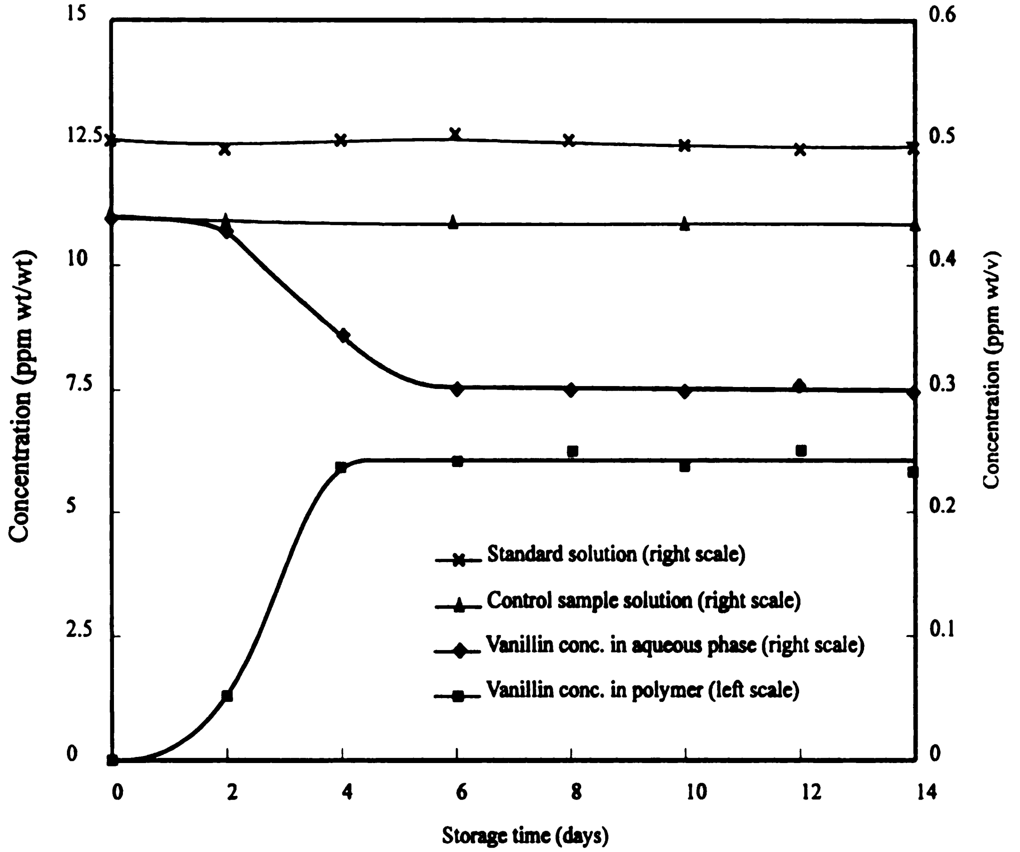


Figure 26: The sample concentration change in both polymer and aqueous phase as a function of time, including control sample and standard solution.

vanillin at 32°C

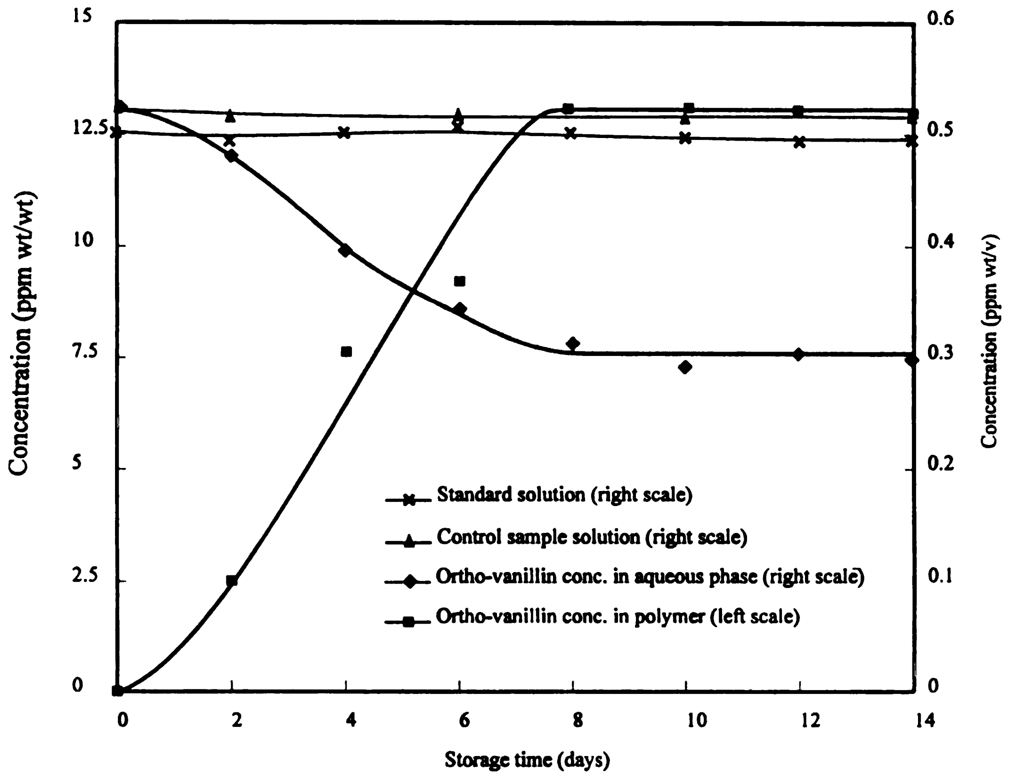


Figure 27: The sample concentration change in both polymer and aqueous phase as a function of time, including control sample and standard solution. ortho-vanillin at 23 °C

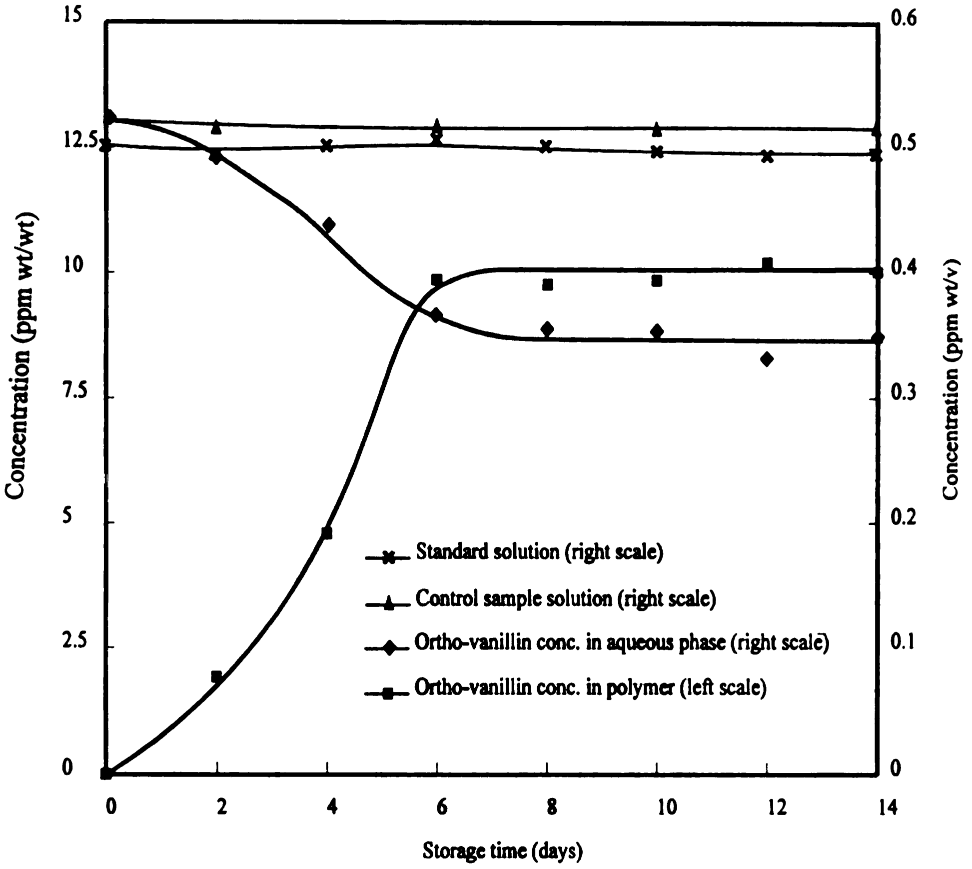


Figure 28: The sample concentration change in both polymer and aqueous phase as a function of time, including control sample and standard solution.

ortho-vanillin at 32 °C

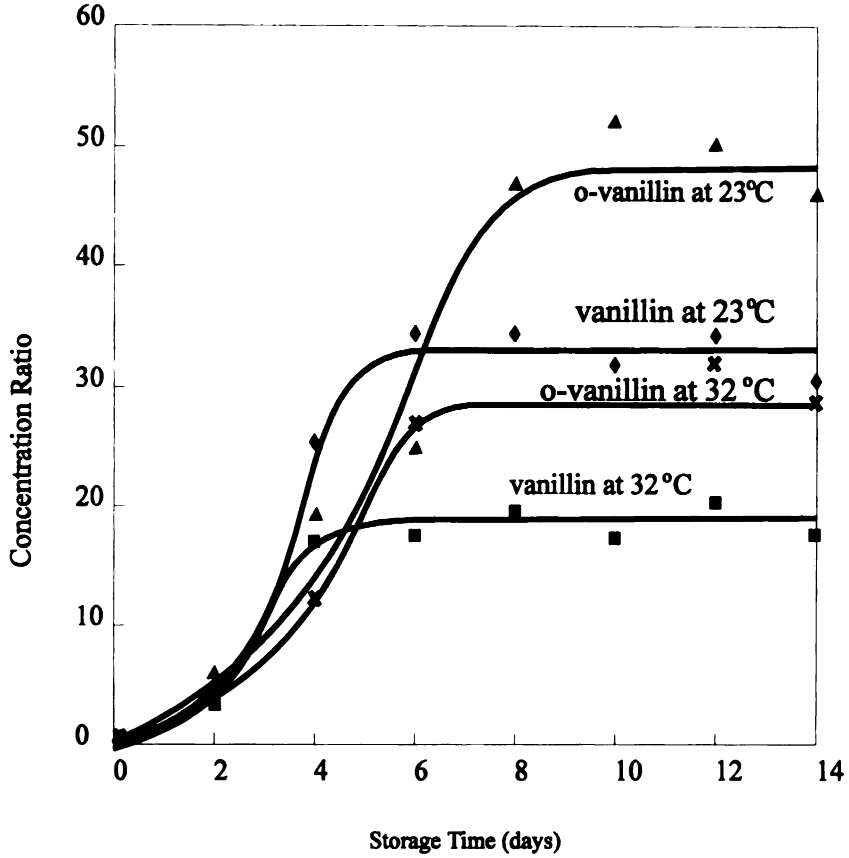


Figure 29: The concentration ratio for both vanillin and ortho-vanillin at different temperature vs. storage time.

6.3.2 Estimation of diffusion coefficient (D) of vanillin and ortho-vanillin in low density polyethylene

For the aqueous phase/LDPE system, sorbate equilibrium is shown experimentally when the liquid phase sorbate concentration remains constant after a given contacting time, such as the case for determination of the equilibrium partition coefficient values ($K_{A/P}$) in the present studies. In Figures 30 to 33, the fraction or percent of equilibrium reached is plotted as a function of contact time and indicates that the phase equilibrium was reached after 6 - 8 days, as shown by the vanillin and ortho-vanillin concentration levels in the aqueous phase remaining constant after this contact period (See Table 8).

In most cases, the diffusion coefficient of a sorbate in the polymer determines the kinetics of the process and , therefore, the time to reach equilibrium. According to Crank (1975), the dynamics of the sorption process can be described by:

$$\frac{M_t}{M_\infty} = \sum_{n-1}^{\infty} \frac{2\alpha(\alpha+1)}{1+\alpha+(\alpha q_n)^2} \exp.\left(\frac{-Dq_n^2 t}{l^2}\right) \qquad (14)$$

where, M_t/M_∞: the fraction of equilibrium reached at time t

α: the ratio of volumes of polymer film and solution divided by partition coefficient

D: the diffusion coefficient of sorbate in LDPE

l: the half thickness of the polymer film

q_n: non-zero positive roots of tan $q_n = -\alpha q_n$

In this study, the fraction of equilibrium reached at time t was determined from the experimental data. The results are summarized in Table 8 and presented graphically in Figure 30 to 33. The time needed to reach a certain value of the fraction of equilibrium was obtained directly from Figures 30 to 33, for vanillin and o-vanillin in the aqueous phase/LDPE system at 23 and 32°C storage conditions, respectively. Diffusion coefficient values for vanillin and o-vanillin in LDPE were calculated for equilibrium fraction values of 0.6, 0.7, and 0.8 respectively by solution of Equation 14. The results are presented in Table 9.

The values in Table 9 were calculated from Equation 14 with enough terms to produce an accuracy of > 99% using values of $K_{A/P}$ and $Mt/M\infty$ determined in the present study. The average diffusion coefficients values (D) determined at 60%, 70%, and 80% of equilibrium for vanillin at 23°C and 32°C were 4.4×10^{-16} m^2/sec, 5.4×10^{-16} m^2/sec, respectively, while the average diffusion coefficient values for o-vanillin were 2.5×10^{-16} m^2/sec and 2.9×10^{-16} m^2/sec, respectively. Both vanillin and ortho-vanillin had lower diffusion coefficients values at 23°C storage temperature, as compared with the diffusion coefficient values at 32°C storage temperature.. The effect of temperature is not unexpected, since temperature plays an important role in the equilibrium partition process. The higher the temperature, the larger the expected diffusion coefficient (Crank, 1975).

Table 8: Mt/M∞ vs storage time of vanillin and ortho-vanillin

storage time (days)	Mt/M∞ of vanillin at 23°C	Mt/M∞ of vanillin at 32°C	Mt/M∞ of ortho-vanillin at 23°C	Mt/M∞ of ortho-vanillin at 32°C
2	0.129	0.197	0.169	0.157
4	0.817	0.914	0.552	0.492
6	1.017	0.944	0.651	0.975
8	1.057	1.018	1.002	0.941
10	0.986	0.953	0.993	0.954
12	1.038	1.049	1.034	1.074
14	0.917	0.980	0.969	1.030

Table 9: The diffusion coefficient (D) values determined to reach Mt/M∞= 0.6, Mt/M∞=0.7, and Mt/M∞=0.8, according to Eq.14

	Vanillin			Ortho-vanillin		
Temp. °C	Mt/M∞	time (day)	Diffusion coef. (m^2/s)	Mt/M∞	time (day)	Diffusion coef. (m^2/s)
23	0.6	3.2	7.1×10^{-16}	0.6	4.5	4.5×10^{-16}
	0.7	3.3	4.0×10^{-16}	0.7	5.1	2.1×10^{-16}
	0.8	3.4	2.0×10^{-16}	0.8	5.7	1.0×10^{-16}
		avg.	***4.4×10^{-16}***		avg.	***2.5×10^{-16}***
		std.	2.1×10^{-16}		std.	1.5×10^{-16}
32	0.6	3.1	8.6×10^{-16}	0.6	4.2	4.6×10^{-16}
	0.7	3.2	5.1×10^{-16}	0.7	4.6	2.9×10^{-16}
	0.8	3.3	2.6×10^{-16}	0.8	4.8	1.2×10^{-16}
		avg.	***5.4×10^{-16}***		avg.	***2.9×10^{-16}***
		std.	2.5×10^{-16}		std.	1.4×10^{-16}

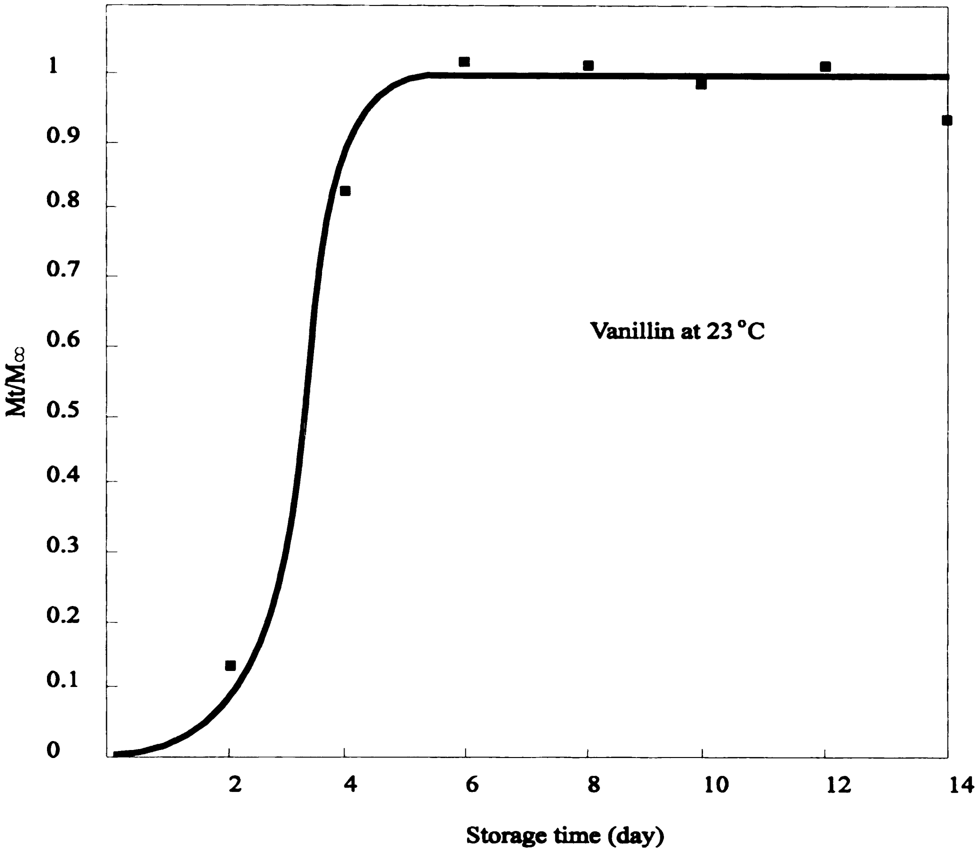


Figure 30: The Mt/M∞ vs. time for sorption of vanillin by LDPE at 23°C

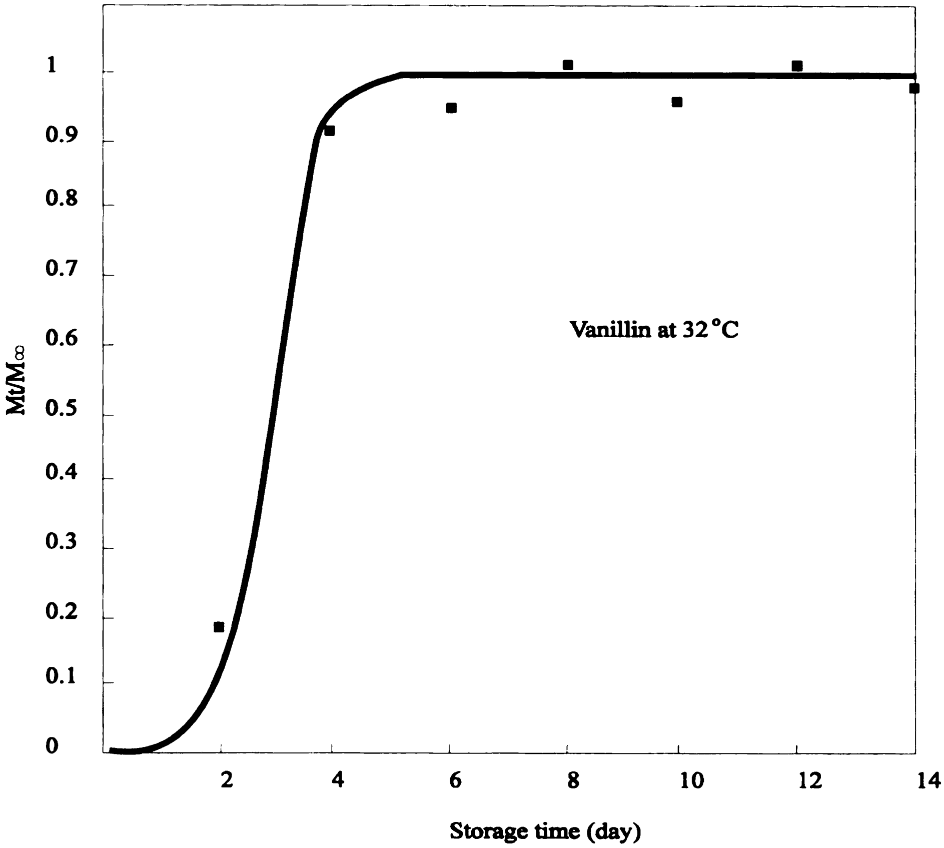


Figure 31: The Mt/M∞ vs. time for sorption of vanillin by LDPE at 32°C

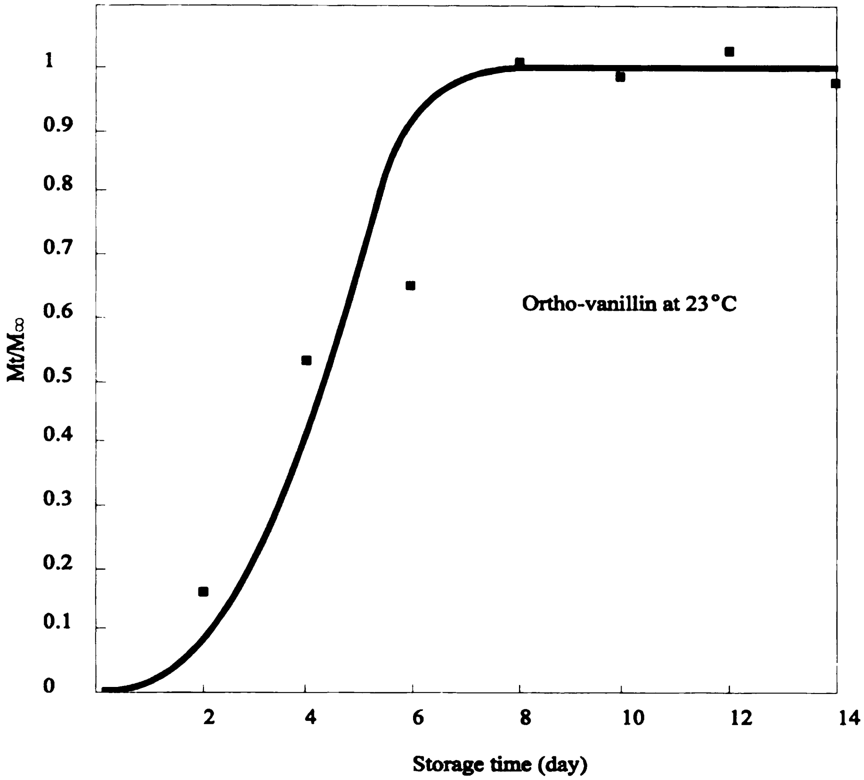


Figure 32: The Mt/M∞ vs. time for sorption of ortho-vanillin by LDPE at 23°C

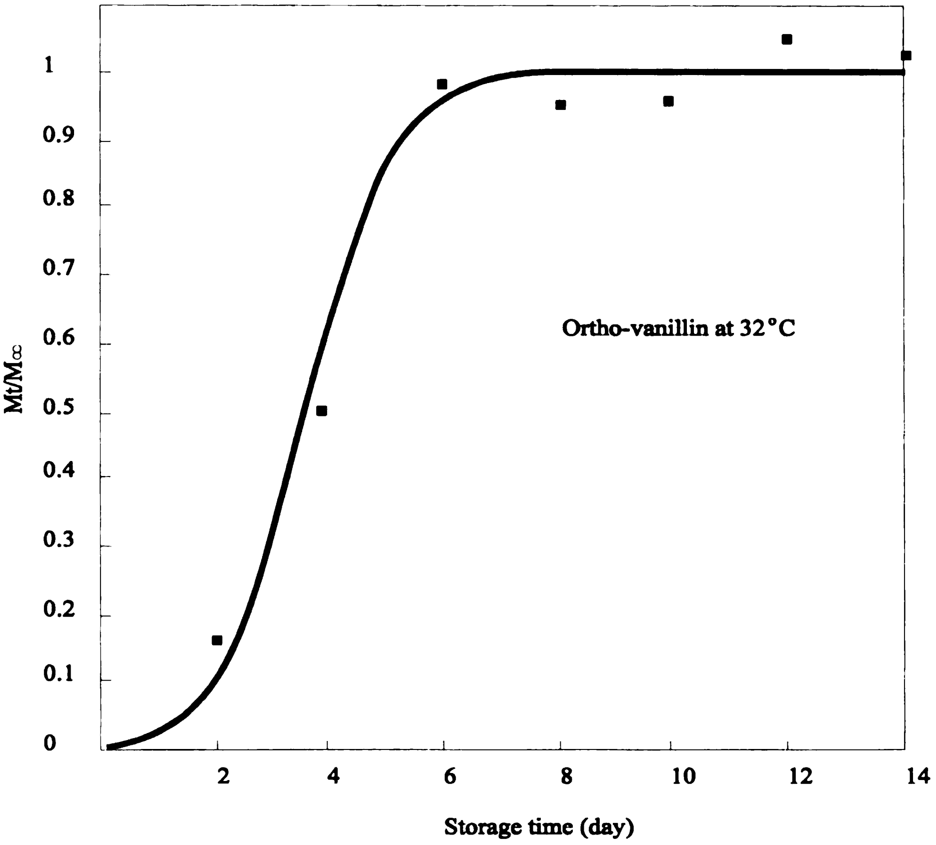


Figure 33: The Mt/M∞ vs. time for sorption of ortho-vanillin by LDPE at 32°C

6.3.3 The solubility parameter (δ) of vanillin and ortho-vanillin in LDPE

Hoy's method was employed to determine solubility parameter values, δ, in this study. The equations to be used in Hoy's system for estimation of the solubility parameter and its components are given as follows (van Krevelen, 1990):

For low-molecular Liquids (Solvents):

$$\delta_d = \frac{F_d + B}{V} \qquad (B = 277) \qquad (15)$$

$$\delta_p = \delta_d \left(\frac{1}{\alpha} \frac{F_p}{F_d + B} \right)^{½} \qquad (16)$$

$$\delta_h = \delta_d \left(\frac{\alpha - 1}{\alpha} \right)^{½} \qquad (17)$$

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{½} \qquad (18)$$

$$\log \alpha = 3.39\,(0.567 + \Delta_T - \Delta_T^2) - 0.1585 - \log V \qquad (19)$$

For amorphous Polymers:

$$\delta_d = \frac{F_d + B/\tilde{n}}{V} \qquad (B = 277) \qquad (20)$$

$$\delta_p = \delta_d \left(\frac{1}{\alpha^{(P)}} \frac{F_p}{F_d + B/\tilde{n}} \right)^{½} \qquad (21)$$

$$\delta_h = \delta_t \left(\frac{\alpha^{(P)} - 1}{\alpha^{(P)}} \right)^{½} \qquad (22)$$

$$\delta = (\delta_t^2 + \delta_p^2 + \delta_h^2)^{1/2} \qquad (23)$$

$$\alpha^{(P)} = 777\ \Delta_T^{(p)} / V \qquad (24)$$

$$\tilde{n} = 0.5 / \Delta_T^{(p)} \qquad (25)$$

F_d is the molar attraction function, F_p is its polar component: V is the molar volume of the solvent molecule or the structural unit of the polymer. $\alpha^{(P)}$ can be derived for Δ_t, which is the Lyderson correction for non-ideality, used in the auxiliary equations. α is the molecular aggregation number and ñ is the number of repeating units per effective chain segment of the polymer. B is a constant base value. All the values of F_t, F_p, V, Δ_t, and $\Delta_T^{(p)}$ for the monomer unit of a group of polymers or solvents were given by van Krevelen (1990). A computer program was created by Fayoux (1997) to calculate the solubility parameters for organic volatiles and polymers. The program was employed to calculate the solubility parameters for water, LDPE, and the sorbates vanillin and o-vanillin, which were evaluated in the present study. The results are summarized in Table 10:

Table 10: The solubility parameter $(J/cm^3)^{1/2}$ of water, LDPE, vanillin, and o-vanillin

	water	LDPE	vanillin	o-vanillin
δ_d	48.1	17.57	16.44	15.94
δ_p	14.3	0	13.68	13.66
δ_h	31.3	0	15.43	15.14
δ	34.4	17.57	26.38	25.88

The solubility parameters (δ) for vanillin and o-vanillin are 26.38 and 25.88 $(J/cm^3)^{1/2}$, respectively. Water and LDPE have solubility parameter values of 34.34 $(J/cm^3)^{1/2}$ and 17.57 $(J/cm^3)^{1/2}$, respectively. According to solubility theory developed by Hildenbrand (Van Krevelen, 1990), the enthalpy of mixing is given by:

$$\Delta H_m = \phi_1 \phi_2 (\delta_1 - \delta_2) \qquad (26)$$

Where: ΔH_m: enthalpy of mixing per unit volume

ϕ_1 and ϕ_2: volume fraction of components

δ_1 and δ_2: solubility parameters of the components

Equation (26) predicts that $\Delta H_m = 0$, if $\delta_1 = \delta_2$, so that two substances with equivalent solubility parameters should be mutually soluble or, substances with similar chemical structures should be quite likely to dissolve in each other (Van Krevelen, 1990). Equation 27 provides an estimation of the solubility or compatibility of a sorbate molecules in a polymer, when dispersion, polar, and hydrogen bonding contributions are considered (van Krevelen, 1990).

$$\Delta\delta = [(\delta_{d.p} - \delta_{d.s})^2 + (\delta_{p.p} - \delta_{p.s})^2 + (\delta_{H.p} - \delta_{H.s})^2]^{1/2} \quad (27)$$

For high compatibility or solubility of a sorbate molecule in a polymer matrix, $\Delta\delta$ should be less than 5. The $\Delta\delta$ values for the respective LDPE/vanillin or ortho-vanillin in water systems were calculated by substitution of the parameters summarized in Table 10 into Equation 27, and the results summarized in Table 11. As shown, the $\Delta\delta$ value between LDPE and vanillin or ortho-vanillin is about 20 $(J/cm^3)^{1/2}$, and between water and vanillin or ortho-vanillin is 35 - 36 $(J/cm^3)^{1/2}$.

Table 11: The solubility parameter $(J/cm^3)^{1/2}$ difference between water, LDPE, vanillin, and o-vanillin

	water/vanillin	water/o-vanillin	LDPE/vanillin	LDPE/o-vanillin
$\Delta\delta$	35	36	20	20

Since the $\Delta\delta$ for the respective sorbate/polymer, sorbate/aqueous phase system are greater than 5, it is difficult to draw a conclusion regarding the relative affinity or partitive distribution of vanillin and o-vanillin between LDPE and aqueous phase, respectively.

6.3.4 Modeling the equilibrium distribution of vanillin or ortho-vanillin in a paperboard/headspace/LDPE/an aqueous phase system

Paperboard may contain organic molecules, such as vanillin and ortho-vanillin volatiles, ink constituents from printing, and other residual organic compounds from the production process, such as the toxic dioxin (Foulke, 1990). Figure 34 shows a typical storage and transportation environment for a shipper/polymer packaging system. Based on the following assumptions: (1) the aqueous phase does not react with the volatiles, (2) the initial concentration of the volatile in the system is initially present only in the paperboard, and (3) volatilization of vanillin or ortho-vanillin from corrugated board to headspace is inward, expressions to allow estimation of the equilibrium concentration of volatiles in the paperboard, shipper headspace, polyethylene ampule, as well as the aqueous phase were derived by Maekawa (1994) according to Cramer's rule (Kreyszig, 1979). The derived expressions are summarized below:

$$C_{eB} = \frac{W_B \cdot C_{iB}}{W_B + \frac{V_H}{K_{B/H}} + \frac{S \cdot \beta \cdot V_L}{K_{B/H}} + \frac{S \cdot \beta \cdot V_L}{K_{B/H} \cdot K_{P/A}}} \qquad (28)$$

$$C_{eB} = \frac{W_B \cdot C_{iB}}{W_B \cdot K_{B/H} + V_H + S \cdot \beta \cdot V_L + \frac{S \cdot \beta \cdot V_A}{K_{P/A}}} \qquad (29)$$

$$C_{eB} = \frac{W_B \cdot C_{iB}}{V_L + \frac{W_B \cdot K_{B/H}}{S \cdot \beta} + \frac{V_H}{S \cdot \beta} + \frac{V_A}{K_{P/A}}} \qquad (30)$$

$$C_{eB} = \frac{W_B \cdot C_{iB}}{V_A + V_L \cdot K_{L/A} + \frac{K_{B/H} \cdot K_{P/A} \cdot W_B}{S \cdot \beta} + \frac{K_{P/A} \cdot V_L}{S \cdot \beta}} \qquad (30)$$

where:

$$\beta = \frac{R \cdot T}{M}$$

C_{iB}: initial concentration of volatile in the shipper paperboard.

C_{eB}, C_{eH}, C_{eL}, C_{eA}: equilibrium concentration of volatile in the paperboard (μg/g), in the shipper headspace (μg/cc), in the LDPE container (μg/g), and in the aqueous phase (μg/cc), respectively.

W_B, V_H, V_L, V_A: weight or volume of the paperboard, of the shipper headspace, of the LDPE container, and of the aqueous phase, respectively (g, cc).

S: solubility coefficient between sorbate vapor and LDPE.

$K_{B/H}$: partition coefficient between paperboard and headspace.

$K_{P/A}$: partition coefficient between LDPE and aqueous phase.

In this study, values for C_{iB}, $K_{B/H}$, $K_{P/A}$, for vanillin and ortho-vanillin were determined as a function of temperature. Maekawa (1994) reported the solubility coefficient of vanillin in LDPE was 0.3 (kg/m^3Pa) at 23 °C and 0.23 (kg/m^3Pa) at 32 °C, and for ortho-vanillin, the solubility coefficient was 11.8 (kg/m^3Pa) at 23 °C, respectively. The parameters for vanillin and ortho-vanillin in the present study are as follows:

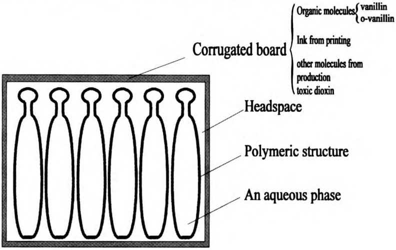
vanillin C_{iB}: 0.96 ppm (wt/wt)
$K_{B/H}$: 179 at 23 °C and 125 at 32 °C
$K_{P/A}$: 33 at 23 °C and 19 at 32 °C
o-vanillin C_{iB}: 0.28 ppm (wt/wt)
$K_{B/H}$: 663 at 23 °C and 450 at 32 °C
$K_{P/A}$: 48 at 23 °C and 28 at 32 °C

For a designed packaging system shown in Figure 34, that was provided by Dey laboratories, Inc (Napa, CA) with weight of the paperboard, W_B = 90.3g, a volume of the headspace V_H = 1797 cc. In this case, the corrugated shipper was unitized to 120, 5 cc LDPE ampules to give a total volume of LDPE V_L = 200 cc, and aqueous phase V_A = 600 cc, respectively. The equilibrium concentrations of vanillin and ortho-vanillin in the packaging system was determined by substitution of the parameters above into Equations 28 to 30. The results are summarized in Table 12. For vanillin in a paperboard/LDPE/aqueous phase packaging system, the higher the storage temperature, the greater the possibility of organic molecules migrating from the paperboard to an aqueous phase product.

Table 12: Prediction of equilibrium concentration in the paperboard and in an aqueous phase.

	vanillin 23°C,	vanillin 32°C	o-vanillin 23°C
CeB	0.82 (μg/g)	0.77 (μg/g)	0.17 (μg/g)
CeH	4.56×10^{-3}(μg/cc)	6.24×10^{-3}(μg/cc)	2.25×10^{-4}(μg/cc)
CeL	2.20×10^{-2}(μg/g)	2.40×10^{-2}(μg/g)	4.59×10^{-2}(μg/g)
CeA	6.70×10^{-4}(μg/cc)	14.33×10^{-4}(μg/cc)	1.42×10^{-3}(μg/cc)

* Corrugated board/Headspace/LDPE packaging system



* Storage stacks

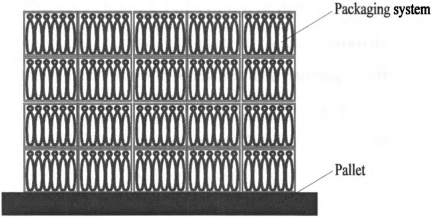


Figure 34: Typical storage and transportation environment of a shipper/polymer packaging system.

SUMMARY AND CONCLUSIONS

The partition coefficients, K values, of vanillin and ortho-vanillin between corrugated board and headspace, and between low density polyethylene (LDPE) and aqueous phase were investigated. The diffusion coefficients (D) and solubility parameter of vanillin and ortho-vanillin in LDPE were studied as well.

1) The partition coefficient, K values, for vanillin and o-vanillin between corrugated board and headspace study was carried out with sorption cells and the concentrations of vanillin or ortho-vanillin in headspace and in corrugated board were determined by a gas chromatograph and thermal stripper/thermal desorption procedure. The partition coefficients, K values, of vanillin were 179 (μg/g / μg/v) at 23°C, 98 (μg/g / μg/v) at 38°C, and 48 (μg/g / μg/v) at 50°C, respectively. The K values of ortho-vanillin were 663 (μg/g / μg/v) at 23°C, 353 (μg/g / μg/v) at 38°C, and 223 (μg/g / μg/v) at 50°C, respectively. The K value that defined as the equilibrium concentration in the paperboard over the equilibrium concentration in the headspace decreaseed for both vanillin and ortho-vanillin while the storage temperature increased. The higher temperature the storage condition was, the more volatile the paperboard lost which means that the more volatile went into headspace.

2) The partition coefficients, K values, between low density polyethylene and contacting aqueous phase were determined by a HPLC

procedure. Data showed that the steady state could be reached after 6 days storage time for vanillin and 8 days storage time for ortho-vanillin in the designed sorption cells. The storage temperature affected the result significantly during the absorption process. The K values were approximately twice as bigger at 23°C compared with 32°C for both vanillin and ortho-vanillin, which were 32.72 (μg/g / μg/v) at 23°C compared with 18.71 at 32°C (μg/g / μg/v) for vanillin and 48.49 (μg/g / μg/v) at 23°C compared with 28.36 at 32°C (μg/g / μg/v) for ortho-vanillin.

3) The diffusion coefficients (D) of vanillin and ortho-vanillin in LDPE were determined according to Crank's method (1976). They are 2.0×10^{-13} cm^2/sec at 23°C and 3.9×10^{-13} cm^2/sec at 32°C for vanillin; and 6.0×10^{-14} cm^2/sec at 23°C and 1.5×10^{-13} cm^2/sec at 32°C for ortho-vanillin. The diffusion coefficients tend to be bigger when the temperature increase. Therefore, the time needed to reach the equilibrium state during the experiment was shorter if the samples stored in the higher temperature condition. The storage times needed to reach equilibrium state for vanillin in this polymer / aqueous phase system was four (4) days at 32°C and six (6) days at 23°C. For ortho-vanillin, six (6) days needed at 23°C and eight (8) days needed at 32°C.

4) Hoy's method (1976) was employed to determine the solubility parameter, δ, in this study. The results show that water has the solubility parameter of 34.4 $(J/cm^3)^{1/2}$, LDPE 17.57 $(J/cm^3)^{1/2}$, vanillin 26.38 $(J/cm^3)^{1/2}$, and ortho-vanillin 25.88 $(J/cm^3)^{1/2}$. According to solubility theory developed by Hildenbrand, two substances with equivalent solubility parameters should by mutually soluable or, be quite likely to dissolve in each other. The solubility parameter difference between LDPE and vanillin is 8.81 $(J/cm^3)^{1/2}$, between

LDPE and ortho-vanillin is 8.31 $(J/cm^3)^{1/2}$. Therefore, the LDPE and ortho-vanillin system is more equivalent than that of LDPE and vanillin system. That explained that the K values of ortho-vanillin is larger than that of vanillin at the same storage temperature.

APPENDICES

APPENDIX A

APPENDIX A

Calibration factors for gas chromatography

Gas chromatography analysis required construction of two kinds of calibration curves based on sample handling, standard calibration curves and thermal stripper/thermal desorption (TS/TD) procedure calibration curves. The vanillin and ortho-vanillin standard solutions were made by a serial dilution technique to give the known concentration in acetonitrile. The condition of gas chromatography was as follows:

The condition of gas chromatography:

Type:	HP 5890A, Hewlett Packard, Avondale, PA.		
Column:	Fused silica capillary column (30m x 0.32 mm ID) intermediate polarity stationary phase SPB-5 (Supelco Co., Bellefronte, PA)		
Injector:	5 µl liquid syringe, 500 µl gas tight syringe (Hamilton)		
Flow rate:	Helium	7.0	ml/min.
	Air	400	ml/min.
	Hydrogen	40	ml/min.
	Nitrogen	30	ml/min.
Temp:	Initial	60	°C
	Final	200	°C
	Rate	7.5	°C/min.

The conditions of DT/ST system:

Type: Model 1000, Dynatherm Analytical Instruments Inc., Kelton, PA.

Dynamic thermal stripper:

Temperature:	oven	80	°C
	block	105	°C
	sorption tubes	50	°C
Purging time:		46	min

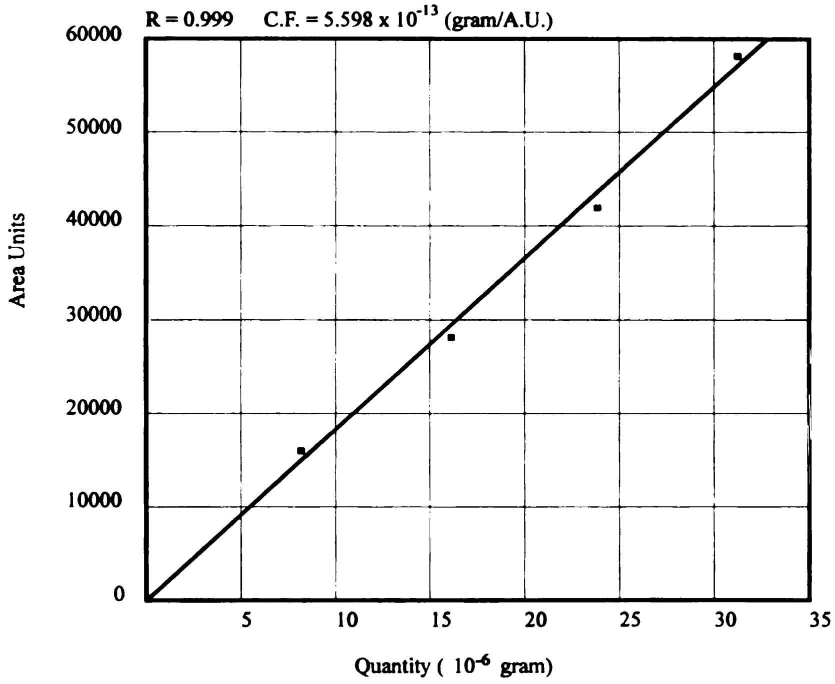
Thermal desorption unit:

Temperature:	transfer line	230	°C
	desorber	340	°C
	valve	230	°C
Desorption time:		8	min

Peak areas and retention time were recorded by the use of a computer integrator. Calibration factors (C.F.) were determined by the slope of the linear calibration curve. The calibration factors are summarized in following table, and calibration curves are shown in Figure 35, 36, 37, and 38.

Standard and TS/TD process calibration factors

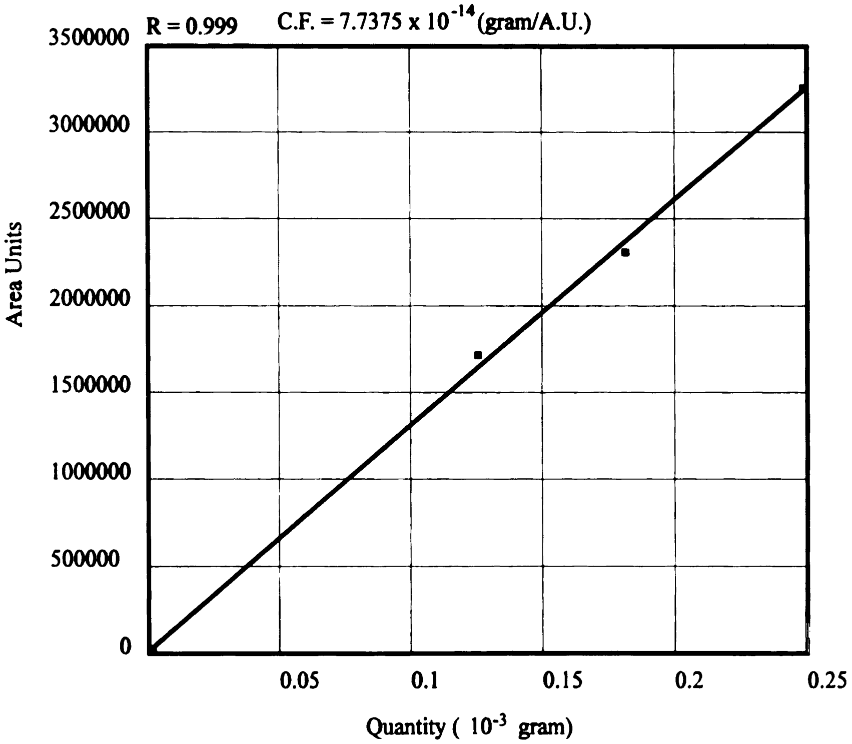
Samples	Process	Calibration Factor
Vanillin	standard	5.598×10^{-13}
	TS/TD	7.757×10^{-13}
Ortho-vanillin	standard	5.921×10^{-13}
	TS/TD	1.327×10^{-13}



Standard calibration data of vanillin

Quan. Inj. (μg)	Area Units
0	0
8	15671
16	27651
24	41451
32	58568

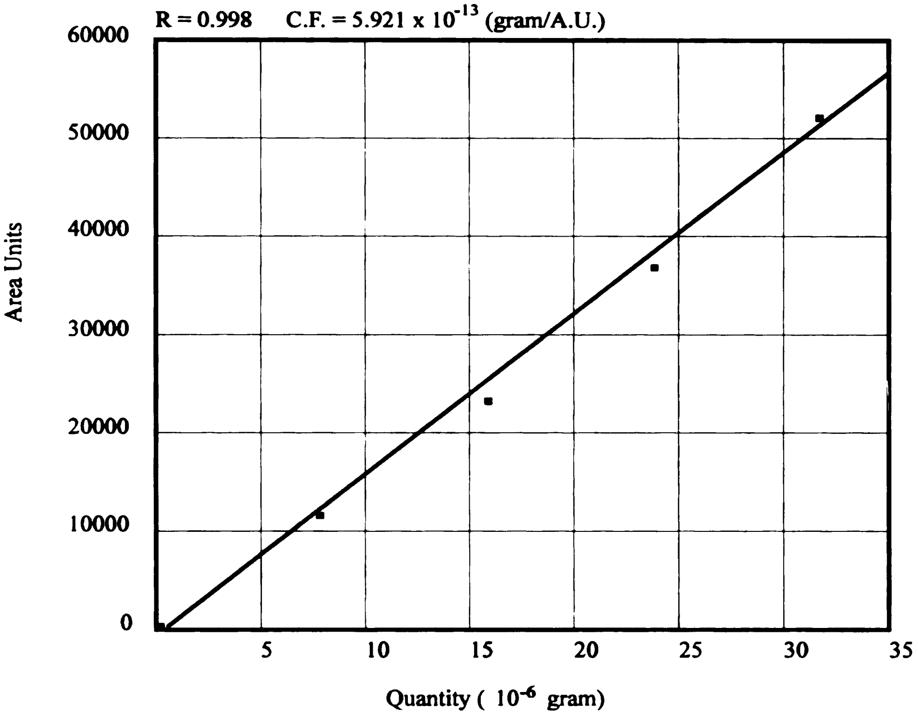
Figure 35: standard calibration curve of vanillin



TS/TD calibration data of vanillin

Quan. Inj. (μg)	Area Units
0	0
0.125	1682271
0.188	2366638
0.250	3267948

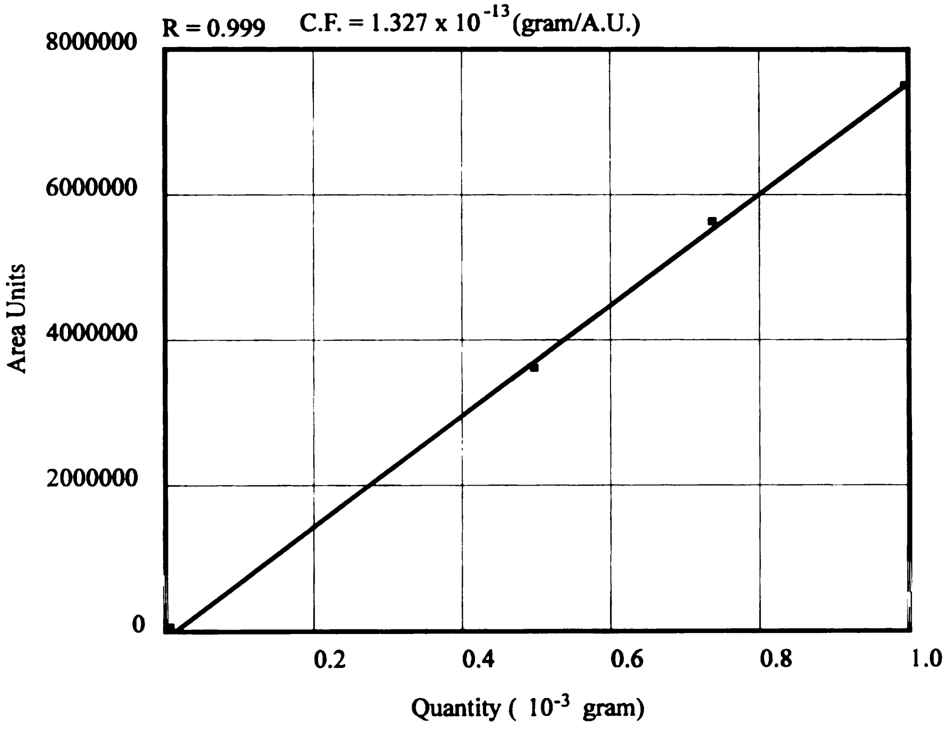
Figure 36: TS/TD calibration curve of vanillin



Standard calibration data of ortho-vanillin

Quan. Inj. (μg)	Area Units
0	0
8	11061
16	23177
24	37600
32	53966

Figure 37: standard calibration curve of ortho-vanillin


R = 0.999 C.F. = 1.327 x 10^{-13}(gram/A.U.)

TS/TD calibration data of ortho-vanillin

Quan. Inj. (μg)	Area Units
0	0
0.50	3602843
0.75	5663324
1.00	7507108

Figure 38: TS/TD calibration curve of ortho-vanillin

APPENDIX B

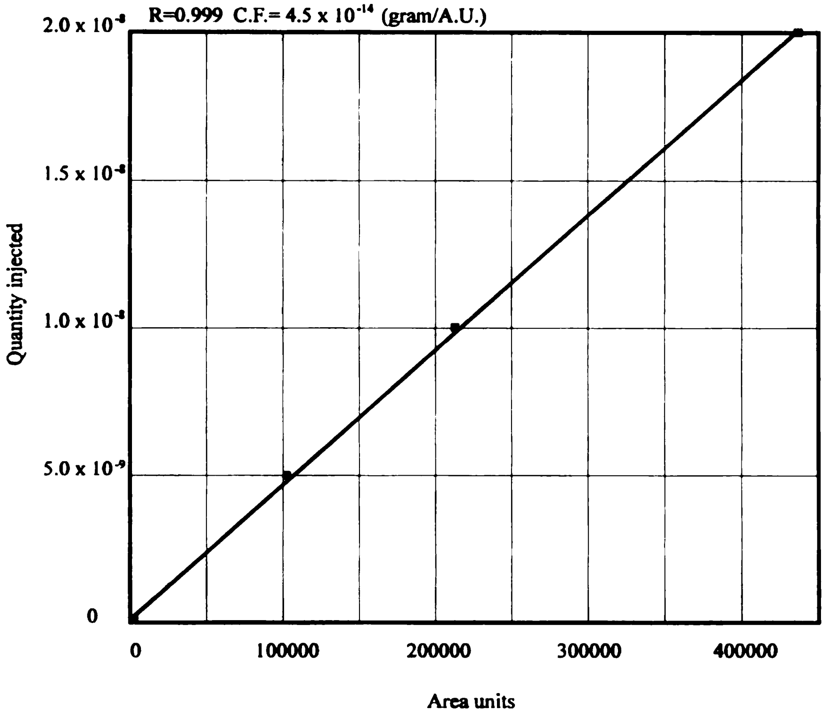
APPENDIX B

Calibration factors for HPLC process

The calibration factors of vanillin and ortho-vanillin for HPLC procedure were determined by the analysis of 0.5, 1.0, and 2.0 ppm (wt/volume) standard vanillin- and ortho-vanillin- acetonitrile solution. The conditions for HPLC analysis was as follows:

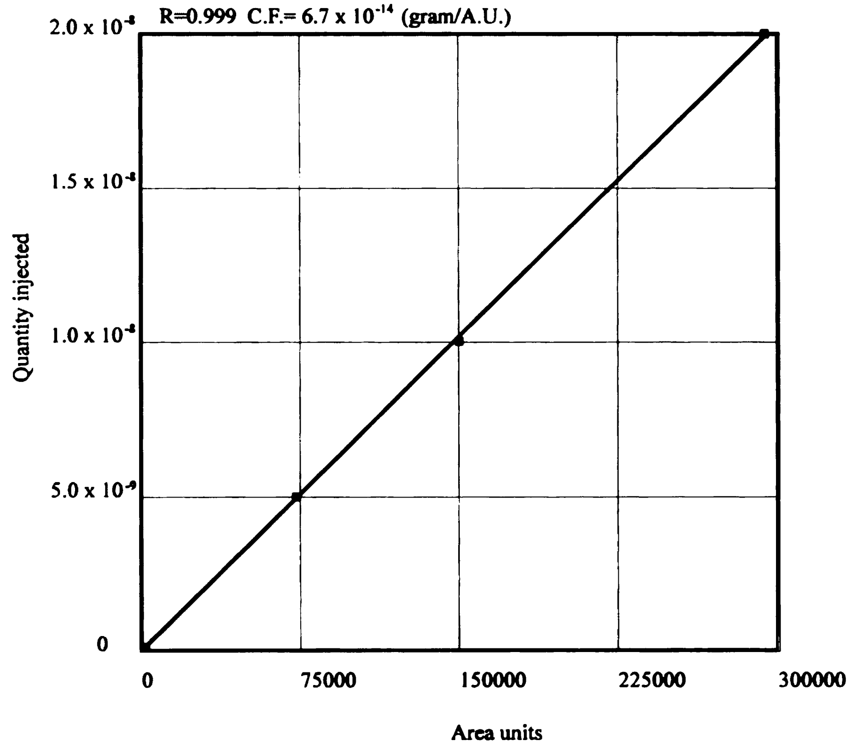
Model: Waters™ 150-C ALC/GPC
Detector: Waters™ Tuable Absorbance Detector
Wavelength 275
Column: Delta-Pak™, C^{18} 300Å, 3.9 x 150 mm
Mobile phase: 40% Methanol & 60% HPLC grade water (v/v %)
Temperature: 23 °C
Flow rate: 1 ml/min.
Inj. Vol.: 10 μl

The calibration factor for vanillin and ortho-vanillin was 4.5×10^{-14} gram/A.U. and 6.7×10^{-14} gram/A.U., respectively. The curves are shown in Figure 39 and 40.



Area units	Quantity injected
0	0
102070	5.0 x 10^{-9}
209128	1.0 x 10^{-8}
437636	2.0 x 10^{-8}

Figure 39: Vanillin calibration curve of HPLC process



Area units	Quantity injected
0	0
102070	5.0 x 10^{-9}
209128	1.0 x 10^{-8}
437636	2.0 x 10^{-8}

Figure 40: Ortho-vanillin calibration curve of HPLC process

APPENDIX C

APPENDIX C

Time needed to reach a steady state within a paperboard/headspace sorption cell

To determined the time needed to attain a steady state concentration level in the sorption cells, a 500 µl aliquot was withdrawn from the headspace of the sorption cell following 2 days storage, and the sample injected directly into gas chromatograph for quantitation. This process was repeated every two days until the headspace concentration of vanillin and o-vanillin reached a steady state level. Every sorption cell could just be withdrawn one time. For both vanillin and ortho-vanillin samples, the results showed that the system had equilibrated within 7 days period. The results were summarized in following Table. The concentration levels change as a function of storage time was illustrated graphically in Figure 41 as well.

The concentration change as a function of storage time until a steady state was reached.

Storage time (days)	vanillin conc. in headspace (ppb)	avg. (ppb)	O-vanillin conc. in headspace (ppb)	avg. (ppb)
3	10.5	12.40	3.5	3.20
	14.3		2.9	
5	19.7	18.80	4.6	5.10
	17.9		5.6	
7	18.4	17.65	6.1	5.85
	16.9		5.6	
9	16.7	18.40	6.0	5.50
	20.1		5.0	

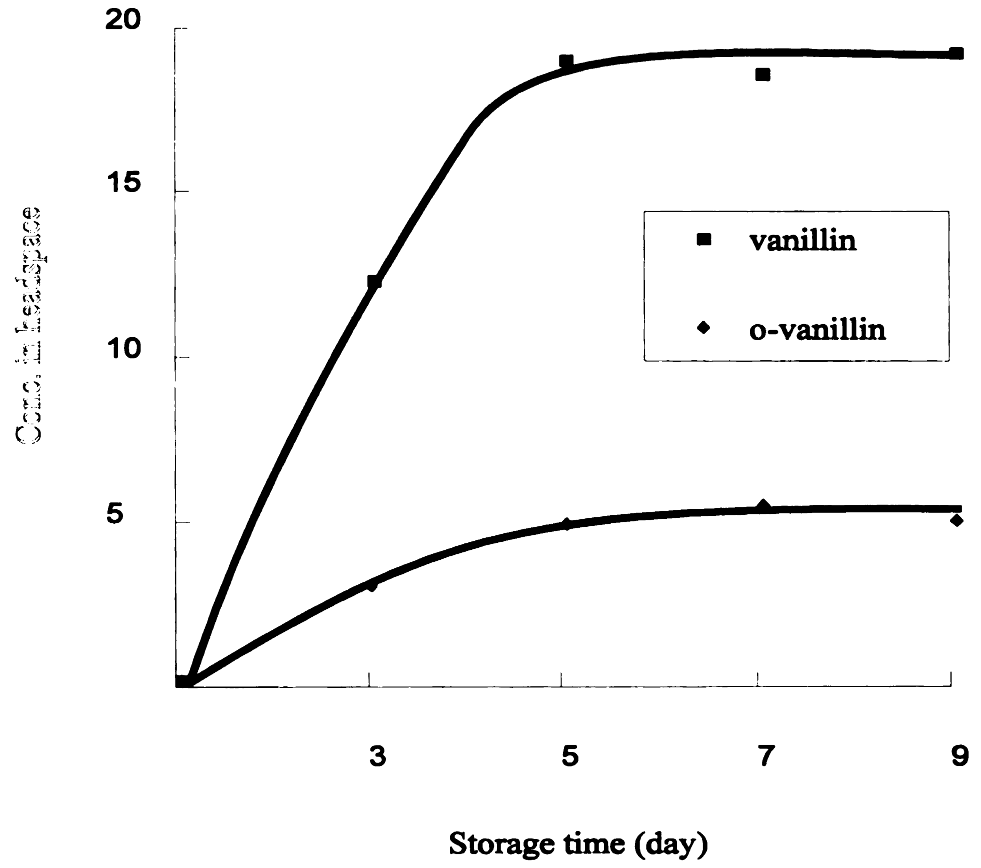


Figure 41: The time needed to reach a steady state within a paperboard/headspace sorption cell

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