Chapter 18

Diffusion and Sorption of Linear Esters in Selected Polymer Films

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Polymers are being used in more sophisticated food-packaging
applications. These applications must do more than keep the food
safe from oxygen damage. They must preserve the attractive flavor
profile of the food. In short, the package must assist in flavor
management.

Permeation of flavor (and aroma) compounds in polymers can be
part of flavor management in two general ways. First, unintended
species can enter the food by permeation from the environment or by
migration from the package itself.

Second, the flavor and aroma molecules of the food may leave by
permeation through the package or by simple sorption by the package.
The flavor profile may be made unacceptable by broad diminution or
by selective removal of a few components.

This paper will describe experiments that concern this second
area of flavor management. The experiments were directed toward the
interactions between linear esters and some of the films that are
important for food-packaging applications. The analysis of the data
will focus on the important solution process with special attention
for the thermodynamics.

Framework for Experiments

Aromas. Nine linear esters were included in this study. They are
listed in Table I. Esters comprise an important flavor group. Not
all of these esters are found in food. These specific esters
provide a systematic approach to a complex problem. They were
purchased from Aldrich Chemical Company as part of the "Flavors and
Fragrances Kit #1: Esters."

Table I
Linear Esters for Permeation

Ester Name	Number of Carbons	Boiling Point °C	% Purity	CAS Number
Methylbutyrate	5	102	98+	623-42-7
Ethylpropionate	5	99	97+	105-37-3
Ethylbutyrate	6	120	98+	105-54-4
Propylbutyrate	7	142	98+	105-66-8
Ethylvalerate	7	144	98+	539-82-2
Ethylhexanoate	8	168	98+	123-66-0
Ethylheptanoate	9	188	98+	106-30-9
Ethyloctanoate	10	206	98+	106-32-1
Hexylbutyate	10	208	98+	2639-63-6

Films. Three films were included in this study. Low density polyethylene (LDPE) was included as a representative polyolefin. It is not considered to be a barrier polymer. It has permeabilities to selected aroma compounds slightly higher than the permeabilities of polypropylene and high density polyethylene (1). A vinylidene chloride copolymer (co-VDC) film was included as an example of a barrier that is useful in both dry and humid conditions. The film was made from a Dow resin which has been designed for rigid packaging applications. A hydrolyzed ethylene-vinylacetate copolymer (EVOH) film was included as an example of a barrier film that is humidity sensitive. The polymer was a blend of resins with total composition of 38 mole% ethylene.

These films were tested as monolayers about 2.5×10^{-5}m(=1 mil) thick. They would typically be used in multilayer structures; however, the individual permeabilities can be combined to predict the behavior of multilayers.

Instrument. The analytical instrument for these experiments is shown schematically in Figure 1. This instrument was designed and built at The Dow Chemical Company for measuring the permeation of flavor and aroma compounds through polymer films. The gas handling section of the instrument contains the plumbing, containers of aroma solutions, and the experimental film. This enclosure is insulated, and the temperature can be controlled, $\pm$ 1°C, from subambient to about 150°C. The detector is a Hewlett-Packard 5970 mass spectrometer. More details are available (2).
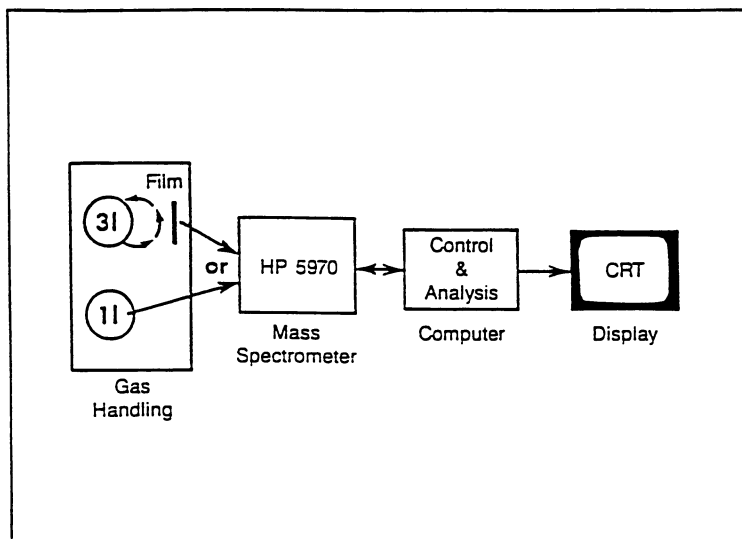
Figure 1. Schematic of Instrument

This instrument is used in two general ways. First, with each new compound, a mass spectrum is generated to identify the most populous and unique ion fragments. Second, for actual permeation experiments, the instrument is programmed to monitor selected ion fragments, typically three, for each of the aromas involved. When a single permeant is used, the three most populous ion fragments may be chosen. However, when mixed permeants are used, significant degeneracies are avoided. All the experiments of this study were done with a single permeant. The response of the instrument was determined to be linear in the operating range and beyond, both at higher and lower concentrations.

In all experiments, the following sequence was used. First, a calibration experiment was completed by preparing a very dilute solution of the permeant in nitrogen in the one liter flask and introducing some of the gaseous solution directly to the mass spectrometer via a specially designed interface. A known concentration and a measured response yield a calibration constant.

Then a permeation experiment was completed by preparing a dilute solution of the permeant in nitrogen in the three liter flask and routing this gaseous solution past the purged, experimental film. The detector response was recorded as a function of time for subsequent analysis.

The computer was used to program and control the mass spectrometer and to collect and analyze the data. The computer was equipped with a CRT and a printer.

The advantages of this instrument are a) it can be used with very dilute solutions of permeants, b) multiple permeants may be used in a single experiment, c) humidity may be used by adding water or a saturated salt solution to the three liter flask, d) the entire progress of the experiment can be monitored as a function of time, and e) a wide range of temperatures can be used.

Variables. A range of temperatures was used with the barrier films -- co-VDC and EVOH. Warm temperatures were used because these barrier polymers had low permeabilities and low diffusion coefficients at cooler temperatures. Experiments at lower temperatures would have taken prohibitively long and may have been below the detection limit of the instrument. Data at several temperatures allow a more sophisticated analysis of the permeation process. The LDPE film was tested at a single, low temperature.

A single concentration of permeant was used for all the experiments. Approximately two microliters of flavor/aroma compound were used in the three liter flask. This corresponds to about 150 ppm(molar) and varies from ester to ester depending upon the molecular weight. Previous experiments have shown that, in this range of concentrations, the permeation process is not a strong function of the permeant concentration (3,4). Table II lists the partial pressure (P_x) at the experimental temperatures for the five carbon ester and the nine carbon ester. Also included are the vapor pressures (P_o) at these temperatures, and the ratio P_x/P_o.

Table II. Partial Pressure at the Experimental Temperature for Five-and Nine-Carbon Esters

Ester	T(C)	P_o (Pa)[1]	P_x (Pa)[2]	P_x/P_o
C-5	105	1.1×10^5	19	1.7×10^{-4}
C-5	95	8.1×10^4	18	2.2×10^{-4}
C-5	85	5.9×10^4	18	3.0×10^{-4}
C-5	25	4.5×10^3	15	3.3×10^{-3}
C-9	105	7.1×10^3	12	1.7×10^{-3}
C-9	95	4.5×10^3	12	2.7×10^{-3}
C-9	85	2.8×10^3	11	3.9×10^{-3}
C-9	25	8.3×10^1	9	1.1×10^{-1}

1) From the Antoine equation[5]
2) For a 2 μL sample

Humidity was tested only qualitatively in a single experiment. In an experiment with the EVOH film and ethylvalerate at 110°C, 0.25 milliliters of water was injected into the three liter flask after the permeation experiment had reached steady state. Within seconds, the permeation rate increased to above the detection limit of the mass spectrometer. This was consistent with prior experience wherein the permeability and the diffusivity in an EVOH film increase by a factor of about 1000 in the presence of moisture (6). No more experiments were done with humidity for this study.

Framework for Analysis.

For a thorough analysis of aroma transport in food packaging, the permeability (P) and its component parts - the solubility coefficient (S) and the diffusion coefficient or diffusivity (D) are needed. These three parameters are related as shown in Equation 1.

$$P = D \times S \tag{1}$$

The permeability is useful for describing the transport rate at steady state. The solubility coefficient is useful for describing the amount of aroma that will be absorbed by the package wall. The diffusion coefficient is useful for describing how quickly the permeant aroma molecules move in the film and how much time is required to reach steady state.

Equation 2 describes steady state permeation where ΔM_x is the

$$\frac{\Delta M_x}{\Delta t} = \frac{P \; A \; \Delta p_x}{L} \tag{2}$$

quantity of permeant x that goes through a film of area A and thickness L in a time interval Δt. The driving force for the permeation is given as the pressure difference of the permeant across the barrier, Δp_x. In an experiment, $\Delta M_x / \Delta t$ is measured at steady state while A and L are known and Δp_x is either measured or calculated separately.

The diffusion coefficient can be determined from the transient portion of a complete permeation experiment. Figure 2 shows how the transport rate or detector response varies with time during a complete experiment. At the beginning of an experiment, t = 0, a clean film is exposed to the permeant on the upstream side.

Initially, the permeation rate is effectively zero. Then "break through" occurs, and the transport rate rises to steady state. The diffusion coefficient can be calculated in either of two ways. Equation 3 uses $t_{1/2}$, the time to reach a transport rate that is one-half of the steady state rate (7).

$$D = \frac{L^2}{7.2 \; t_{1/2}} \tag{3}$$

Equation 4 uses the slope in the transient part of the curve and the

$$D = \frac{0.176 \ L^2 \ (slope)}{Rss} \qquad (4)$$

steady state response Rss (8).   After P has been determined with
Equation 2 and D has been determined with Equation 3 (or 4), and
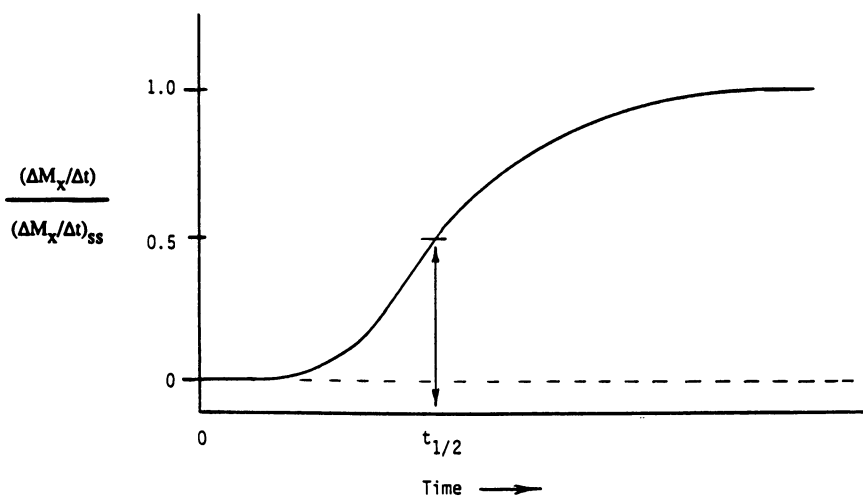then S can be determined with Equation 1.

Figure 2.   Relative Transport Rate as a Function of Time

Many sets of units are used to report the permeability in the
literature. This paper will use SI units in the following way. For
Equation 2 to be valid, the permeability must have dimensions of
quantity of gas times thickness divided by area-time-pressure. If
the kilogram is used to describe the quantity of gas and the pascal
is used as the unit of pressure, then units of permeability are
$kg \cdot m/m^2 \cdot s \cdot Pa$. This unit is very large and a cumbersome exponent
often results. A more convenient unit, the Modified Zobel Unit, (1
MZU = 10^{-20} $kg \cdot m/m^2 \cdot s \cdot Pa$), was developed for flavor permeation.
Zobel proposed a similar unit earlier (9). The units of the
diffusion coefficient are m^2/s. The units of the solubility
coefficient are $kg/m^3 Pa$.

Equations 1, 2, and 3 are working definitions of P, D, and S. No corrections are made for the crystallinity in any of the experimental samples of this study.

For most simple cases, P, D, and S are simple functions of temperature as given in Equations 5, 6, and 7.

$$P\ (T) = P_o \exp\ (-E_p/RT) \tag{5}$$

$$D\ (T) = D_o \exp\ (-E_D/RT) \tag{6}$$

$$S\ (T) = S_o \exp\ (-\Delta H_s/RT) \tag{7}$$

where, P_o, D_o, and S_o are constants, T is the absolute temperature, and R is the gas constant. E_p is the activation energy for permeation. E_D is the activation energy for diffusion, and ΔH_s is the heat of solution. If log P data are plotted on the vertical axis of a graph and T^{-1} is plotted on the horizontal axis, a straight line will result. The slope will be $-0.43\ E_p/R$. The diffusion coefficient and solubility coefficient behave similarly. Equations 1, 5, 6, and 7 can be manipulated to yield equation 8 which relates the activation energies and the heat of solution.

$$E_p = E_D + \Delta H_s \tag{8}$$

Equations 1-7 were developed for gas permeation through rubbery polymers. They must be used with caution with glassy polymers and/or organic vapors that interact strongly with the barrier.

The heat of solution can be separated into two basic parts – namely, the heat of condensation (ΔH_c) and the heat of mixing (ΔH_m). Equation 9 expresses the relationship

$$\Delta H_s\ \ =\ \ \Delta H_c\ +\ \Delta H_m \tag{9}$$

The heats of solution can be determined experimentally in these experiments, and the heats of condensation are available in the literature. The heat of mixing can then be calculated with Equation 9. The heat of mixing describes the basic thermodynamic relationship between the polymer and the penetrant.

EXPERIMENTS

Typical Experiment. Figure 3 shows the results of a typical experiment with the co-VDC film. The permeant was ethylbutyrate. The experiment was done at 100°C. The warm temperature caused the experiment to progress quickly. Three ions fragments, m/z = 60, 71, and 88 were monitored by the mass spectrometer. The total ion intensity of these three ions is shown here. The first response in Figure 3 is due to calibration. Here 2.4 ul of a 0.5% solution of ethylbutyrate in acetone was injected into the 1-liter flask and diluted with nitrogen. The resulting gaseous solution was introduced into the mass spectrometer via the interface.

     After the baseline was obtained again at 34 minutes into the
run, the permeation experiment began. Here 2.5 ul of ethylbutyrate
had been injected into the 3-liter flask and diluted with nitrogen
before being circulated past the upstream side of the film.
Breakthrough occurred at about 38 minutes, and steady state was
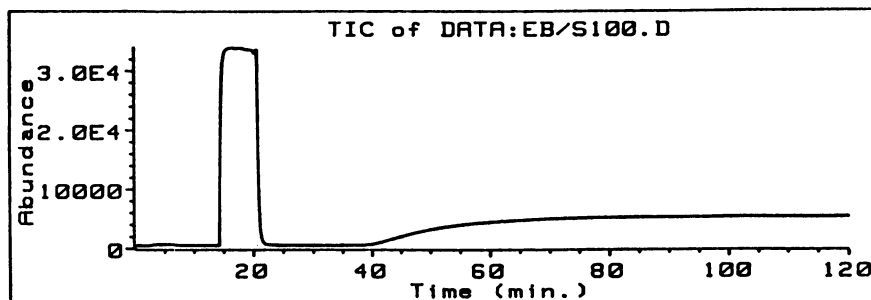reached at 90 to 100 min.

Figure 3.   Permeation Experiment for Ethylbutyrate in a
         Vinylidene Chloride Copolymer Film at 100°C

Organized Results. Many combinations of permeant ester, film, and
temperature were studied. Figure 4 shows the permeability results
for a single ester-film combination at 5 different temperatures.
Similar graphs were made for the other ester-film combinations.
     Figure 5 shows permeabilities of all the esters at 85°C in the
co-VDC film. These data were taken from graphs like Figure 4.
Figure 6 shows the diffusion coefficients of all the esters at 85°C
in the co-VDC film. Figure 7 shows the solubility coefficients of
all the esters in the co-VDC film. Figure 8 is a re-plot of the
data in Figure 7 with the boiling point of the ester as the
horizontal axis.
     The activation energies for permeation in the co-VDC film were
all positive. The activation energies for the diffusion coefficient
are shown in Figure 9. The heats of solution for the esters are
shown in Figure 10.
     Fewer esters were used in experiments with the EVOH because the
trends observed with the co-VDC film were apparent. Figures 11, 12,
and 13 show the permeabilities, diffusion coefficients, and
solubility coefficients for the esters at 85°C in the EVOH film.
Figures 14 and 15 show the activation energies for diffusion and the
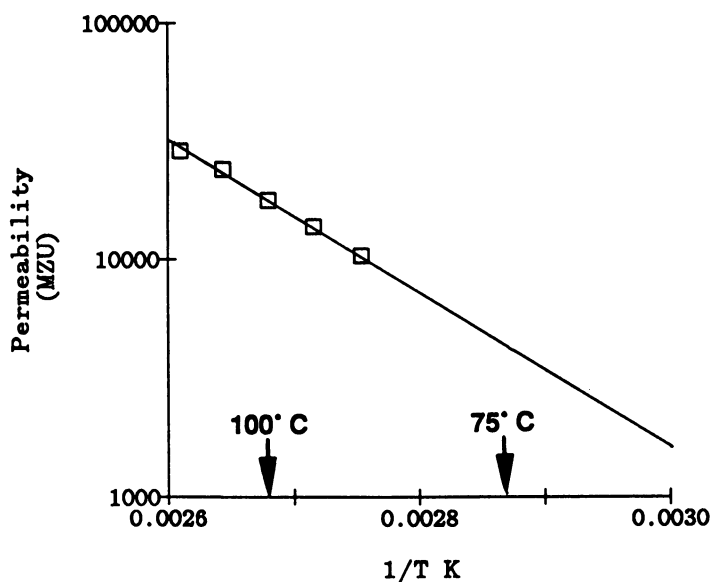heats of solution.

Figure 4.   Permeability of Ethylbutyrate in a
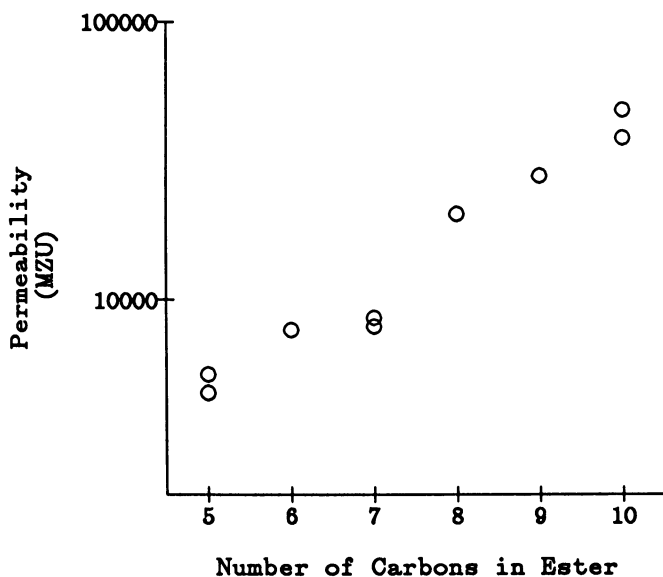Vinylidene Chloride Copolymer Film

Figure 5.   Permeability of Esters at 85°C in a
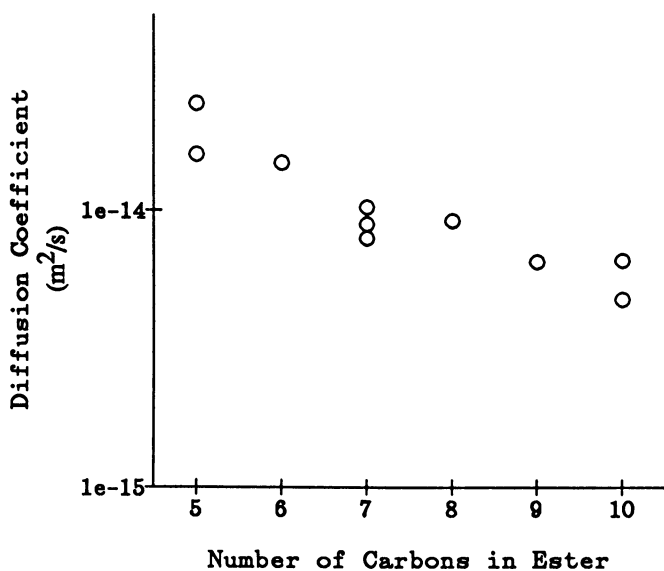Vinylidene Chloride Copolymer

Figure 6.   Diffusion Coefficient at 85°C of Esters
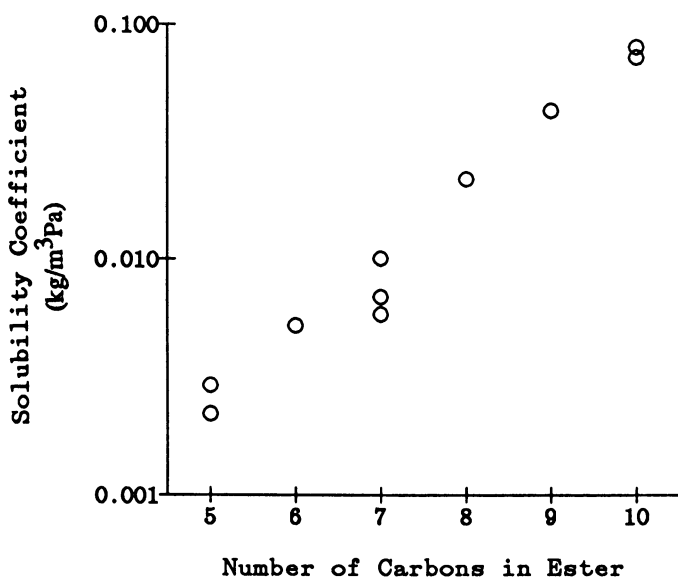in a Vinylidene Chloride Copolymer Film

Figure 7.   Solubility Coefficient at 85°C of Esters
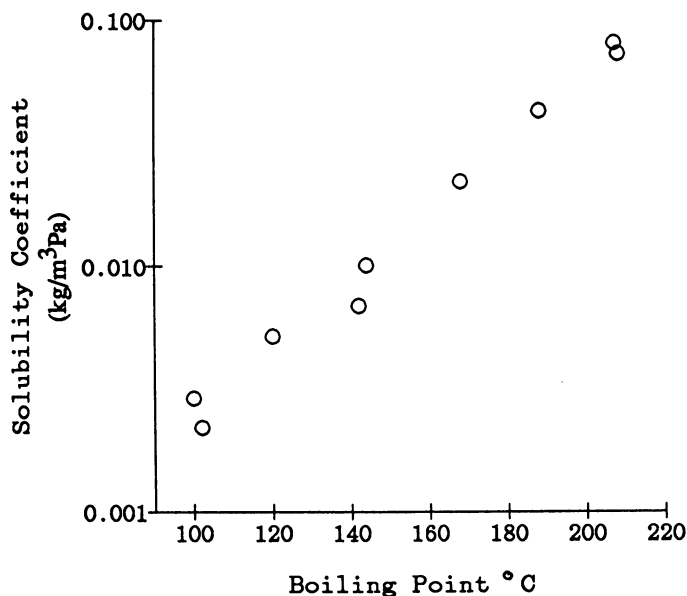in a Vinylidene Chloride Copolymer Film

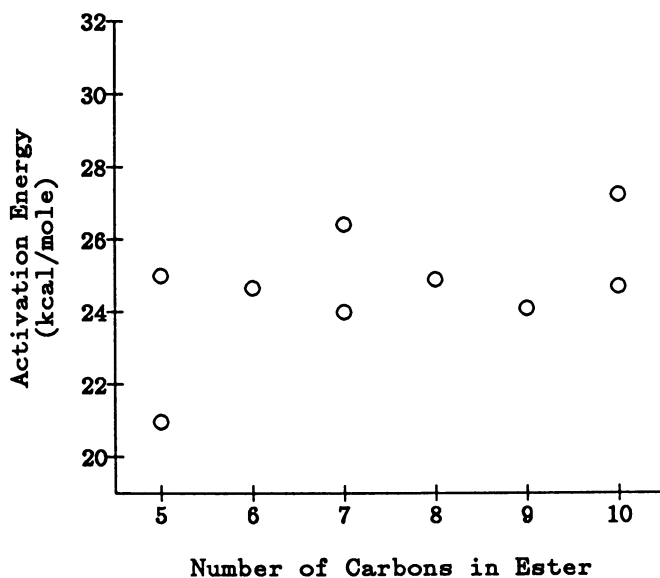Figure 8. Solubility Coefficients of Esters at 85°C in a Vinylidene Chloride Copolymer Film

Figure 9. Activation Energy for Diffusion of Esters in a Vinylidene Chloride Copolymer Film
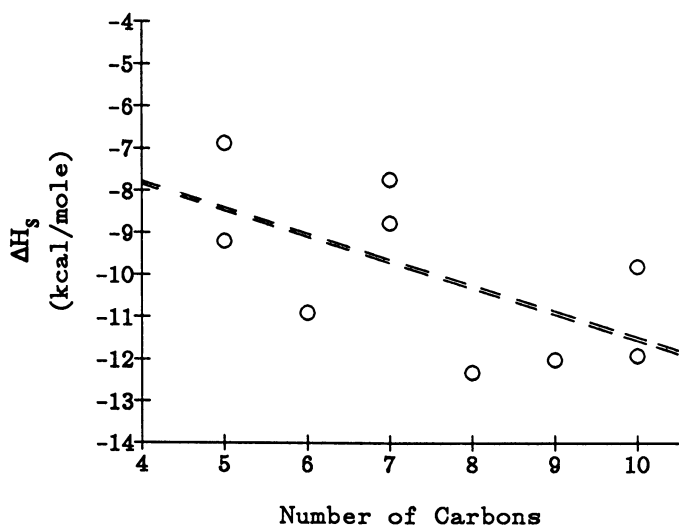
Figure 10.   Heats of Solution for Esters
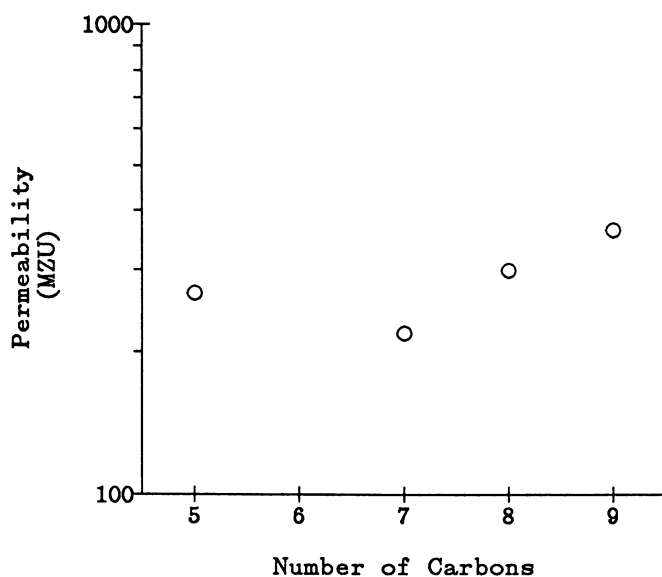in a Vinylidene Chloride Copolymer Film

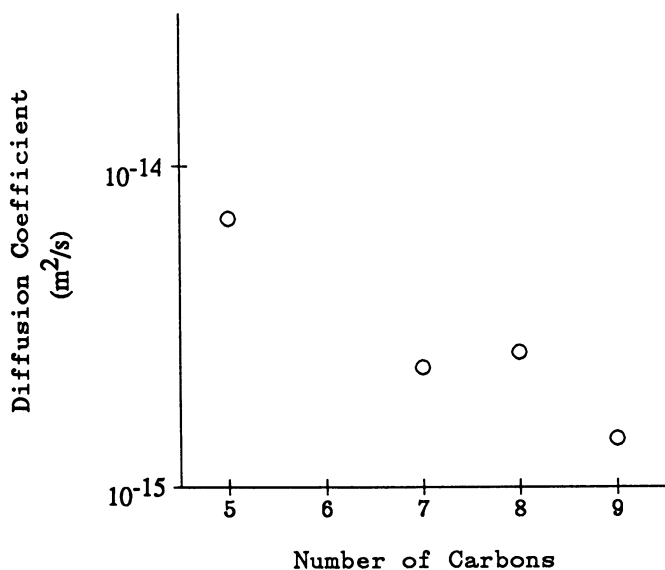Figure 11.   Permeability Coefficient at 85°C
of Esters Through EVOH

Figure 12. Diffusion Coefficient at 85°C
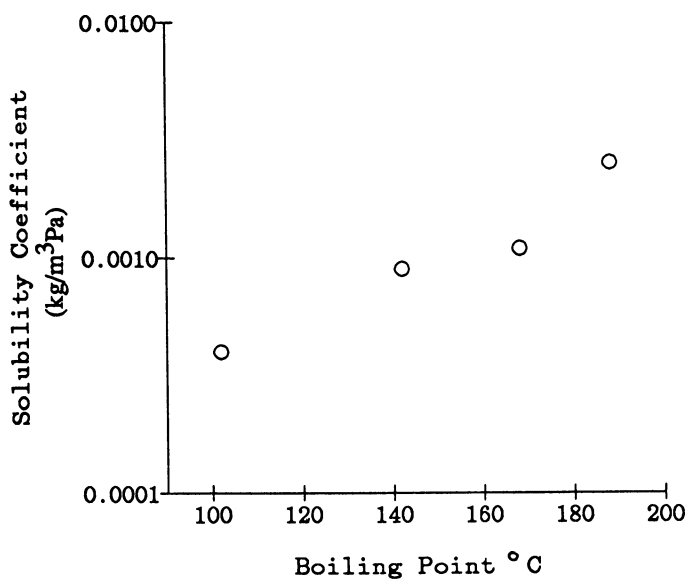of Esters Through EVOH

Figure 13. Solubility Coefficient at 85°C vs
Boiling Point of Esters in EVOH
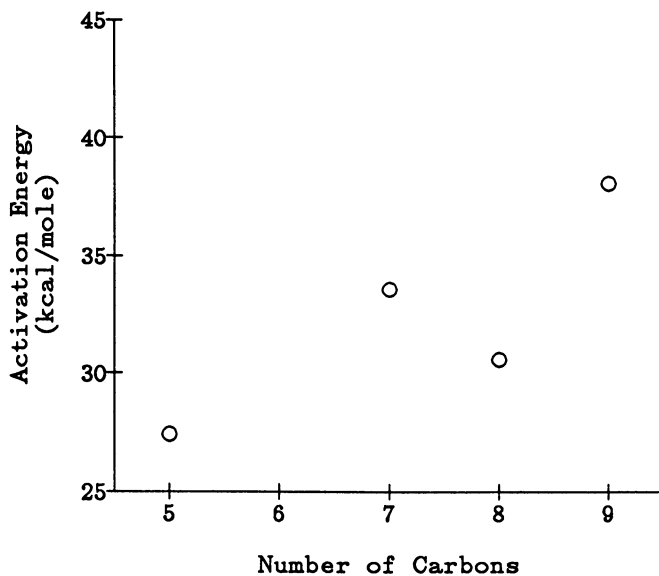
Figure 14.   Activation Energy of Diffusion
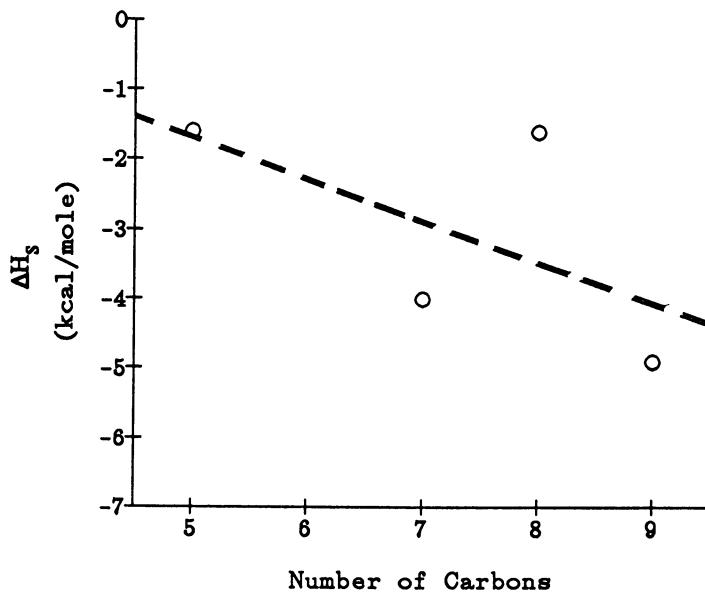   for Esters Through EVOH

Figure 15.   Heats of Solution for Esters
         in an EVOH Copolymer Film

Figures 16 through 18 show the results for the LDPE film.

Discussion. In each film the permeabilities increase as the size of the ester increases. The data show that this result is driven by the solubility coefficient. The diffusion coefficients decrease as the size of the ester increases; however, the solubility coefficients increase greatly as the size of the ester increases.
    The qualitative effect of permeant size on the diffusion coefficient was expected. A recent simple analysis quantified the relationship between D and permeant size for spherical permeants up to C_6 in several polymers (10). That analysis is not directly applicable here since these permeants are linear and larger. Another study quantifies the relationship between D and permeant size for linear alkanes in polyethylene (11). The diffusion coefficient at 25°C was observed to decrease from 3.9×10^{-11} m^2/s for n-hexane to 2.2×10^{-11} m^2/s for n-nonane.
    The diffusion coefficients for the esters in the present studies seem to change comparable amounts. At 85°C in co-VDC and EVOH, the diffusion coefficients for the esters decrease by about 3x as the number of atoms (excluding hydrogen) in the backbone increases from 6 to 9 (5 carbons plus one oxygen to 8 carbons plus one oxygen). The difference would be greater at 25°C because the activation energies for diffusion are larger for the larger esters. This is consistant with the results of Landois-Garza and Hotchkiss for an ester series in polyvinyl alcohol (12).
    At 30°C in LDPE, the diffusion coefficients decrease by about 30% as the number of atoms in the backbone of the ester increases from 6 to 9. Studies of alkanes in low density polyethylene show similar trends (13).
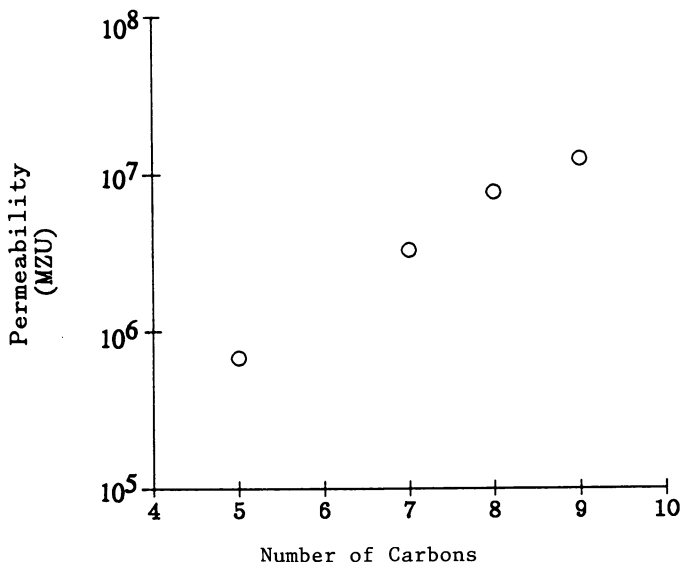

Figure 16. Permeability at 30°C for
Esters in a LDPE Film
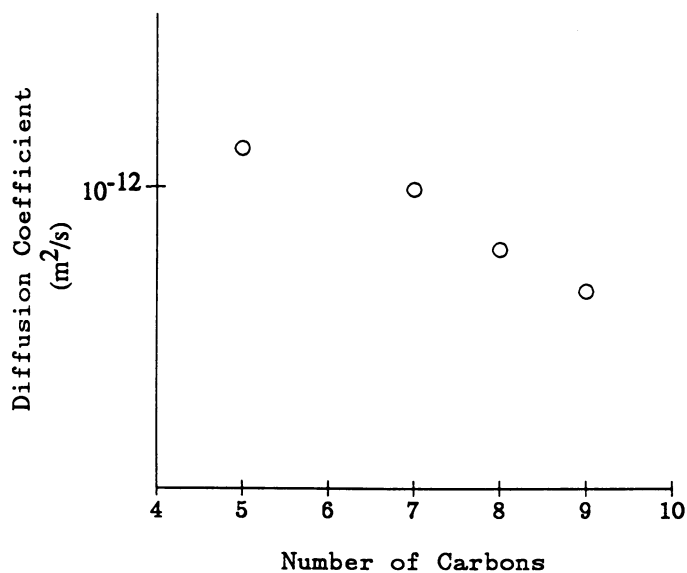
Figure 17. Diffusion Coefficient at 30°C
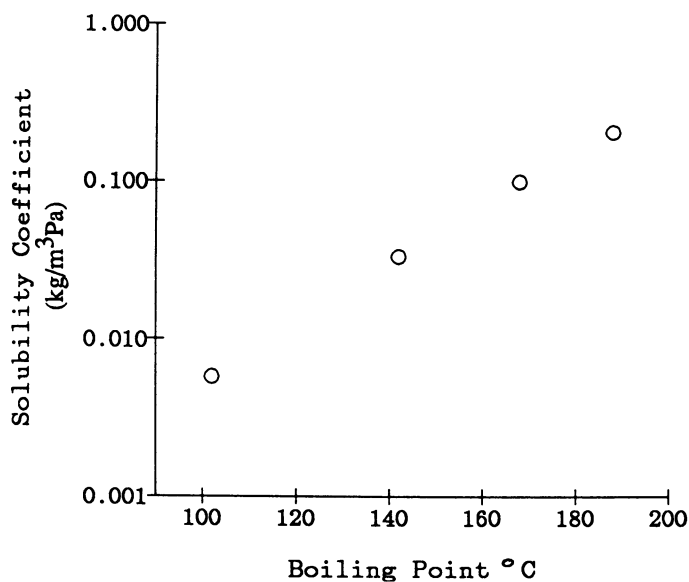   of Esters in a LDPE Film

Figure 18. Solubility Coefficient at 30°C vs.
           Boiling Point of Ester in a LDPE Film

The activation energies for diffusion in the co-VDC and EVOH films increase as the size of the ester increases. This is expected since cooperative motion of larger zones of the polymer matrix are necessary to create larger holes for passage. The activation energies for diffusion in LDPE were not determined.

The solubility coefficients make interesting contributions to the permeabilities. The solution process of these gas phase permeants can be separated for analysis into two components – condensation and mixing. Table III contains the heats of condensation for the experimental esters. Table III also contains the heats of solution in the polymer films from linear fits of the data in Figures 10 and 15. Finally, Table III contains the heats of mixing for the esters in the films. The heats of mixing were calculated using equation 9.

Table III Heats of Condensation and Solution for Experimental Esters

Number of Carbons	ΔH_c	ΔH_s co-VDC	ΔH_s EVOH	ΔH_{mix} co-VDC	ΔH_{mix} EVOH
5	-8.88^1	-8.4	-1.6	0.4	7.3
6	-9.47	-9.1	---	0.4	---
7	-10.48^1	-9.7	-2.8	0.8	7.7
8	-11.20^2	-10.3	-3.5	0.9	7.7
9	-11.92	-10.9	-4.1	1.0	7.9
10	-12.87^2	-11.5	---	1.4	---

a) kcal/mole
1) average of two values
2) extrapolated values

The heats of condensation are reliable data: On the other hand, there is considerable experimental uncertainty in the heats of solution. The trends in the heat of solution are more certain; however, the actual values are not so certain. This uncertainty arises from two sources. First, the solubility coefficients are derived from the permeabilities and the diffusion coefficients. Hence, the relative uncertainties of both P and D transfer to S. The heats of solution are derived by fitting equation 7 to only 3 or 4 data. This is not ideal. Future work will expand the data base to test this preliminary analysis.

Nevertheless, the trends for the heats of mixing are probably correct as shown in Table II. As the esters get larger, the molecule becomes more like an alkane, and the polar ester group is diluted. The trend in the heats of mixing for the co-VDC film is interesting. As the esters become larger the heats of mixing become less favorable in the co-VDC film. This is a reflection of the

dilution of the ester function. Esters are known to interact well
with chlorine containing polymers. The heats of mixing for the
esters in the EVOH film are unfavorable. They are more unfavorable
than the heats of mixing in the co-VDC film. The heats of mixing in
the EVOH film became more unfavorable as the size of the ester
increases. This behavior may be predicted by solubility parameters.
Future work will include a variety of functional groups to study the
specific interactions of polymer and permeant.

SUMMARY

1. The diffusion coefficient decreases modestly as the ester size
    increases for low density polyethylene, EVOH and co-VDC films.
2. The solubility coefficient undergoes a much greater change with
    increasing ester size.
3. Thus the permeability increases with increased ester size.
4. Plasticizing the polymer film can result in a dramatic increase
    in the diffusion coefficient.
5. Important flavor and aroma compounds can be lost to the food
    package by sorption.
6. The amount of flavor loss to the package is dependent on both
    diffusion and solubility coefficients.
7. The heats of mixing are dependent on specific interactions
    between polymer and permeant.

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