Articles

Solubility and Diffusion of Water in Low-Density Polyethylene

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ABSTRACT: Solubility (*S*) and diffusion (*D*) of water in low-density polyethylene have been studied by means of desorption experiments. The dependence of *S* and *D* on the state of oxidation of the polymers has been measured. A model has been developed to describe the bound-oxygen dependence of *S* and *D*. Physically the oxygen groups act as traps that are strong enough to bind the water but not so deep as to remove the water from the diffusion process. Hydroxyl, hydroperoxide, and carboxylic acid groups form the strongest traps, ketone groups are weaker, and ester groups exhibit negligible trapping. Permeation is unaffected by bound oxygen. Trap volumes deduced from the analysis lie in the range of a few cubic angstroms. Some restriction of rotational motion of the trapped water is required by the analysis, and independent NMR evidence is presented to support this result.

I. Introduction

Water and saturated hydrocarbons are mutually incompatible to a high degree. While good data[1] exist for the solubility of water in low molecular weight hydrocarbons, the inherent solubility of water in polyethylene has proved to be difficult to establish. The explanation[2-6] of this difficulty appears to lie in the presence of trace impurities in polyethylene that are not easily avoided or removed in the high molecular weight hydrocarbon. Even very low concentrations of impurities, including foreign groups bound to the polymer chains, can give rise to water solubility that is large compared with the inherent solubility in the hydrocarbon. Oxygen-containing groups are of central interest in this connection.

A graph of Schatzberg's results[1] for the solubility of water in linear paraffins plotted as a function of $1/n$ where n is the number of carbons (ranging from 7 to 16), is approximately linear. Extrapolation to high molecular weight, $1/n = 0$, yields a solubility of about 20 ppm. A number of this magnitude is entirely consistent with Masterton's[7] results for the solubility of low molecular weight paraffins in water. Thus, recognizing that water is probably substantially excluded from the crystalline regions of polyethylene, an inherent solubility of 10 ppm or less is expected on the basis of low molecular weight studies.

In the present study[8] solubilities as low as 18 ppm have been observed in branched polyethylenes chosen for their high purity. The solubility of water has been studied as a function of polymer oxidation and it is found to increase by about 1 ppm for every 30 ppm of bound oxygen in the polymer. The limit of sensitivity for oxygen analysis is about 50 ppm, which would correspond to an upper limit of about 2 ppm water associated with bound oxygen. Thus, present results support an inherent solubility for water in branched polyethylene in the range of 15–20 ppm.

The dependence of water solubility on oxygen content of the polymer was expected on the basis of earlier investigations. A less obvious result of the present study is the strong dependence of the coefficient of diffusion of water on bound-oxygen concentration. Empirically it is observed that the product of solubility and diffusion, DS,[30] is independent of oxygen concentration and thus the increase in solubility with oxygen content is balanced by a decrease in diffusion. In view of the fact that solubility is a thermodynamic quantity and diffusion is a kinetic phenomenon this was not an expected result. The principal purpose of this paper is to describe a model for these oxygen dependences. Physically the model involves oxygen-containing groups on the polymer that act as traps of intermediate depth, i.e., a few kcal/mol.

Numerous models have been proposed earlier that correlate diffusivity data for systems composed of a polymeric material and a solvent or low molecular weight species.[9] An important part of this work that is directly relevant to the experiments reported herein comprises the "dual-sorption" treatments presented by Paul and Koros,[10] Petropoulos[11] and Vieth and Sladek.[12] In these models the penetrant is viewed as existing in two kinds of states within the polymer: a mobile form, akin to a solute in a viscous liquid, and a partially immobilized form in which the penetrant is localized by some kind of molecular binding. These treatments apply to the present work on a macroscopic level. On a microscopic level, however, the "dual-sorption" models have treated the immobilized form as adsorbed on internal surfaces. In this paper we consider immobilization in terms of more specific binding of water molecules to oxygenated groups attached to the polymer. It is possible that the water-oxidized polyethylene system reported here is unique. Although the earlier "dual-

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Table I
Properties of Polyethylenes Studied

sample	process	density,[a] g/cm^3	melt flow index, g/10 min	T_m, °C	$\Delta H_f{}^*$,[b] cal/g
B	low pressure	0.923	0.46	114	34
C	high pressure	0.920	0.22	109	32
D	high pressure	0.920	0.59	108	32

[a] At 23 °C. [b] Apparent heat of fusion, $\Delta H_f{}^*$, was determined by DSC at a heating rate of 10 °C/min after cooling each sample from the melt to 0 °C at 20 °C/min.

sorption" models[10-12] are more applicable to the *general* problem of solubility and diffusion of penetrants in polymers, they do not address the important case of an immobilized penetrant as it relates to *specific* association with oxygen-containing groups on the polymer. The present oxygen trap model is suggested by early studies[13,14] that have yielded consistent data for nonpolar penetrants while results for water have varied widely. The largely undefined state of oxidation of the earlier polyethylene specimens is presumably a central factor as suggested by Myers et al.[15] In the present study the total oxygen content is a controlled variable. In addition, individual oxygen-containing roups are identified and measured.

II. Experimental Section

Three branched polyethylenes have been studied, sample B, a linear low-density material prepared at low pressure, and samples C and D, typical high-pressure, low-density polyethylenes. Physical property data are given in Table I. Although these samples are of commercial origin they are extremely pure. Chemical analysis for metals and halogens have failed to reveal impurities above the ppm range. Oxygen analyses have been carried out by a neutron analysis procedure with a detectability limit of about 50 ppm.[16] Samples B and D show no oxygen at this level. Sample C contains about 500 ppm oxygen, presumably present as an additive.

Sheets of the polymers were molded in 0.127-cm thickness at 150 °C under clean conditions between fluorocarbon (FEP) backing sheets and cooled rapidly to room temperature. Specimens measuring about 1.3 cm by 15 cm and weighing roughly 2.2 g each were immersed in water until saturated. The water content, S, and diffusion coefficient, D, were found by following the desorption from the slabs in dry nitrogen (dew point = −50 °C).

Prior to weighing, samples were quickly wiped clean with a lint-free cloth and blown dry with a stream of fast-flowing nitrogen. Following this procedure, samples were rapidly placed in an electromagnetic microbalance (Perkin-Elmer Autobalance AR-2). Weight changes were displayed continuously on a recorder with a precision of 0.5 ppm. Drift with a 2-g standard load was established to be as low as 4 μg in 24 h.

A polonium α source was kept in the balance to provide ions to neutralize any static charges on the polymer slabs. Water was lost during the time the sample was removed from the water bath until the first weight changes were observed in the microbalance. The amount was determined from a plot of weight loss vs. $t^{1/2}$ extrapolated to $t = 0$.

In addition, S and D were measured by coulometry using a Du Pont moisture analyzer (Model 26-321A).[17,18] Desorption in this instrument was carried out at 100 °C or lower. All measurements of D at temperatures above 25 °C were made in the moisture analyzer.

Both of these techniques yield consistent results with a sensitivity of about 2 ppm for the microbalance and 5 ppm for the moisture analyzer. The lowest solubilities observed were close to 20 ppm for each type of polymer.

It is well-known that water solubility increases substantially as polyethylene is oxidized. We have oxidized the polyethylenes in the present study by shearing the material in air at 160 °C on a two-roll laboratory mill. Even after the oxygen content of sample C was raised from 550 to 11 000 ppm, the resulting apparent heat of fusion, determined by differential scanning calorimetry (DSC), for the two samples was the same, namely, 32 cal/g. However, small differences in the shape of the DSC melting curves between 30 and 80 °C for these two samples indicate that their morphologies are slightly different. In addition, differences in the isothermal crystallization behavior of the two samples at 103 °C and higher were observed. These results suggest that some oxidized portions of the polyethylene chains are drawn into the crystal structure. The method employed for oxygen analysis requires bulk specimens and gives no information concerning the distribution of oxygen within the polymer. We believe that the oxygen is distributed throughout the bulk of the samples used in the desorption studies but this is difficult to prove conclusively.

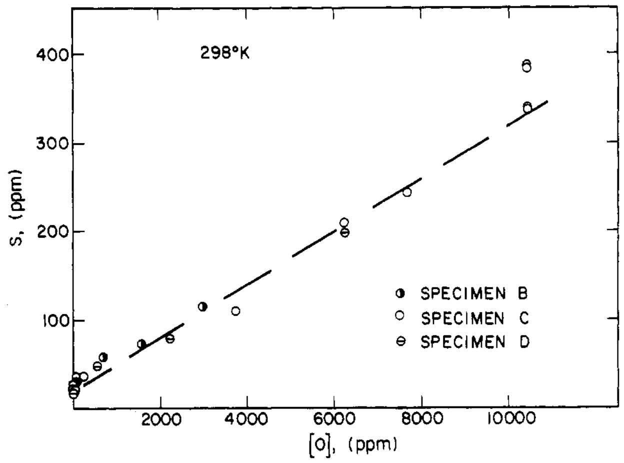

Figure 1. Water solubility in low-density polyethylene as a function of the concentration of oxygen bound to the polymer.

III. Results

Figure 1 exhibits the solubility as a function of oxygen concentration at room temperature. Samples C and D both dissolve water to about 20 ppm although sample D has less than 50 ppm oxygen and sample C has over 500 ppm oxygen, as received. Infrared results suggest that the initial oxygen in sample C may be present as an ester, which apparently has a negligible effect on water absorption. Oxidation by milling at 160 °C gives rise to other chemical forms of oxygen that strongly affect the solubility of water. About 1 water molecule is dissolved for every 30 oxygen atoms added by the thermal oxidation.

Diffusion of water in polyethylene has been studied by following the kinetics of the desorption experiment.[19] At short times, the weight loss follows a $t^{1/2}$ form while at long times the dependence is exponential. Desorption curves obtained in the present study were closely described by the simple theoretical equations involving only the specimen thickness and the diffusion coefficient. Thus, diffusion coefficients calculated from the initial ($t^{1/2}$) slope, the "half-time", or the final (semilog) slope are identical. This provides strong evidence that the diffusion coefficients are independent of time and water concentration, although they exhibit a strong dependence on the oxygen content of the polyethylene. At low oxygen contents desorption occurs relatively rapidly. This can lead the experimenter to underestimate the very low solubility in this region. Even so, with care diffusion coefficients are reproducible to within about 10%.

Figure 2 displays the reciprocal of the diffusion coefficients for water in branched polyethylenes as a function of oxygen concentration. D decreases by an order of magnitude as the oxygen content increases to about 1%. This relatively strong dependence was unexpected but understandable in terms of the model presented below.

Figure 3 shows a plot of D vs. S and it is clear that DS is constant over a wide range of oxygen concentrations. If polyethylene sheets are arranged as barriers to the escape

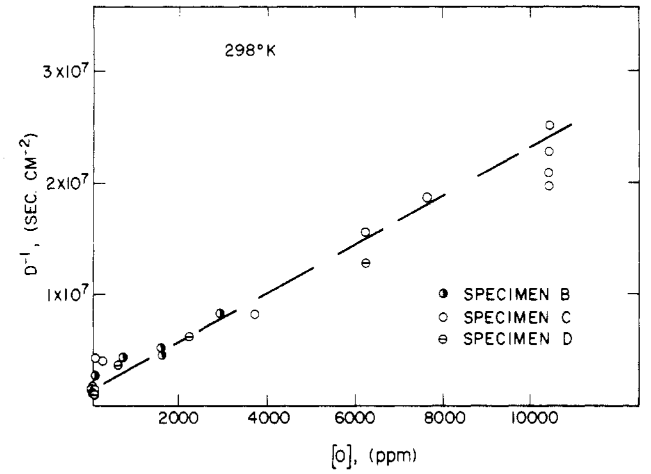

Figure 2. Reciprocal of the diffusion coefficient of water in low-density polyethylene as a function of the concentration of oxygen bound to the polymer.

of a vapor, the transmission rate at steady state is governed by the permeation coefficient, which is proportional to *DS*. Thus, permeation is unaffected by oxidation of the polymer over the range of concentration attained in this study.

The effect of temperature on *S* and *D* was determined between room temperature and 60 °C for sample C, as received and after oxidation, [O] = 550 and 8200 ppm, respectively. Results are shown in Figures 4 and 5. The activation energies for diffusion of as-received and oxidized material are 9 and 14 kcal/mol.

IV. Oxygen Trap Model

The model to be developed in this section involves polymer-bound oxygen traps that are deep enough to bind the water but not so deep as to remove water from the diffusion process. Following thermal oxidation a variety of oxygen species are present[20,21] and these groups are expected to differ significantly in their affinity for water. The solubility and diffusion results shown in Figures 1, 2, 4, and 5 can be described by the following equations:

$$S = 7.5 \times 10^{7} \exp(-10500/RT)F([\mathrm{O}],T) \qquad (1)$$

$$D^{-1} = 0.35 \exp(7500/RT)F([\mathrm{O}],T) \qquad (2)$$

where

$$F([\mathrm{O}],T) \equiv 6.1 \times 10^{-8}[\mathrm{O}] \exp(7500/RT) + \exp(1500/RT) \qquad (3)$$

$$DS = 21 \times 10^{7} \exp(-18000/RT) \qquad (4)$$

S is the solubility of water and [O] is the concentration of oxygen bound to the polymer as analyzed by neutron activation analysis techniques, both expressed as micrograms per gram of polymer. *D* is the diffusion coefficient, cm^2/s, *T* the absolute temperature, and *R* is given in calories/(mole degree). The agreement between eq 1 and 2 and the experimental results is illustrated in Figures 1–5 (dashed lines from eq 1 and 2). As discussed previously, the oxygen concentration of the as-received sample C is thought to be present as an ester having negligible effect on water absorption. The initial concentration of 550 ppm was thus subtracted from the total oxygen concentration in obtaining fits to the equations.

The striking feature of these equations is the commonality of the [O]-dependent term, and consequent [O] independence of *DS*, eq 4 and Figure 3. The energy 10 500 cal/mol is the heat of vaporization of water and thus accounts for the vapor pressure with which the polymer is initially equilibrated. The energy 1500 cal/mol is a measure of the slight attraction that the water molecules feel for the hydrocarbon matrix. This exponent is small but a satisfactory fit cannot be obtained with a value of zero. The energy 7500 − 1500 = 6000 cal/mol is a measure of the depth of the oxygen traps relative to the hydrocarbon medium. Note that the heat of vaporization was not treated as an adjustable parameter in this fit. The energy 7500 cal/mol in the diffusion coefficient is an activation energy component that does not have a simple interpretation in the present model.

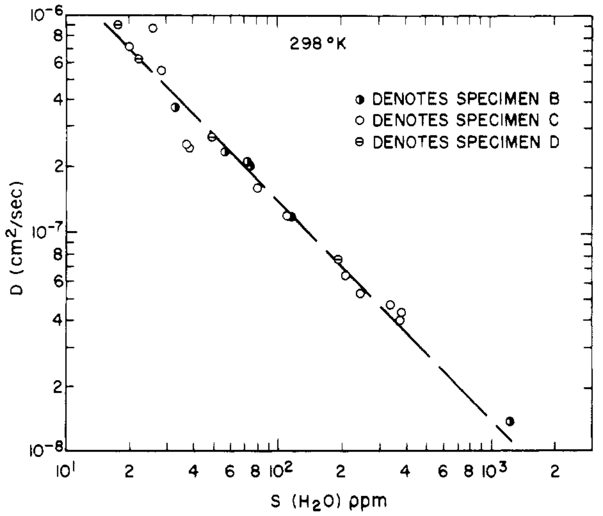

Figure 3. Diffusion of water vs. solubility of water for low-density polyethylenes of varying oxygen content. *DS* is seen to be independent of oxygen content.

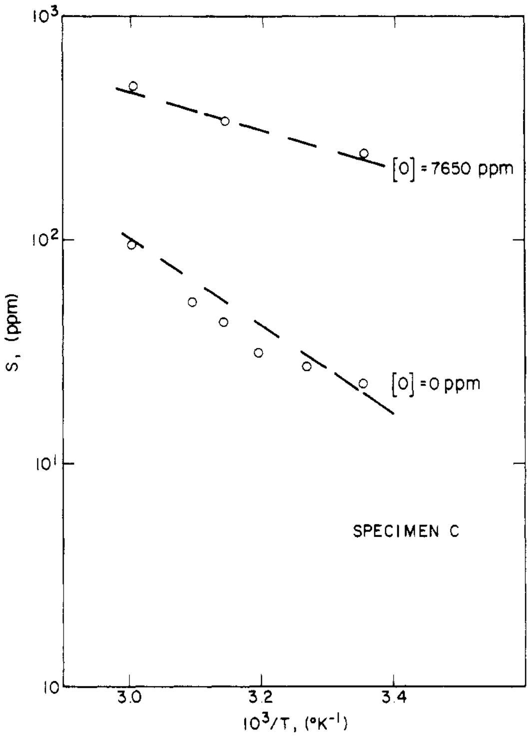

Figure 4. Water solubility in low-density polyethylene as a function of reciprocal temperature.

The trap energy 6000 cal/mol is deep enough that the molecules of water have a strong tendency to enter the traps. The Boltzmann factor, relative to the hydrocarbon matrix, is

$$\exp(6000/RT) > 10^{4} \qquad (5)$$

The population of water in the traps, however, will depend upon other factors, including the trap volume and

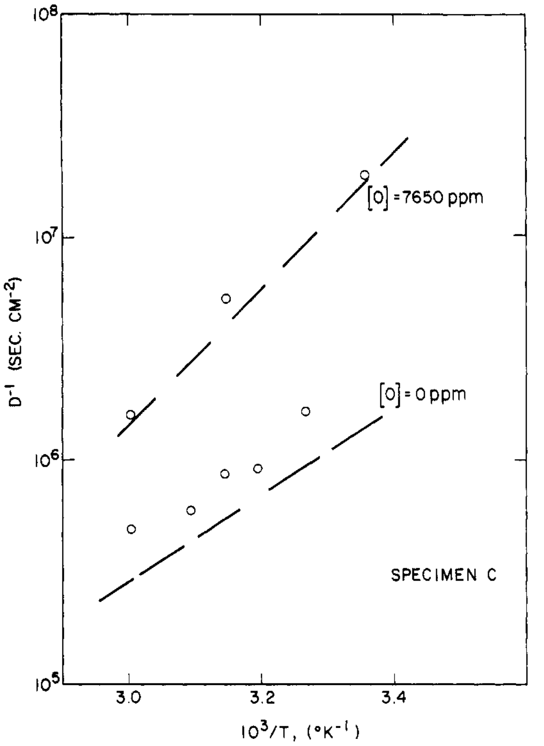

Figure 5. Reciprocal of the diffusion coefficient of water in low-density polyethylene as a function of reciprocal temperature.

the volume available to the water in the hydrocarbon. We assume that water can only enter the amorphous regions of the polymer and a liquid-like free volume will be available. The concentration of bound oxygen is small in these experiments and thus the volume of available hydrocarbon does not vary appreciably over the range of oxidation considered.

In its simplest form the model considers two kinds of water inside the polymer: water associated relatively strongly with bound oxygen traps and water dissolved in the amorphous regions of the polymer. The dissolved or "hydrocarbon" water is mobile and responsible for observed permeation. Water is immobile in the traps but a given molecule tends to escape from a trap in a time of order

$$(kT/h)^{-1} \exp(6000/RT) \sim 4 \times 10^{-9}\ \mathrm{s} \qquad (6)$$

Thus, as a water molecule diffuses through an oxidized polyethylene it moves rapidly through the hydrocarbon environment but spends part of its time immobilized in the traps. As the concentration of traps increases, a given water molecule spends more time in traps, thereby impeding diffusion. The number of water molecules dissolved in the polymer increases, however, and the effects of oxygen on S and D cancel one another. Thus the resultant permeation rate is independent of oxygen.

The number of water molecules in a given state (i.e., vapor, hydrocarbon, or trap) is given by[22,23]

$$f_i = (V_i/Q) \exp(-\epsilon_i/kT) \qquad (7)$$

where V_i is the volume of the state, ϵ_i the energy, and Q the partition function. If molecular rotation is neglected

$$Q = V_t \exp(-\epsilon_t/kT) + V_h \exp(-\epsilon_h/kT) \qquad (8)$$

considering only the water inside the polymer. It follows that the coefficient $6.1 \times 10^{-8}[O]$ in eq 1–3 is to be identified with V_t/V_h. V_t is equal to the number of traps multiplied by the individual trap volume:

$$V_t = v_t n_t = v_t \times 0.3 \times 10^{17}[O] \qquad (9)$$

where [O] is the oxygen concentration in parts per million by weight (as in eq 1 and 2) and we have assumed each oxygen to be a trap. Therefore

$$v_t \sim 2.0 \times 10^{-24} V_h \qquad (10)$$

Following a similar line of reasoning for the equilibrium between saturated water vapor and the "hydrocarbon" water in the unoxidized polymer,

$$Q = V_v \exp(-\epsilon_v/kT) + V_h \exp(-\epsilon_h/kT) \qquad (11)$$

From eq 1, $\epsilon_h - \epsilon_v = -1500$ cal/mol. Empirically the number of water molecules in the polymer is roughly equal to the number of water molecules in an equal volume of saturated vapor. Thus

$$V_h \exp(1500/RT) \sim 12 V_h \sim 1$$

and $V_h \sim (1/12)$ cm^3/g of polymer.

Note that the exclusion of water from the crystalline regions does not affect this estimate if the bound oxygen is distributed uniformly throughout the polymer bulk. It is likely that the oxygen in distributed uniformly throughout the bulk, as the samples were oxidized well above the melt and molded into sheets. V_h is not unreasonable as a "free volume" magnitude.

Combining this result with eq 10 we find

$$v_t \sim (1/6) \times 10^{-24}\ \mathrm{cm}^3$$

which is very small for an elementary trap volume.

A more reasonable trap volume can be obtained if the water molecules are assumed to be subjected to hindered rotation in the dissolved and trapped states. Independent NMR evidence supports this assumption (see section VI). With the inclusion of restricted rotation, the equilibrium between saturated vapor and unoxidized polymer is characterized by a partition function

$$Q = V_v \exp(-\epsilon_v/kT) Q_{vr} + V_h \exp(-\epsilon_h/kT) Q_{hr} \qquad (12)$$

where Q_{vr} and Q_{hr} are the vapor and hydrocarbon rotational partition functions. Reasoning as before

$$V_h \sim (1/12)(Q_{vr}/Q_{hr}) \qquad (13)$$

for $\epsilon_h - \epsilon_v = -1500$ cal/mol.

$$Q_r = 4\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}/h^3 \qquad (14)$$

for a freely rotating molecule with moments of inertia A, B, and C. For water[22]

$$Q_r = 43 = Q_{vr}$$

and

$$V_h \sim (1/Q_{hr})(43/12) \qquad (15)$$

Similarly, as in eq 10

$$v_t \sim 2.0 \times 10^{-24}(Q_{hr}/Q_{tr}) V_h$$

$$v_t \sim 2.0 \times 10^{-24}(1/Q_{tr})(43/12) \qquad (16)$$

If the rotation is substantially quenched in a trap, $Q_{tr} \sim 1$, yielding a trap volume of 7×10^{-24} cm^3. Q_{hr} is presumably intermediate between Q_{tr} and Q_{vr}, i.e., 1 and 43, but the magnitude of Q_{hr} does not affect the trap volume.

Other factors must be considered. The foregoing analysis has been carried through on the assumption that each oxygen atom that is bound to the polymer constitutes a trap. There is evidence, below, that some forms of polymer-bound oxygen bind water more effectively than others. It is only necessary to assume an approximate proportionality of trap concentrations with [O], and the preceding estimate of the trap volume will be modified by

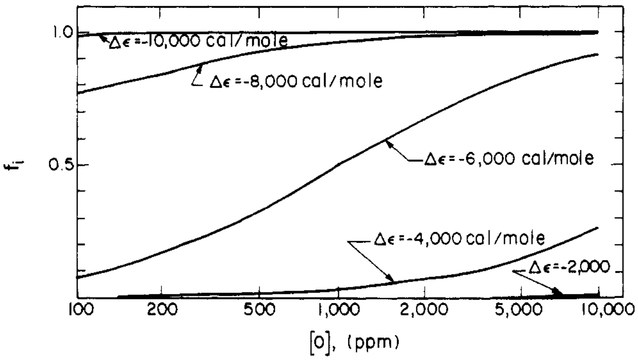

Figure 6. Fractional occupancy of traps at room temperature as a function of the concentration of oxygen bound to the polymer.

the coefficient of proportionality. In any case, the volume of the traps is plausible when viewed as some weighted average of the various traps present.

The fraction of water in traps (as opposed to "hydrocarbon water") is given directly by the bracket term of eq 1:

$$f_t = \frac{6.1 \times 10^{-8}[\mathrm{O}] \exp[-(\epsilon_t - \epsilon_h)/RT]}{6.1 \times 10^{-8}[\mathrm{O}] \exp[-(\epsilon_t - \epsilon_h)/RT] + 1} \qquad (17)$$

This function is illustrated graphically in Figure 6. It is apparent that the trap occupancy traverses the range zero to one (near room temperature) in the energy range $\epsilon_t - \epsilon_h = -4000$ to -8000 cal/mol. Deeper traps will bind the water tightly, as a hydrate. Shallower traps will have no observable effect on solubility or diffusion.[31]

V. Molecular State of the Bound Oxygen

Oxygen-containing carbons have been identified and analyzed in some of the more heavily oxidized samples of branched polyethylene studied. A detailed account of these experiments is given in the following paper,[24] but a brief report of the results will be included here because it bears on our conclusions concerning the molecular nature of the oxygen traps.

Concentrated (24–30%) solutions of the polymers in 1,2,4-trichlorobenzene were prepared. Care was taken to avoid further oxidation during the solution process.[32] Carbon-13 spectra were collected at 120 °C on a Varian XL-200 NMR spectrometer employing Overhauser enhancement. About 20000 transients were accumulated for adequate signal-to-noise in heavily oxidized specimens (of the order of 10^4 ppm oxygen). Duplicate spectra were found to be in good agreement. Assignments were made according to the method of Cheng et al.[21]

Analytical data for samples B, C, and D are exhibited in Table II. These results reveal the presence of the expected molecular forms: ketones, alcohols, hydroperoxides, and carboxylic acids. Samples C and D are similar, as expected, when one takes account of the hydroperoxide-to-alcohol conversion process.[21] The rather large differences between C and D on the one hand and B on the other were not anticipated in view of the similarity of the behavior of all three materials illustrated in Figures 1 and 2.

Copolymers of ethylene and carbon monoxide are known to contain oxygen predominantly as ketone groups.[25] A copolymer of this type, shown by ^{13}C NMR to contain only keto oxygen, has been studied, yielding $S = 87$ ppm for $[\mathrm{O}] = 7900$ ppm. This is about one-third of the water solubility expected for thermally oxidized polyethylene, Figure 1. Appealing to eq 17, one concludes that ketone traps are 4000–5000 cal/mol deep, compared with 6000 cal/mol for the dominant species. Consistent conclusions can be drawn from diffusion results for the copolymer.

Table II
Relative Distribution of Carbons Attached to Oxygen

	sample B	sample C	sample D
% ketone	57	21	18
% secondary alcohol	14	55	40
% tertiary alcohol	7	6	7
% secondary hydroperoxide[a]		15	32
% carboxylic acid	22	4	4

[a] Note that the secondary hydroperoxide can decompose to yield secondary alcohol during sample preparation and NMR measurement.

Similarly, unoxidized polymer C contains $[\mathrm{O}] = 550$ ppm, which has been identified as ester (possibly added by the supplier) by infrared spectroscopy, but exhibits no corresponding solubility of water. It can thus be concluded that ester traps are less than 4000 cal/mol deep.

Therefore alcohol, hydroperoxide, and carboxylic acid groups are identified as the dominant traps in branched polyethylene. Referring to polymer C, the results exhibited in Figures 1, 2, 4, and 5 support the strong conclusion that the alcohol traps are about 6000 cal deep. From the data for polymer B it is concluded that carboxylic acid traps are at least as deep, and likely deeper. Hydroperoxide traps are probably strong traps as well.

VI. Motional State of Trapped Water

In section IV it was found necessary to invoke some restriction of molecular rotation of trapped water in order to obtain a reasonable interpretation in terms of the model. In this section independent evidence will be presented in support of the assumed hindrance. In the first experiment polymer C, oxidized, $[\mathrm{O}] = 8200$ ppm, and saturated with water, $S = 240$ ppm, was examined in the solid state by proton NMR analysis. The proton signal was sought, employing the decoupler coil of a high-sensitivity probe using a Varian XL-200 spectrometer operating at 200 MHz. "Block averaging" was used to avoid dynamic range problems. Pulses of 90° and 5-s relaxation delay were employed. No narrow proton signal was observed on the very strong signal (~1 kHz wide) from the protons in the amorphous regions of the polymer. Sufficient accumulations were collected so that an unbroadened water peak should have been visible at a signal-to-noise ratio of a least 3:1. No narrow resonance was observed. From this negative result it is concluded that the proton resonance is broadened by damping of its motion.

In a second experiment D_2O was absorbed by the same polymer, $[\mathrm{O}] = 8200$ ppm, D_2O concentration 135 ppm. The solid polymer was examined by deuterium NMR at 30.7 MHz on the Varian XL-200 spectrometer (84085 scans, 1-s relaxation interval). A broad signal was observed with no sharp features, suggesting that the water is not isotropically mobile on a time scale of the order of 10^{-11} s.

In a third experiment a deuterium signal was observed at 20 °C in a solid sample of polymer B which was saturated with D_2O ($S = 630$ ppm D_2O, $[\mathrm{O}] = 18900$ ppm). This experiment was carried out at 55.26 MHz on a solid-state deuterium spectrometer[26] employing a quadrupole echo pulse sequence[27,28] (10-MHz digitization rate, 30-μs intrasequence delay and a 2-s repetition rate, 36604 scans). The resonance consists of a central peak (width 3 kHz) and a superimposed doublet of width 87 kHz. The central peak is ascribed to dissolved D_2O with a correlation time in the range of 10^{-9} s at 20 °C. This correlation time is interpreted as a characteristic time for rotation of the water molecules, in agreement with conclusions drawn from the model for solubility and diffusion (see section IV). The doublet is ascribed to deuterium that has exchanged with polar groups in the polymer.

Parallel NMR experiments were performed with the nonpolar penetrant, cyclohexane, diffused into oxidized and unoxidized polyethylene in approximately the same concentrations as water. Cyclohexane was chosen for these measurements because it most closely resembles polyethylene but does not have the added complication of segmental hopping that would be introduced by a small linear alkane.[29]

In contrast to the broad (3 kHz) line width observed for D_2O in the oxidized polymer sample, the deuterated cyclohexane line width is so narrow that it is determined primarily by magnetic field inhomogeneities. The deuterated cyclohexane in oxidized polyethylene readily gives a signal under high-resolution conditions, whereas the D_2O associated with polyethylene does not. This result suggests that the respective mobilities of D_2O and cyclohexane-d_6 are different by at least 2 orders of magnitude. Furthermore, the NMR signals for deuterated cyclohexane in oxidized and unoxidized polyethylene are similar. Taken together, these results show that cyclohexane as a diffusant in oxidized polyethylene behaves in a significantly different manner than does water. These data provide strong support for the oxygen trap model.

VII. Conclusions

The oxygen dependence of water solubility and diffusion in branched polyethylene has been treated in terms of a model in which the polymer-bound oxygens act as traps or binding points for the water. The molecular nature of the traps has been identified and an approximate measure of the strength of the binding has been deduced. Physical parameters of the model are reasonable within the limitations of present knowledge of structural details of the partially crystalline polymers. Alcohol, hydroperoxide, and carboxylic acid groups bind the water most strongly, ketone groups are markedly weaker traps, and ester groups have a negligible effect.

It is a result of the model, in agreement with experimental results, that the oxygen effect on solubility and diffusion cancels out in the permeation coefficient *DS*. That is, when polyethylene serves as a barrier to water vapor transmission, the rate of transmission does not depend upon bound-oxygen content. Physically, there are always the same number of "hydrocarbon" waters which are unaffected by oxygen in their rate of diffusion. An individual water molecule, however, samples the "hydrocarbon" state and the "trap" state many times during an experiment and its rate of movement is diminished as it spends more and more time in traps.

The simplicity and success of the model in branched polyethylene suggest many further experiments. Preliminary results indicate that linear polyethylene can be treated similarly. Extension of the model to polyethylenes containing other polar groups should follow directly. It remains to be shown that these ideas will be useful in polymers that contain oxygen groups as part of their basic structure.

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Registry No. Polyethylene (homopolymer), 9002-88-4; water, 7732-18-5.

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(30) We choose to define *S* as a solubility in units of grams of water per gram of polymer, rather than the more conventional designation as a solubility coefficient with units cm^3 of water vapor (STP) per cm^3 of polymer per atm pressure. The solubility coefficient is not central to the analysis, and *S* is convenient in discussing the concentration of water (in equilibrium with saturated water vapor) in the context of bound-oxygen concentration.

(31) Note that even for traps as deep as −6000 cal/mol (i.e., those dominant in branched polyethylene) only a small fraction are occupied at any moment. This probability of occupancy is given by $[S - S(0)]/[O] \sim {}^{1}/_{30}$, where $S(0)$ is the hydrocarbon solubility of water, <20 ppm.

(32) Samples were prepared under nitrogen in degassed solvents. Santonox-R antioxidant was added at 0.05% concentration.