A Method for the Determination of the Solubility of Hydrogen in Polyethylene

Shigeo Kubo and Malcolm Dole*

Department of Chemistry, Baylor University, Waco, Texas 76703. *Received June 26, 1973*

ABSTRACT: A new method and perhaps the only method suitable for the measurement of the solubility of hydrogen in single crystalline polyethylene is described. The new technique consists in freezing in the soluble hydrogen by plunging the solubility cell containing the equilibrium mixture of hydrogen and polyethylene into liquid nitrogen at which point the ambient hydrogen can be pumped out at leisure and the soluble hydrogen later determined at room temperature as previously described. This method is also applicable to ordinary bulk polyethylene and yields, we believe, more accurate data. The solubility of hydrogen in single crystalline polyethylene is about ten times greater than in bulk polyethylene when the solubilities are compared at equal amorphous volume fractions as measured by density determinations. This method can be applied in addition to measurements of the solubility of helium in polyethylene.

Our initial interest in measuring the solubility of hydrogen in polyethylene was stimulated by the marked effect of molecular hydrogen in catalyzing the decay[1] of alkyl radicals in irradiated polyethylene. From this interest arose our development[2] of a new semimicro method for the measurement of hydrogen in ordinary bulk polyethylene. More recent data[3] on the decay of free radicals in single crystals of PE demonstrated that the alkyl radical decay was considerably faster than in ordinary bulk polyethylene in the presence of hydrogen. Thus it became imperative to know the solubility of hydrogen in single crystalline polyethylene. Unfortunately our original semimicro method was inappliable to polyethylene single crystals. The reason for our inability to apply the new method to single crystalline polyethylene is illustrated by the data of Figure 1 where the grams of hydrogen/100 g of polyethylene, σ, remaining in the polyethylene after flushing the ambient hydrogen out of the solubility cell is plotted as a function of the square root of the flushing time. In our solubility method it is necessary, of course, to separate as cleanly as possible the ambient hydrogen from the hydrogen actually dissolved in the polyethylene at equilibrium. In the original work[2] this was accomplished by sweeping nitrogen gas through the cell at high velocity for a period of usually 5 sec, but when this method was attempted using single crystal mats of polyethylene, the dissolved hydrogen diffused out of the single crystals with such rapidity, that it was impossible to separate even roughly the ambient hydrogen from that which was dissolved. It is clear from Figure 1 that it would have been quite impossible to extrapolate with any certainty the curve for the single crystals back to zero time so as to obtain the equilibrium solubility value. Hence a new method applicable to single crystals had to be invented. Such a method, which is also applicable to other forms of polyethylene, is described in detail below.

Knowing the activation energy (6.71 kcal/mol) for diffusion of hydrogen in low-density polyethylene of 56% amorphous content by volume as determined by Ash, Barrer, and Palmer,[4] it is easy to estimate that at −196° the diffusion coefficient would be less by a factor of 10^{-14} than that at 25°. This calculation suggests that the diffusion of hydrogen in polyethylene would be negligible at −196° if the data for bulk polyethylene could be transferred to single crystalline polyethylene. Actually, our new method described below was suggested by an observation made many years ago[5,6] in work on the radiation chemistry of polyethylene, namely that in the irradiation of polyethylene at −196°, the evolved hydrogen was "frozen in" the polyethylene and could not diffuse out until the polyethylene was heated to higher temperatures, about 150°K. Hence we decided to see if it could be possible to freeze the soluble hydrogen in the polyethylene samples by quickly plunging the solubility cell containing hydrogen gas at solubility equilibrium with the polyethylene sample into liquid nitrogen after which the ambient hydrogen could be pumped out at leisure. It was hoped that the cooling rate would be fast enough so that the amount of dissolved hydrogen would not be changed during the cooling period. Actually, the temperature coefficient of hydrogen solubility in single crystalline polyethylene is practically zero, at least over the temperature range 0–45° as will be demonstrated by data given in a later publication. Another refinement was to replace all glass tubing and greased glass stopcocks with all metal tubes and valves so as to remove the possibility of some hydrogen dissolving in the stopcock grease.

Except for these modifications the technique was the same as that used previously.[2]

Experimental Section

Materials. All samples were prepared from the Marlex-6002 film which was used in the previous work.[2] The bulk sample was recrystallized from the melt by cooling in air under vacuum in an 8-mm Pyrex tube. Density of this sample as measured at 25° in a toluene–monochlorobenzene density gradient column was 0.962 g/cm^3 which corresponds to a weight fraction of the amorphous part (α_w) equal to 0.229 based on the relation described in the previous publication.[2] The single crystalline sample was prepared from a 0.2 wt % solution of polyethylene in *p*-xylene at 90°. The single crystalline structure of the sample was supported by electron micrographs of one-stage replicas which showed the typical single crystal layering. The density of the single crystal sample was 0.978 giving α_w equal to 0.124.

Sample Loop and Vacuum System. The sample loop and vacuum system were essentially the same as those previously[2] used except that metal valves (Nupro SS-4TW) replaced the glass stopcocks, copper tubing of 0.25-in. diameter replaced the glass tubing and the sample loop was also made of copper tubing. The latter was U-shaped, 15 cm long with a total volume of approximately 3 cm^3. Copper tubing was used for the sample loop to make the thermal conductivity as high as possible. A separate vacuum line with a diffusion pump was used to pump out the ambient hydrogen at −196°.

Experimental Technique. The polyethylene was placed in the bottom part of the U tube in order to obtain good thermal contact with the copper and to ensure as rapid a cooling rate as possible.

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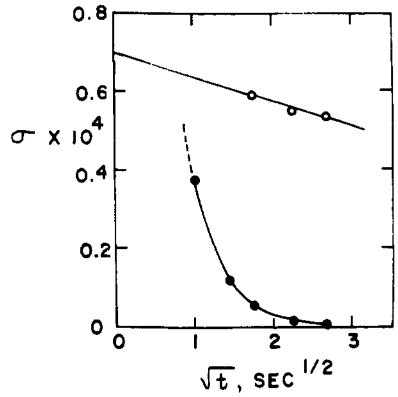

Figure 1. Grams of hydrogen/100 g of polyethylene × 10^4 as a function of the square root of the time of flushing nitrogen gas through the solubility cell. Open circles, film polyethylene of α_w equal to 0.245^2. Closed circles, single crystals of polyethylene of α_w equal to 0.124. Initial hydrogen pressure 1 atm.

The bottom part of the U tube made the first contact with the liquid nitrogen. Before admitting hydrogen, the air was removed from the U tube by repetitive evacuation, then hydrogen admitted to a pressure such that on placing the sample into a constant-temperature bath at a selected temperature, the pressure would be 1 atm (except in the experiments in which the appliability of Henry's law was tested when the hydrogen pressure was varied from 0.25 to 1 atm). After solubility equilibrium had been attained (after 2 hr or more), the sample loop was plunged into the liquid nitrogen bath and cooled for 5 min at this temperature. Both a closed loop system and another in which the loop was connected to a reservoir of hydrogen gas at 1-atm pressure (an open loop system) were tried. In the former the volume of hydrogen gas was constant so that on cooling the pressure dropped in accordance with the perfect gas law. Such a drop in pressure would cause the solubility of the hydrogen in the polyethylene to be reduced. In the open system the hydrogen pressure was maintained at 1-atm pressure during the entire cooling period (5 min). It turned out, however, that no significant difference could be detected between the results obtained by these two methods. Evidently, the small polyethylene sample, from 30 to 300 mg in weight, cooled more rapidly than the entire loop system so that the diffusibility of the hydrogen in the sample fell essentially to zero before any hydrogen diffused out of the polyethylene sample. On the basis of these tests most of the experiments were made with the closed loop system whose operation was more convenient than that of the open loop system.

After the sample had been cooled to −196°, the evacuation of the ambient hydrogen could be carried out for as long a period as desired without losing any of the dissolved hydrogen. This fact is demonstrated by the data of Figure 2 where the amount of dissolved hydrogen remaining in the single crystalline polyethylene, σ, is plotted as a function of the square root of the time. Analogous results obtained during flushing at −78, 0, and 25° are included in the same figure for comparison. It is seen that σ is independent of the evacuation time only at −196°. In fact at the latter temperature it is unnecessary to apply any correction for the diffusive loss of dissolved hydrogen as was required in the previous work.[2] Although shorter or longer times could have been adopted, 20 min was selected as a standard evacuation time at −196°. A vacuum as low as 3×10^{-5} Torr was usually attained during this standard evacuation procedure after which the loop was closed, and then later subjected to the desorption process at 25°. Approximately as long a time as the sorption process was applied to this desorption process, after which the loop was connected to the gas chromatograph input system to measure the quantity of hydrogen gas which diffused out of the polymer sample. After the injection the loop was closed again and kept for as long as 15 hr to test if any significant amount of hydrogen had remained for further desorption. Whenever this was found to be the case, new experimental conditions were adopted with longer sorption and desorption times as required for attaining sorption or desorption equilibrium. In this way a second desorption period and injection of hydrogen into the gc as used in the first work[2] were avoided. This demonstrates that use of an all metal loop and valve system eliminated the uncertainty due to hydrogen dissolving in the stopcock grease.

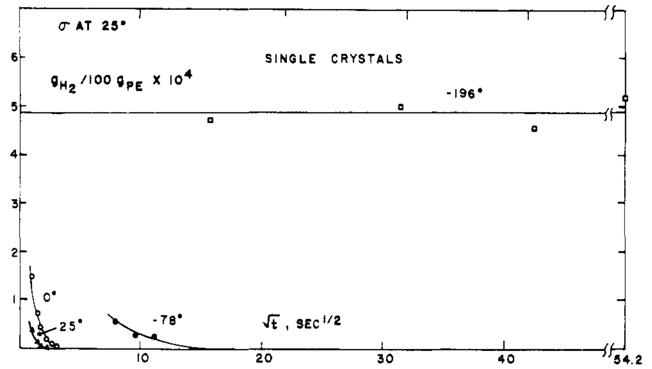

Figure 2. Same as Figure 1 except limited to single crystalline polyethylene. Data at 0 and 25° by the nitrogen flushing method. Data at −78° obtained after quenching in Dry Ice-methanol mixture and at −196° after quenching in liquid nitrogen.

Table I
Hydrogen Solubility in Polyethylene as Obtained by Three Different Methods at 25° and 1-Atm Pressure of Hydrogen for a Bulk Polyethylene Sample of Amorphous Weight Fraction Equal to 0.229

Method	σ (10^{-4} g of H_2/100 g of PE)	σ_a[a]
Flushing method with glass system[2]	0.767	3.35
Flushing method with metal system[b]	0.807	3.52
Quenching method with metal system[b]	0.876	3.82

[a] σ_a is σ divided by the amorphous weight fraction. [b] Average of four experiments.

The sorption and desorption times varied from 3 hr for bulk polyethylene to 6 hr for a compressed cylinder of polyethylene single crystals and to 2 hr for single crystal mats of polyethylene of diameter less than 0.1 cm. These small mats were separated from larger crystals by sieving. No difference was detected in the solubility of hydrogen between these two samples of the single crystals.

Experimental Results

Comparison of Data from the Liquid Nitrogen Quenching Method with Those Obtained by the Earlier Method.[2] In order to check on the reliability of this new method we repeated the solubility measurements on the bulk polyethylene sample at 25° first using the old method but with the glass stopcocks and sample tube replaced by metal valves and tube. Blank tests of the empty copper tube system were carried out to make sure that no hydrogen would be sorbed by the copper tubes or metal valves. A small amount of sorbed hydrogen was found and a correction of about 1% due to hydrogen retained in the empty cell was subtracted from subsequent measurements.

The next experiments were done at 25° on the same sample using the liquid nitrogen quenching method. The data obtained by these two modifications are compared in Table I with the solubility estimated at α_w equal to 0.229 from the data of the previous work.[2]

The data of Table I demonstrate that the new liquid nitrogen quenching method gives results in reasonable agreement with those obtained previously. The new value for the bulk polyethylene as measured by the flushing method, which should have been improved by the use of the all metal system is slightly higher than that estimated from the earlier work.[2] The value of σ_a calculated for 100% amorphous content is 3.52×10^{-4} g of H_2/100 g of polyethylene at 1-atm pressure compared to the mean

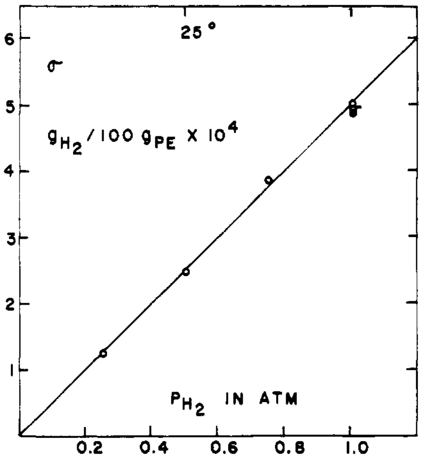

Figure 3. Solubility of hydrogen in single crystals of polyethylene at different equilibrium pressures of hydrogen gas. Liquid nitrogen quenching method. Open circles, data for compressed cylinders in the closed loop system. Circle with dash, σ for the compressed cylinder in the open loop system. Solid circle, sieved polyethylene in the closed loop system.

value of 3.35×10^{-4} from the previous study. The value of σ_a calculated from data obtained by the liquid nitrogen quenching method is 3.82×10^{-4} g of H_2/100 g of polyethylene which is about 10% higher than that obtained in the all metal system by the flushing method. As the flushing method required an uncertain extrapolation to zero flushing time, we believe that the liquid nitrogen quenching method gives the most reliable results.

We have also tested this method with helium and found it to yield very consistent data. By appropriate choice of the quenching temperature it should in principle be applicable to many other gases.

Application of the Liquid Nitrogen Quenching Method to Single Crystalline Samples. Returning now to the problem of measuring the hydrogen gas solubility in single crystals of polyethylene, which stimulated this work, values of σ as a function of the hydrogen gas pressure at 25° are shown in Figure 3. The nice agreement of the data with Henry's law and the fact that the line extrapolates to the origin at zero gas pressure lend support to the reliability of the data. As far as we know this new method is the only one by which the solubility of hydrogen in single crystals can be measured.

From Figure 3 it is possible to calculate that the solubility of the hydrogen in single crystals of polyethylene is about ten times greater than in bulk polyethylene when the comparison is made at equal amorphous weight fractions as measured by density determinations. More extensive data on the solubility of hydrogen in single crystals as well as in extended chain crystals and bulk polyethylene as obtained by the new method of this paper will be submitted for publication later.

We turn now to a consideration of the mechanism of diffusion of hydrogen in the single crystalline polyethylene. Unfortunately, we do not know the diffusion path of the hydrogen molecules, thickness of diffusion layer or other details necessary for a theoretical interpretation of the abnormally high rate of diffusion of hydrogen in single crystals of polyethylene. Inasmuch as the diffusion equations[7] for diffusion out of a sphere involve the product *Dt*, where *D* is the diffusion coefficient and *t* the time, we should be able to obtain an estimate of the activation energy of diffusion by plotting the logarithm of the time for 90% of the gas to diffuse out, $t_{0.9}$, as a function of the reciprocal absolute temperature. This assumes that as we lower the temperature, the increased time required for diffusion out of a sphere is due solely to the decrease of *D* with temperature, in other words that *Dt* is a constant for 90% desorption. Such a plot is shown in Figure 4 and from the slope of the line an activation energy of 5.4 kcal/mol was calculated.

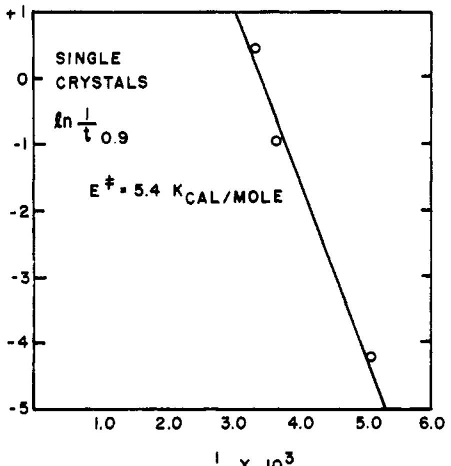

Figure 4. Arrhenius plot of the logarithm of the time necessary to desorb 90% of the hydrogen, $t_{0.9}$, as a function of the reciprocal absolute temperature.

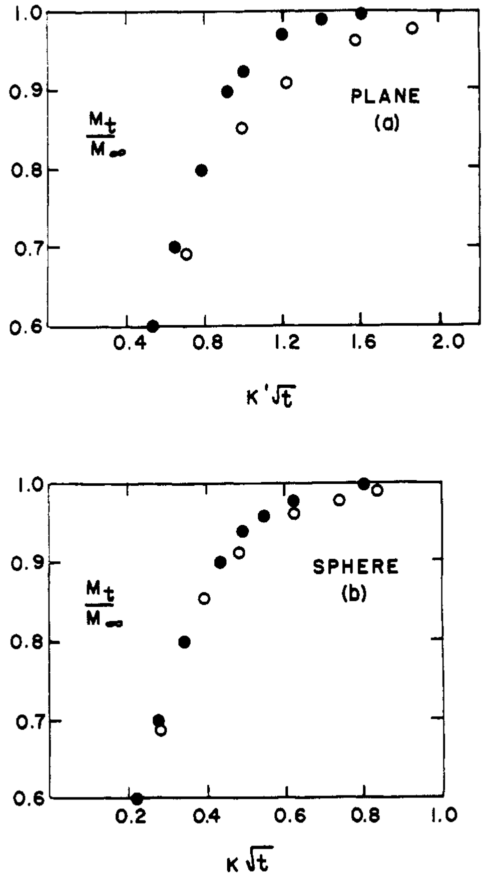

Figure 5. Comparison of our observed rates of desorption, open circles, with those theoretically estimated, solid circles, from (a) a plane sheet and (b) a sphere.

The diffusion data illustrated in Figure 2 correspond more nearly to diffusion from a sphere than from a plane sheet. This is roughly shown by comparing our values of M_t/M_∞ estimated from Figure 2 with values read off the theoretical curves of Crank, his Figures 4.7 for the plane sheet and 6.5 for the sphere. His data were chosen for *L*

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(7) See J. Crank, "The Mathematics of Diffusion," Oxford Univ Press, Oxford, 1970, p 86.

equal to infinity where L equals $a\alpha/D$ in which a is the radius of the sphere and α is given by the expression

$$3M_\infty/4\pi a^3C_0 = 1/(1 + 1/\alpha) \qquad (1)$$

C_0 is the initial concentration in the sphere, *e.g.*

$$C_0 = M_\infty/(4/3)\pi a^3 \qquad (2)$$

hence α must equal infinity for these boundary conditions. The ratio M_t/M_∞ is the ratio of hydrogen that has diffused out of the single crystals at time t divided by the initial amount of hydrogen. In Crank's terminology our M_t/M_∞ is equal to his $1 - (M_t/M_\infty)$. Comparison of the data of Figure 2 with the theoretical values are shown in Figure 5. In order to make such a comparison our observed times have been multiplied by a factor such that at M_t/M_∞ equal to 0.5, the observed and theoretical points agreed. At M_t/M_∞ equal to 0.5 there is not much difference between the sphere and the plane sheet data; it is at high values of M_t/M_∞ that the differences between the two assumed shapes become apparent. We conclude that diffusion out of the mats of polyethylene single crystals is more like that from a sphere than from a plane sheet.

Because our estimated activation energy for diffusion from the single crystals is not greatly different from that found for the bulk polyethylene samples,[2,4] the excessively rapid loss of hydrogen from the single crystals on flushing the ambient hydrogen out of the solubility cell as illustrated by the data of Figures 1 and 2 must be the result of a very short diffusion path. We imagine that the hydrogen diffuses for a short distance through the amorphous regions separating the single lamellae. As a single crystal lamella is typically 1–2 μm along one exterior edge of the crystal[8] it is apparent that the diffusion path for hydrogen molecules can be very short.

Acknowledgments. This research was supported by income from the chair in Chemistry at Baylor University endowed by a gift from The Robert A. Welch Foundation. We are indebted to the Phillips Petroleum Co. for the Marlex-6002 polyethylene.

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(8) See, for example, B. Wunderlich, "Macromolecular Physics," Academic Press, Inc., New York, N. Y., 1973, p 190.

The Nature of Asymmetry in Reverse Osmosis Membranes

Manuel Panar,* Harvey H. Hoehn, and R. R. Hebert

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ABSTRACT: The micellar morphology which may constitute a definition of asymmetry in a common class of reverse osmosis membranes is proposed. The structure, general to a range of polymer classes, is that of a partially fused but nearly pore-free monolayer of deformed spheres (400–800 Å) supported by a substrate composed of the same spheres randomly packed and less deformed so as to leave 75–100 Å interstices. This structure has elements in common with the solution from which the membranes are cast, and the unquenched cast, unprecipitated polymer solution. The morphology of the permeate side of the membrane, in contrast to that of the functioning feed side, can vary with composition and preparation.

This paper proposes a morphology of asymmetric reverse osmosis (RO) membranes of the type prepared by casting from mixed, or salt-containing solutions as first described by Loeb and Sourirajan.[1] The proposed structure is general to a range of polymer classes and, as such, may constitute a practical definition of this most common type of high flux membrane. The membranes are composed of a surface monolayer of polymeric spheres having diameters of several hundred ångstrom units. These spheres are deformed and partly fused so that few permanent pores remain. The surface monolayer is supported by a substrate of similar spheres randomly packed, less perfectly fused and relatively undeformed so that 75- to 100-Å interstices remain. This concept of asymmetry has implications with respect to the permeation mechanism in that it seems most consistent with mechanisms which invoke free volume (dynamic pores) rather than permanent pores. Moreover, the ability to characterize a new membrane class as having the desired morphology, prior to time-consuming optimization, represents an aid to membrane research.

Significant similarities exist between the morphology of the membrane, the structure of the solution from which the membrane is cast and the structure of the cast but unprecipitated protomembrane. Because of this relationship we will refer to the structural units as micelles. They are detected by electron microscopy in the casting solution when it is rapidly frozen to a clear glass and, even more significantly, the surface monolayer can be seen in the protomembrane within seconds after it is cast at room temperature. We suggest that the asymmetric morphology is determined by the liquid phase, and that the procedures used in membrane casting[2,3] perform their function largely by retaining the morphology of the cast solution without permitting total fusion of the micelles. The casting procedure must obviously also control the internal morphology of the micelles and the quantitative degree of fusion of micelles in the surface layer so as to yield the optimum free volume (dynamic pores). These latter topics will not be dealt with in this paper.

The micellar morphology is consistent with the well-established concept that a surface layer of roughly 1000 Å thickness is the functioning part of an asymmetric reverse osmosis membrane.[4] However, most descriptions of the surface layer treat it as being a thin layer which otherwise

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