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Solubilities and Diffusivities of Permanent Gases in Poly(phenolphthalein terephthalate)

R. T. Chern* and N. F. Brown

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695.
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ABSTRACT: Solubility and diffusivity of pure carbon dioxide, methane, ethane, oxygen, argon, and nitrogen in solution-polymerized poly(phenolphthalein terephthalate) [PPha-tere] were determined from independent sorption and permeation measurements. PPha-tere absorbs ~8 wt % carbon dioxide at 35 °C (20 atm), roughly 80% more than polycarbonate or polysulfone does. The carbon dioxide permeability of PPha at 35 °C exceeds 20 Barrers. The permselectivities, defined as the ratio of pure-gas permeabilities, for CO_2/CH_4 and CO_2/C_2H_6, respectively, are greater than 28 and 59 at 35 °C. The dual-mode model formalism was adopted to analyze the sorption and permeation data. Inference regarding the physical state of absorbed gas molecules is made. The equilibrium sorption parameters and the diffusion coefficients are correlated with the critical temperature of the gas and the dimension of the gas, respectively.

Introduction

Recent intensified searches for better gas-separation membrane and permeation barrier materials has led to the discovery of many polymers exhibiting extraordinary transport properties.[1-4] Our interest has been in the relationship between molecular features (including packing density, local chain mobility, and functional groups of the polymer and dimensions and the donor–acceptor nature of the penetrants) and transport parameters (including the diffusion and solubility coefficients of penetrants in the polymer). One of the polymers which we found to exhibit transport properties superior to commercial materials is the polyester of phenolphthalein and phthalic acid chloride. The effects of the nature of the phthalate (tere-, iso-, or a mixture of them) on the various properties of the polymer have been reported in a previous paper.[5] It was found that the para linkage in poly(phenolphthalein terephthalate) (to be called PPha-tere in this paper) resulted in a lower mass density of the polymer relative to its isophthalate counterpart (PPha-iso). The lower mass density of PPha-tere was considered equivalent to poorer packing since PPha-tere and PPha-iso are essentially isomers made of the same constituent atoms.

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* To whom correspondence should be addressed.

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Table I
Source and Purity of the Gases

gas	supplier	grade and purity
CO_2	MG Scientific Gases	Coleman, 99.99%
C_2H_6	Linde Specialty Gases	CP, >90.0%
Ar, N_2	Linde Specialty Gases	Ultra-high, >99.99%
CH_4	Air Products	Instrument, 99.7%
O_2	Air Products	Ultra-pure, >99.947%

In this paper, we report the solubilities and diffusivities of pure CO_2, N_2, O_2, CH_4, Ar, and C_2H_6 in PPha-tere at 35 °C up to 21 atm. Comparison with commercially available glassy polymers is included. Correlations for the solubility, diffusivity, and other properties of the gases following the formalism of the dual-mode theory[6] is also examined.

Experimental Section

Materials. Phenolphthalein and reagent-grade triethylamine were purchased from Fisher Scientific Co., while terephthaloyl chloride, HPLC-grade 1,2-dichloroethane, and the methanol were purchased from Aldrich Chemical Co. Gases used in this study are N_2, CO_2, CH_4, Ar, C_2H_6, and O_2. The suppliers and purities of the gases are listed in Table I. Poly(phenolphthalein terephthalate) was synthesized by reacting phenolphthalein with terephthaloyl chloride, following a slightly modified solution polymerization method developed by Morgan.[7] The polymerization protocol is described below.

Phenolphthalein was dissolved in 1,2-dichloroethane in a 1000-mL four-neck round-bottomed flask into which triethylamine was added. A nitrogen bubbler and an outlet tube were inserted through a rubber stopper, the stopper was placed in the first opening of the flask, a thermometer was inserted in the second opening, a stirrer with a Teflon impeller blade was inserted in the center opening, and a 100-mL graduated, stoppered addition funnel, which was connected to another nitrogen bubbler, was placed in the last opening. Terephthaloyl chloride dissolved in 1,2-dichloroethane was placed in the addition funnel. The flask was immersed in an ice/water bath. Medium speed stirring was started, and after about 10 min, the addition of the terephthaloyl chloride solution was begun at a rate that allows addition to complete in about 1 h. Additional 1,2-dichloroethane was then added to rinse the terephthaloyl chloride residue in the funnel. This mixture was added slowly to the reaction vessel. After the reaction, the solution was yellow, and a precipitate of a byproduct salt, triethylamine hydrochloride, was also formed. The mixture was allowed to stand for 1 h at room temperature. 1,2-Dichloroethane was then added to the mixture to dilute it. This mixture was then filtered with a glass filter with an average thickness of 47 mm and 4 μm pores to remove the solid contaminants. The filtrate was poured in methanol to precipitate the polymer, which was then recovered by filtration with a Buchner funnel. The polymer was washed with hot methanol and filtered again. The washed polymer was placed in a glass dish and dried in a vacuum oven at 80 °C for approximately 16 h. The dissolution, precipitation, washing, and drying sequence was repeated twice more. The dry, clean polymer was then stored in a dessicator for future use.

A Cannon-Ubbelohde viscometer in a constant temperature bath of 20 °C was used to determine the intrinsic viscosity of the polymer in s-tetrachloroethane. The Mark-Houwink constants, K and a, were taken from literature[8] to be 5.09×10^{-4} and 0.69, respectively. The intrinsic viscosity and viscosity-averaged molecular weight thus determined are 0.6961 dL/g, and 35 064, respectively.

Sorption and Permeation. Steady-state permeability to pure gases was measured with a barometric type of device where the pressure in a known downstream volume is monitored as the gas permeates through the film and accumulates in the downstream volume.[6,9] The downstream pressure was kept below 10 mmHg, and the upstream pressure was varied up to 21 atm. Sorption isotherms of the pure gases were measured with a dual-transducer barometric device.[10,11] Detailed procedures for the construction, operation, and calibration of the apparatus can be found in the literature.[6,9-12]

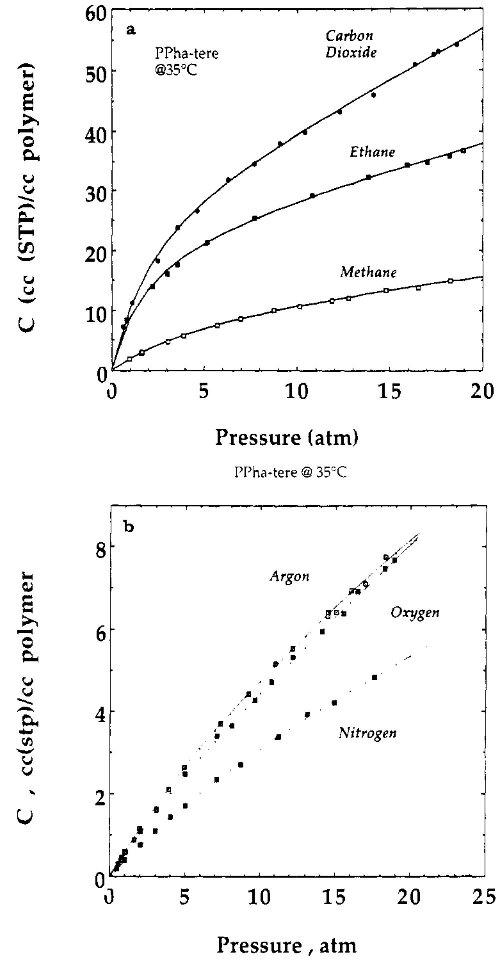

Figure 1. Equilibrium sorption isotherms for (a) CO_2, C_2H_6, and CH_4 and (b) Ar, O_2, and N_2 in PPha-tere at 35 °C.

All permeabilities were determined with a 0.8-mil-thick film that had been previously exposed to CO_2 at 21 atm for ~24 h while the downstream pressure was kept well below 10 mmHg. Films with this type of "history" were called "vectored" samples by Paul's group.[13] Specimens placed in the sorption chamber were films of ~0.8 mil thickness. All sorption isotherms reported here were determined after the polymer had been exposed to 21 atm of CO_2 for more than 24 h.

Results and Discussion

I. Equilibrium Solubility. Sorption isotherms of CO_2, CH_4, Ar, C_2H_6, N_2, and O_2 in PPha-tere are presented in Figure 1. The isotherms were analyzed according to the dual-mode model[6]

$$C = k_D p + C_H' bp/(1 + bp) \qquad (1)$$

where C is the molar concentration of the gas in the polymer, cm^3 (STP)/cm^3 polymer, p is the pressure of the gas, and k_D, b, and C_H' are dual-mode parameters, corresponding to Henry's law constant, Langmuir mode affinity constant, and saturation Langmuir capacity, respectively. A SAS nonlinear Marquardt regression routine was used; the program minimizes the sum of squares of the residues to fit the experimental data. The dual-mode sorption parameters for the various gases at 35 °C are listed in Table II. The solid lines in Figure 1 were computed values from eq 1 employing the parameters in Table II. Clearly, the calculated curves fit the experimentally determined points very well. The solubility increases in the order $N_2 < O_2 \approx Ar < CH_4 < C_2H_6 < CO_2$, the same trend as reported for many other glassy polymers. The solubilities of CO_2, CH_4, Ar, and N_2 in

Table II
Dual-Mode Sorption Parameters at 35 °C

gas	k_D, cm^3 (STP)/cm^3 polymer·atm	C_H', cm^3 (STP)/cm^3 polymer	b, atm^{-1}
CO_2	1.44	31.2	0.398
C_2H_6	0.829	23.6	0.497
CH_4	0.311	12.4	0.149
Ar	0.228	6.83	0.056
O_2	0.333	1.93	0.136
N_2	0.160	3.89	0.062

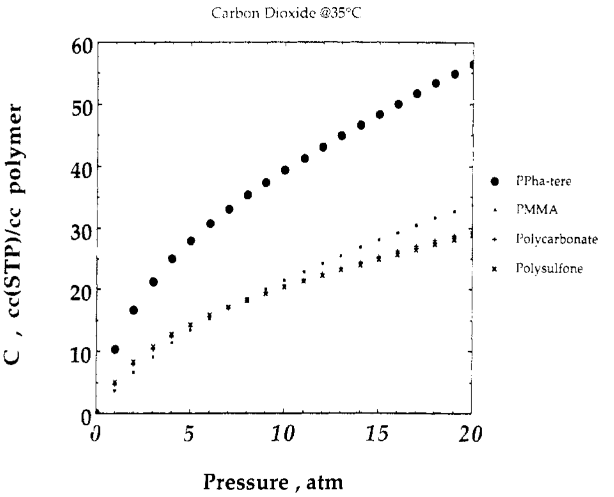

Figure 2. Comparison of CO_2 sorption isotherms for PPha-tere, poly(methyl methacrylate), Lexan polycarbonate, and polysulfone.

PPha-tere are much larger than those in polycarbonate,[14] polysulfone,[15] and poly(methyl methacrylate)[11] as illustrated in Figure 2 where the sorption isotherms of CO_2 in these polymers at 35 °C are compared.

Correlations for the Dual-Mode Parameters. In the absence of chemical reaction or specific interaction, the solubility of supercritical gases in liquids and rubbers typically observes Henry's law. The Henry's law constant, k_D, has been correlated with parameters that represent approximately the condensability of the gas,[16-20] including the critical temperature T_c, the Lennard-Jones potential well-depth, ϵ/K, and T_c^2. It has been reported that the correlation between the Henry's law constant and gas condensability applies to glassy polymers as well; moreover, the quantitative relationship between log k_D and ϵ/K for glassy polymers is similar to that for rubbers or liquids, suggesting a possible similarity in the mechanism of sorption.[17]

According to the assumptions made in the development of the dual-mode model, the apparent affinity constant of the penetrant toward the microvoids in the polymer, b, should show a similar dependence on gas condensability as the Henry's law constant, k_D, does. These correlations for PPha-tere together with data found in the literature for other glassy polymers are demonstrated in Figures 3 and 4, where the critical temperature, T_c, is used for representing the condensability of the gas. The solid lines were drawn to assist visualization of the correlation for PPha-tere. Roughly parallel lines can be drawn for the data of other polymers in the figure. Clearly, the correlation for any of the polymers in Figures 3 and 4 is reasonably good, albeit scattered. The influence of factors other than the condensability on the Henry's law constant cannot be ruled out in cases where specific gas–polymer attractions exist, but it appears to be relatively small in those systems included in Figures 3 and 4. Also clear from Figures 3 and 4 is that the k_D and b values of a given gas in different polymers can vary significantly even among aromatic polymers. The causes for these differences, either of energetic or entropic nature, however, wait to be identified.

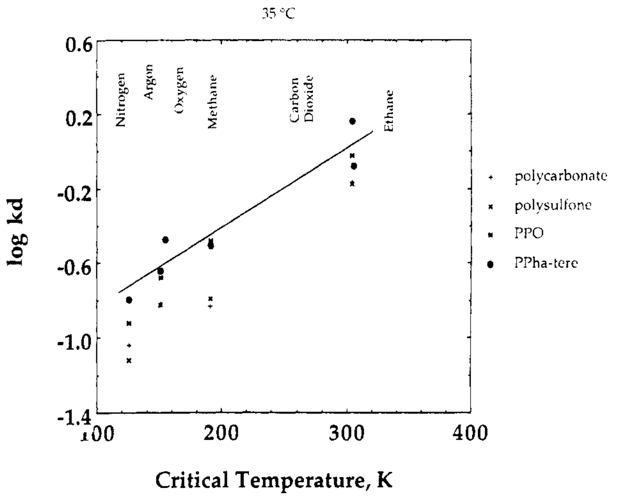

Figure 3. Correlation between the Henry's law constant, k_D, and critical temperature of the gas, T_c.

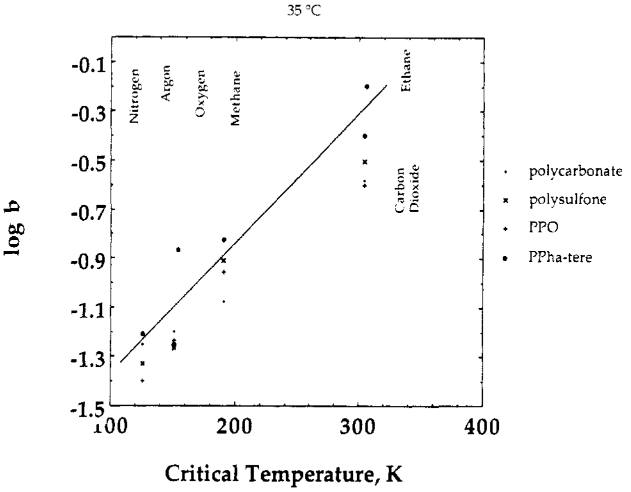

Figure 4. Correlation between the Langmuir affinity constant, b, and critical temperature of the gas, T_c.

The following equation was reported by Koros and Paul,[21] which has been extensively used for interpreting the C_H' data of CO_2 in many glassy polymers

$$C_H' = (\alpha_l - \alpha_g)(T_g - T)\frac{22415}{v^*} \quad (2)$$

where v^* is the sorbed molar volume of the penetrant in cm^3/g·mol and $\alpha_l - \alpha_g$ is the difference in thermal expansion coefficients at temperatures above and below the glass transition of the polymer. From eq 2, the ratio of C_H' for CO_2 over that of C_2H_6 in PPha-tere equals

$$\frac{(C_H')_{CO_2}}{(C_H')_{C_2H_6}} = \frac{v^*_{C_2H_6}}{v^*_{CO_2}} \quad (3)$$

Substituting into eq 3 the respective experimental C_H' values from Table II, one calculates $v^*_{C_2H_6}/v^*_{CO_2} = 1.32$. In other words, the sorbed molar volume of C_2H_6 is 1.32 times as large as that of CO_2 according to eq 3.

Fleming et al.[22] reported that the partial molar volume of CO_2 at 35 °C in polycarbonate is approximately equal to its infinite dilution molar volume in low molecular weight liquids. Ethane is expected to behave similarly since its critical temperature is very close to that of CO_2 and the experimental temperature, 35 °C. The

Table III
Infinite Dilution Partial Molar Volumes, $\bar{v}^{\infty}$, of Gases in Organic Liquids at 25 °C (cm^3/g·mol)

solvent	CO_2	N_2	CH_4	C_2H_6
acetone	55	55	64	46
methyl acetate	54	53	69	46
carbon tetrachloride	53	5	67	48
benzene	53	52	67	47
chlorobenzene	50	49	64	45
average	53	52	66	46

Table IV
Comparison between Equation 3 and Experimental $(C_H')_i/(C_H')_{n\text{-}C_5}$ for Organic Vapors in Poly[1-(trimethylsilyl)-1-propyne][a]

penetrant	exptl $\frac{(C_H')_i}{(C_H')_{n\text{-}C_5}}$	from eq 3	deviatn from exptl value, %
n-nonane	0.91	0.65	−28
CCl_4	1.27	1.18	−7
benzene	1.50	1.31	−13

[a] Data taken from ref 25.

partial molar volumes of CO_2, C_2H_6, CH_4, and N_2 in several organic liquids and their respective averages[23,24] are listed in Table III. Substituting the appropriate average volumes into the right-hand side of eq 3, one gets

$$\frac{(C_H')_{CO_2}}{(C_H')_{C_2H_6}} = \frac{\bar{v}^{\infty}_{C_2H_6}}{\bar{v}^{\infty}_{CO_2}} = \frac{66}{46} = 1.43 \qquad (4)$$

Gratifyingly, the predicted value, 1.43, differs from the experimental value, 1.32, by only 8%.

Further examination of the validity of eq 2 can be made by applying a similar analysis to the sorption data found in literature of several vapors in poly[1-(trimethylsilyl)-1-propyne] at 35 °C.[25] With *n*-pentane taken as the reference, $(C_H')_i/(C_H')_{n\text{-}C_5}$ is calculated from eq 3, where the penetrant "sorbed density" is assumed to be equal to the corresponding liquid density. The results are compared with experimental data in Table IV. The agreement between experimental and predicted values is not as close as for CO_2 and C_2H_6 in PPha-tere but is acceptable considering the approximations made on sorbed density and the experimental uncertainty in the determination of C_H' for the highly sorbing poly[1-(trimethylsilyl)-1-propyne].[25,26]

In contrast, inspection of the data in Tables II and III clearly reveals that v^* cannot be approximated by $\bar{v}^{\infty}$ for penetrants well above their critical temperatures. For example, the $\bar{v}^{\infty}$ value of nitrogen is very close to that of carbon dioxide but the C_H' value for N_2 is only one-eighth that of CO_2. Table V summarizes comparisons similar to those in Table IV, for CO_2, CH_4, and N_2 in a few glassy polymers. Obviously, the agreement between prediction and data is very poor for penetrants well above their critical temperatures at the experimental conditions. (The cause for the relatively small error for the PPO polymers and its implications are unknown at this time.)

The above discussion leads to the following tentative conclusion: the sorbed density of a penetrant in the glassy polymer is similar to its partial density in ordinary liquids only if the penetrant is slightly above its critical temperature or below its critical temperature. One implication of this conclusion is that the thermodynamic states of a sorbed penetrant in glassy polymers and in liquids are similar only if the gas is subcritical. Caution, therefore, must be exercised when thermodynamic parameters obtained from gas/liquid equilibria are used to interpret equilibrium sorption of gases in polymers. Certainly, this tentative conclusion waits to be corroborated by experimental approaches other than sorption isotherms described here.

Table V
Comparison between $(C_H')_i/(C_H')_j$ and Equation 3 for Penetrants above Their Critical Temperatures

	$(C_H')_{CH_4}/(C_H')_{CO_2}$			$(C_H')_{N_2}/(C_H')_{CO_2}$		
polymer	exptl	eq 3	deviatn, %	exptl	eq 3	deviatn, %
PPha-tere	0.40	0.88	+120	0.12	0.87	+625
PC[a]	0.45	0.88	+96	0.11	0.87	+691
PPO[b]	0.68	0.88	+29	0.30	0.87	+190
PPOBr(0.91)[c]	0.72	0.88	+22	0.40	0.87	+118
PAr[d]	0.45	0.88	+96			
PES[e]	0.36	0.88	+144	0.20	0.87	+335

[a] Polycarbonate.[14] [b,c] Poly(2,6-dimethylphenylene oxide) and brominated PPO, respectively: Chern, R. T.; et al. *J. Membr. Sci.* 1987, *35*, 103. [d] Polyarylate: Sheu, F. R.; et al. *J. Polym. Sci., Polym. Phys. Ed.* 1988, *26*, 883. [e] Polyethersulfone: Sanders, E. S. *J. Membr. Sci.* 1988, *37*, 63.

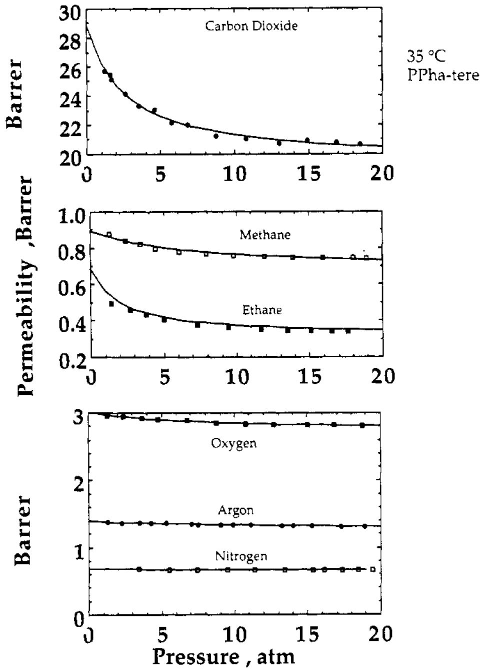

Figure 5. Pressure-dependence of the permeability of PPha-tere at 35 °C to CO_2, C_2H_6, CH_4, Ar, O_2, and N_2. 1 Barrer = 10^{-10} cm^3 (STP)·cm/s·cm^2·cmHg.

II. Steady-State Permeation. The permeability of PPha-tere to pure CO_2, C_2H_6, CH_4, Ar, O_2, and N_2 at 35 °C decreases with increasing upstream driving pressure (Figure 5). Gas permeabilities of many glassy polymers over a range of 1–20 atm have been reported; the magnitude of the permeability is typically $CO_2 > Ar > N_2 > CH_4$. Clearly, this trend also holds for PPha-tere at 35 °C. The permeability ratios of CO_2 to CH_4 and C_2H_6 at 20 atm are 28 and 59, respectively. Coupled with a reasonably high CO_2 permeability of >20 Barrer and good membrane-forming properties, the high permselectivity makes PPha-tere a potential membrane material for CO_2/hydrocarbon gas separations.

Table VI summarizes the dual-mode transport parameters,[27] D_D and D_H, which were evaluated from the permeability and solubility data following the dual-mode equation:

$$P = k_D D_D\left[1 + \frac{(D_H/D_D)C_H'b/k_D}{1 + bp}\right] \qquad (5)$$

The solid lines in Figure 5 are values computed from eq

Table VI
Dual-Mode Transport Parameters for PPha-tere at 35 °C

gas	D_D, $\times 10^8$ cm^2/s	D_H, $\times 10^9$ cm^2/s	F
CO_2	10.20	5.85	0.057
O_2	6.21	8.29	0.133
Ar	4.11	2.96	0.072
N_2	3.08	0.755	0.025
CH_4	1.65	0.893	0.054
C_2H_6	0.283	0.244	0.090

Table VII
Kinetic and Collision Diameters of Gases

gas	kinetic diameter,[a] Å	collision diameter,[b] Å
CO_2	3.30	4.00
Ar	3.40	3.42
O_2	3.46	3.43
N_2	3.64	3.68
CH_4	3.80	3.82
C_2H_6	3.80	4.42

[a] Reference 30. [b] Reference 29.

5 and the parameters in Table VI. Clearly, eq 5 fits the experimental data reasonably well.

Diffusion Coefficient and the Dimension of the Gas. Diffusion coefficients of small molecules in glassy polymers are often found to correlate exponentially with the size of the penetrant.[28] Two parameters are frequently used: Lennard-Jones collision diameter and kinetic diameter. The former is often determined from viscosity data[29] and, therefore, is an average dimension over all possible orientations. The kinetic diameter is the calculated intermolecular distance of the closest approach for two molecules colliding with zero initial kinetic energy and is often taken to correspond to the smallest diameter of a zeolite window that allows the given gas molecule to enter the inner cavity.[30] On the basis of the large diffusion coefficient of CO_2 in many glassy polymers, it has been suggested that this minimal molecular dimension of the gas molecule rather than the collision diameter controls the transport in rigid glassy polymers.[31] This statement will be examined further in the following discussion.

The collision diameters and kinetic diameters for the gases are listed in Table VII. The two diameters differ considerably only for CO_2 and C_2H_6. Ethane has the same kinetic diameter as CH_4 but a significantly larger collision diameter. If indeed the diffusion in glassy polymers is correlated with the kinetic diameter rather than the collision diameter, the diffusion coefficient of C_2H_6 would be similar to that of CH_4, an expectation not supported by the data shown in Table VI. On the other hand, the large diffusion coefficient of CO_2 must be attributed to its small kinetic diameter since its collision diameter is next to only C_2H_6 among the gases studied here.

Whether CO_2 or C_2H_6 is the exception in the size-diffusivity correlation is a subject of future investigation where, for example, C_3H_8 and C_4H_{10} should be included. It is worth noting that reasonable correlation has been reported between the zero-concentration diffusivity and the collision diameter of a large number of gases and vapors in poly(methyl methacrylate), polystyrene, and poly(vinyl chloride).[28] Figure 6 shows a plot of log D_D (the Henry's law mode diffusion coefficient) and log D_H (the Langmuir mode diffusion coefficient) versus the collision diameter, except CO_2, for which kinetic diameter is used. The goodness of correlation is reasonable and is similar to that reported in the literature for other glassy polymers,[14,15,31] where O_2 and C_2H_6 were not studied.

III. Comparison with Existing Data for PPha-tere. The magnitude of the isotherms for CO_2, CH_4, and N_2 is 5–10% smaller than the corresponding isotherms reported in a previous paper.[5] In contrast, the steady-state permeability to pure CO_2 is 10–20% larger than that previously observed.[5] These discrepancies can be traced back to a few possible causes. First, the sorption device has been completely renovated and recalibrated between the two independent studies.[12] The latest calibration is believed to have improved the accuracy of the solubility measurement by ~5% due to a more elaborate calibration procedure. A separate paper is in preparation to address this issue. Second, the PPha-tere sample used in this study was solution-polymerized, while the previous one was interfacially polymerized, which raises the question regarding a possible difference in the molecular weight of the two samples. Molecular weight of the polymer has been shown to have some measurable influence on the gas sorption and permeability of glassy polymers.[32] The absence of molecular weight data and specimens from the previous study, unfortunately, precludes an unequivocal discussion on this issue. Nevertheless, there is little doubt that the two polymer samples are different since the density of the present sample is 0.006 g/cm^3 less than the previous one, i.e., 1.291 g/cm^3 compared with 1.297 g/cm^3. Whether a difference in molecular weight or casting solvent causes the density variation is still to be revolved. The larger gas permeability reported here is a result of larger gas diffusivity, which in turn can be attributed to the lower packing density of the present sample, manifested clearly in its lower mass density.

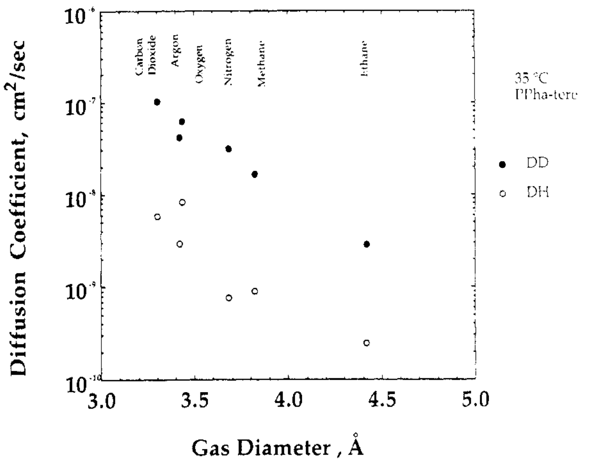

Figure 6. Correlation between the dual-mode diffusion coefficients, cm^2/s, and the dimension of the gas. Collision diameter was used for all the gases except CO_2 for which kinetic diameter was used.

Conclusions

PPha-tere was shown to absorb 60–80% more gases (pure CO_2, CH_4, Ar, C_2H_6, N_2, and O_2) than poly(methyl methacrylate), Bisphenol A polycarbonate, and polysulfone do under the same experimental conditions. PPha-tere is also greater than 3 times more permeable than these polymers. The high permselectivity and permeability, together with good membrane-forming properties not presented here, make PPha-tere a potential membrane material candidate for carbon dioxide/hydrocarbon separations. Following the formalism of the dual-mode model, we inferred that the physical states of the polymer-sorbed gas and liquid-sorbed gas are similar only when the experimental temperature is not much above the critical temperature of the gas. The diffusivity of gases in PPha-tere correlates reasonably well with the collision

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diameter; carbon dioxide is the only exception. Finally, the dual-mode sorption parameters, k_D and b, of all six gases in PPha-tere show a strong dependence on the condensability of the gas, similar to most other systems reported in the literature.

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Tridimensional Profile Functions in Structure Analysis of Crystalline Fibers by the "Whole-Pattern" Method. Dependence on Crystal Size and Crystallite Orientation

Pio Iannelli* and Attilio Immirzi

Dipartimento di Fisica, Universitá di Salerno, I-84100 Salerno, Italy.

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ABSTRACT: With the aim of implementing crystal structure refinement programs applicable to fibrous materials and on the basis of the whole-pattern approach, theoretical functions have been developed expressing the continuous diffraction intensity versus crystal size and misalignment parameters. Applications of this function to two synthetic polymers, polyisobutylene and isotactic polypropylene, has afforded an excellent agreement between observed and calculated intensity.

Introduction

In recent papers[1,2] we have proposed a *whole-pattern* approach in structure refinement of crystalline fibrous materials, viz., a least-squares procedure using, as observations, the *continuous* diffracted intensities instead of the traditional *integrated* ones. To this end, we have studied bidimensional profile functions appropriate for describing the X-ray diffracted intensity recorded on photographic films, considering either cylindrical or flat-camera geometry. Starting from a modified Pearson-VII function, we have found, on empirical grounds, that the product of two Gauss functions is adequate to fit single reflections if a system of curvilinear film coordinates τ and ρ is chosen, which makes the shape of the recorded spots rectangular

$$\Phi(\tau_i, \rho_i) = f_\tau(\tau_i - \tau_k)\, f_\rho(\rho_i - \rho_k) \qquad (1)$$

τ_i and ρ_i being the curvilinear coordinates of any point of the film and τ_k and ρ_k those of the *center* of the kth reflection.

In this paper a more exact approach is reported based on theoretical functions instead of empirical ones, also with the aim of obtaining, besides structural parameters refined, morphological parameters such as crystal sizes

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