

# Sorption and Interactions of Gases in Polyaniline Powders of Different Doping Levels

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## SYNOPSIS

Sorption of different gases (N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>) were performed on as-synthesized polyemeraldine base, on HCl 4M doped, on NH<sub>4</sub>OH 1M undoped, and on HCl 10<sup>-2</sup>M redoped powders. In the pressure range examined (100–700 torr), linear sorption isotherms were observed for N<sub>2</sub> and correspond to an ordinary dissolution in Henry's law state. Concerning O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, nonlinear isotherms were evidenced and could be described by the dual-mode sorption mechanism proposed for glassy polymers, which consists of the combination of a Henry's type dissolution with a Langmuir sorption in unrelaxed gaps between macromolecular chains. Specific interactions between polyaniline (PANi) and O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were studied. Gas permeation experiments were performed by using different upstream pressures,  $P_1$ , and have confirmed the dissolution of Henry's type for N<sub>2</sub> and the dual-mode mechanism for O<sub>2</sub> and CO<sub>2</sub>. From the fits of the sorption isotherms, gas solubilities of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were calculated for three different gas pressures and analyzed in terms of gas separation for permeation experiments. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Considerable effort has already been invested to understand the sorption and diffusion of gases in glassy polymers.<sup>1–10</sup> The impetus of this work comes from applications such as polymeric membranes for gas separation. Recent results have focused attention on the interest in using electronic conducting polymers such as polyaniline (PANi) because large selectivity values for the O<sub>2</sub>/N<sub>2</sub> gas pair have been reported.<sup>11–13</sup> By a treatment of doping in acidic medium, undoping in basic medium, and redoping in a slightly acidic medium, irreversible morphological changes seem to be induced in the macromolecular structure because the selectivity and permeability performances are considerably modified. The aim of this study is to determine whether doping treatments significantly influence gas solubilities and to reveal to what extent the solubility factor is responsible

for the exceptional separation coefficients observed with PANi membranes.

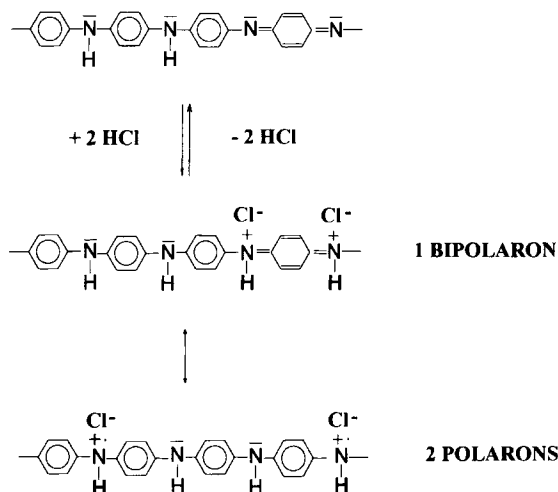
## EXPERIMENTAL

### Materials

PANi in a half-oxidized state (called polyemeraldine) was synthesized by chemical oxidation of aniline by ammonium peroxodisulfate, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, in an acidic medium (H<sub>2</sub>SO<sub>4</sub> 2M).<sup>14</sup> The polymer was deprotonated by immersion in a dilute aqueous ammonia solution under constant stirring and it was purified by washing cycles in distilled water and in tetrahydrofuran, which respectively removes unreacted monomers and oligomers ( $n < 8$ ) from the material. A powder of polyemeraldine in the base form was thus obtained and called as-synthesized (AS) PANi.

Following the method used by Anderson et al.,<sup>11–13</sup> the AS powder was protonated by immersion in a 4M chlorhydric acid solution, which yields a fully

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**Figure 1** Process of doping ( $+ \text{HCl}$ ) and undoping ( $- \text{HCl}$ ) in polyemeraldine.

doped material, that is, 50 chloride counterions per 100 ring nitrogens (Fig. 1). The fully doped material, was undoped by immersion in a  $\text{NH}_4\text{OH}$  1M solution that nearly removed all doping agent from the polymer (by leaving only 1 or 2 chloride ions per 100 ring nitrogens). At last the undoped powder was slightly redoped by immersion in a  $10^{-2}\text{M}$  chlorhydric acid solution, which led to a partially protonated material that had 9–10 chloride ions per 100 ring nitrogens. Each treatment of this acid–base chemistry was undergone in aqueous medium during 2 h and it was followed by drying under dynamic vacuum ( $T < 50^\circ\text{C}$ ,  $P < 1$  torr). The total amount of halide counterions and ring nitrogens was determined by elementary analysis.<sup>14</sup>

The density of AS and undoped powders<sup>15</sup> was  $1.3 \text{ g cm}^{-3}$  and the density of the fully doped material<sup>16</sup> was  $1.4 \text{ g cm}^{-3}$ . If we assume the density of PANi follows a linear variation with the doping level, the density of the redoped powder was estimated at  $1.32 \text{ g cm}^{-3}$ . The PANi pellets were studied under an electron microscope and the average diameter was estimated at  $1 \mu\text{m}$ .

The preparation of PANi membranes for gas permeation was described in Rebbattet et al.<sup>17</sup> A similar doping, undoping, and redoping process was performed on films and powders.

## Apparatus

### Sorption Apparatus

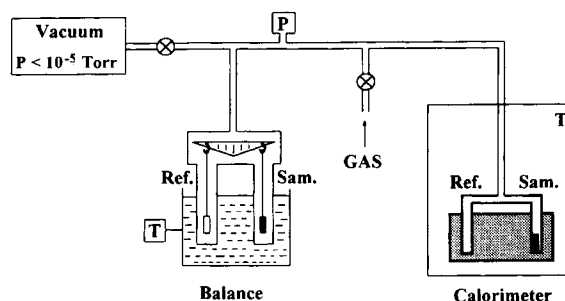
The apparatus consists of a microgravimetric balance (Setaram TGDTA 92) and a microcalorimeter (ARION) that allows the simultaneous determi-

nation of weight uptakes and associated dissolution enthalpies (Fig. 2). The weight uptakes were determined by a constant electromagnetic compensation between the sample and the reference nacelles. The apparatus is unfortunately built up with glass, which forced us to carry out sorption experiments below atmospheric pressure. In order to get good accuracy on weight uptakes, two experimental precautions were taken:

- The Archimede thrust was compensated for by introducing in the reference nacelle a volume of carbon fibers ( $d = 1.8 \text{ g cm}^{-3}$ ) equivalent to that of the powder set in the sample part. Previous experiments have undoubtedly demonstrated that carbon fibers do not present weight uptakes under gas pressure.
- Before each experiment, the PANi powder and the apparatus were strongly outgassed by a long-duration pumping ( $P < 10^{-5}$  torr) with a set of rotary and oil diffusion pumps.

The two nacelles were immersed in a thermostatted bath at  $22.5^\circ\text{C}$  and the microcalorimeter was settled in a cupboard thermoregulated at  $22.5 \pm 0.5^\circ\text{C}$ . Room temperature was maintained at  $24^\circ\text{C}$ .

An amount of approximately 150 mg of PANi powder was set in the sample nacelle of the balance and an equivalent amount (within about 0.1 mg) was set in the sample part of the microcalorimeter. When the gas pressure was supplied to the assembly, it was measured with a MKS Baratron 122B (range 1000 torr) manometer with an accuracy of 0.1 torr. Experimental data were collected with an electronic interface (CS 92) and were processed by a computer (PC 92) using Setaram TGDTA 92 software. The gas concentration versus pressure isotherms were fitted with a Kaleida Graph Software and an error inferior to 0.01% was reached for each fit.



**Figure 2** Gas sorption apparatus.

### Gas Permeation Apparatus

The gas transport cell is described in Rebattet et al.<sup>17</sup> The upstream pressure,  $P_1$ , was measured by using a MKS Baratron 122B manometer.

## THEORY

### Fundamentals of Gas Sorption

Solution of gases is a complex process in glassy polymers and it was satisfactorily described for  $T > T_c$  (where  $T_c$  is the critical temperature of the gas) by means of a "dual-mode" model.<sup>1-10</sup> This model assumes that the penetrant gas molecules dissolved in the polymer can be distinguished in two thermodynamically distinct populations:

- The first population is dissolved following a Henry's type dissolution mechanism. The concentration of the molecules  $C_D$  is related to the penetrant equilibrium pressure  $P$  by a linear isotherm:  $C_D = k_D P$ , where  $k_D$  represents Henry's constant.
- The second population is held in preexisting microcavities (i.e., unrelaxed gaps) between polymeric chains or on preferential sites. The concentration of the gas molecules,  $C_H$  is related to the pressure  $P$  by the equation of the Langmuir isotherm:  $C_H = C'_H b P / (1 + b P)$ , where  $C'_H$  is the maximum capacity of the polymer to the penetrant in the Langmuir sorption mode (or the hole saturation constant) and  $b$  is the affinity constant, the ratio of rate constants of gas absorption and desorption in microcavities.

The overall penetrant concentration  $C_T$  corresponds to the sum of Henry and Langmuir contributions:

$$C_T = C_D + C_H = k_D P + \frac{C'_H b P}{1 + b P}. \quad (1)$$

By fitting the sorption isotherms  $C_T = f(P)$  with eq. (1), the  $k_D$ ,  $C'_H$ , and  $b$  coefficients are determined, which enables the calculation of a pressure-dependent solubility coefficient  $S$ :

$$S = \frac{C_T}{P} = k_D + \frac{C'_H b}{1 + b P} = f(P). \quad (2)$$

When concentration versus pressure isotherms are linear, it means the affinity constant  $b$  is very small. Then  $b P \ll 1$  and eq. (1) becomes:

$$C_T \cong (k_D + C'_H b) \cdot P = k'_D P. \quad (3)$$

The dissolution of the gas molecule obeys Henry's law and the solubility coefficient  $S$  is constant on all the pressure range examined.

### Statements on Gas Permeation

Gas permeation properties are considerably affected by the way gas molecules are dissolved in the polymer matrix and this is particularly obvious by decreasing the upstream pressure<sup>4-10</sup>  $P_1$ :

- When gas molecules are dissolved following Henry's law, the permeability coefficient is independent of  $P_1$ :

$$P_e = k_D D \quad (4)$$

where  $k_D$  is Henry's constant.

- The problem is much more complicated when gas molecules are dissolved according to a dual-mode mechanism because permeability coefficients significantly decrease when upstream pressure increases. To explain these experimental results, Paul et al.<sup>4,5</sup> and Petropoulos<sup>6</sup> suggested that the gas molecules sorbed following Henry's law are completely mobile in the polymer matrix, but the gas molecules sorbed according to a Langmuir type isotherm are only partially mobile. In the Paul et al. model,<sup>4,5</sup> the mobile fraction  $F$  of the Langmuir population is equal to the ratio  $D_H/D_D$ , where  $D_H$  and  $D_D$ , respectively represent the diffusion coefficients of the Langmuir and Henry contributions. The permeability coefficient is defined by the following relation:

$$P_e = k_D D_D \left[ 1 + \frac{F K}{1 + y} \right] \quad (5)$$

where  $K = \frac{C'_H b}{k_D}$  and  $y = b P_1$  ( $C'_H$ ,  $b$ , and  $k_D$  having the previously described meanings).

The above relation has been improved by Nichide et al.<sup>9</sup> by taking into account local exchanges between Henry and Langmuir populations. The overall expression of the permeability coefficient versus  $P_1$  is therefore complicated and it has not been used in the present study.

## RESULTS AND DISCUSSION

### General Statements

From Figure 3, we can notice that for each powder, weight uptakes considerably differ from a gas to another. Gas concentrations can be ordered in the following way:

$$C_{N_2} \cong C_{O_2} < C_{CH_4} < C_{CO_2}$$

The amount of gas sorbed by the polymer is about 4 times higher for  $CO_2$  than for  $CH_4$  and 10 times more important for  $CO_2$  than for  $O_2$  or  $N_2$ . The dissolution enthalpies are presented in Figure 4 and it is necessary to point out that these energies correspond to exothermic processes. In addition to gas concentrations, the molar dissolution enthalpies are very different from one gas to another and can be ordered as following:

$$\Delta H_{N_2} \cong \Delta H_{O_2} < \Delta H_{CH_4} < \Delta H_{CO_2}$$

This result shows PANi has very different affinities to gases. Concerning  $CH_4$  and especially  $CO_2$ , the sorption energies are surprisingly high. The experimental accuracy cannot be questioned: as weight uptakes and heat flows are both very high (therefore very precise), the molar energy is determined with very good accuracy. For each gas, the measured enthalpies are strongly superior to the liquefaction enthalpies (that are equal to  $1.5 \text{ kcal mol}^{-1}$  for  $N_2$  and  $O_2$ ,  $2.1 \text{ kcal mol}^{-1}$  for  $CH_4$ , and  $2.6 \text{ kcal mol}^{-1}$  for  $CO_2$ ). This means the mixing enthalpies are highly exothermic processes for the dissolution of gases. Such a result has already been observed in the literature: from sorption isotherms, Kirchheim<sup>18</sup> has evaluated dissolution enthalpies of  $CO_2$  that are markedly higher than the liquefaction enthalpy.

Sorption isotherms of Figure 3 show that for each gas, concentrations are appreciably modified by the level of doping of the polymer:

$$C_{AS} \leq C_{undoped} < C_{redoped} < C_{doped}$$

Even if the ratio between  $C_{doped}$  and  $C_{AS}$  does not exceed a factor of 2, the doping treatment undoubtedly increases the ability of the powder to sorb gases. It also increases the interaction energies (Fig. 4):

$$\Delta H_{AS} \leq \Delta H_{undoped} < \Delta H_{redoped} < \Delta H_{doped}$$

A difference of approximately 2 or 3  $\text{kcal mol}^{-1}$  is observed between the doped and AS powders. The

sites  $N^+Cl^-$  produced by the protonation represent permanent dipoles that can induce the polarization of the gas molecule according to a Debye type interaction. It may involve a slight increase in the affinity of the polymer for the gas and then a slight increase in both the gas solubility and the dissolution enthalpy.

After having undoped the polymer, it appears the gas concentrations are significantly higher than those measured for the AS powder, which tends to evidence that the doping treatment leaves an irreversible mark within the polymer.

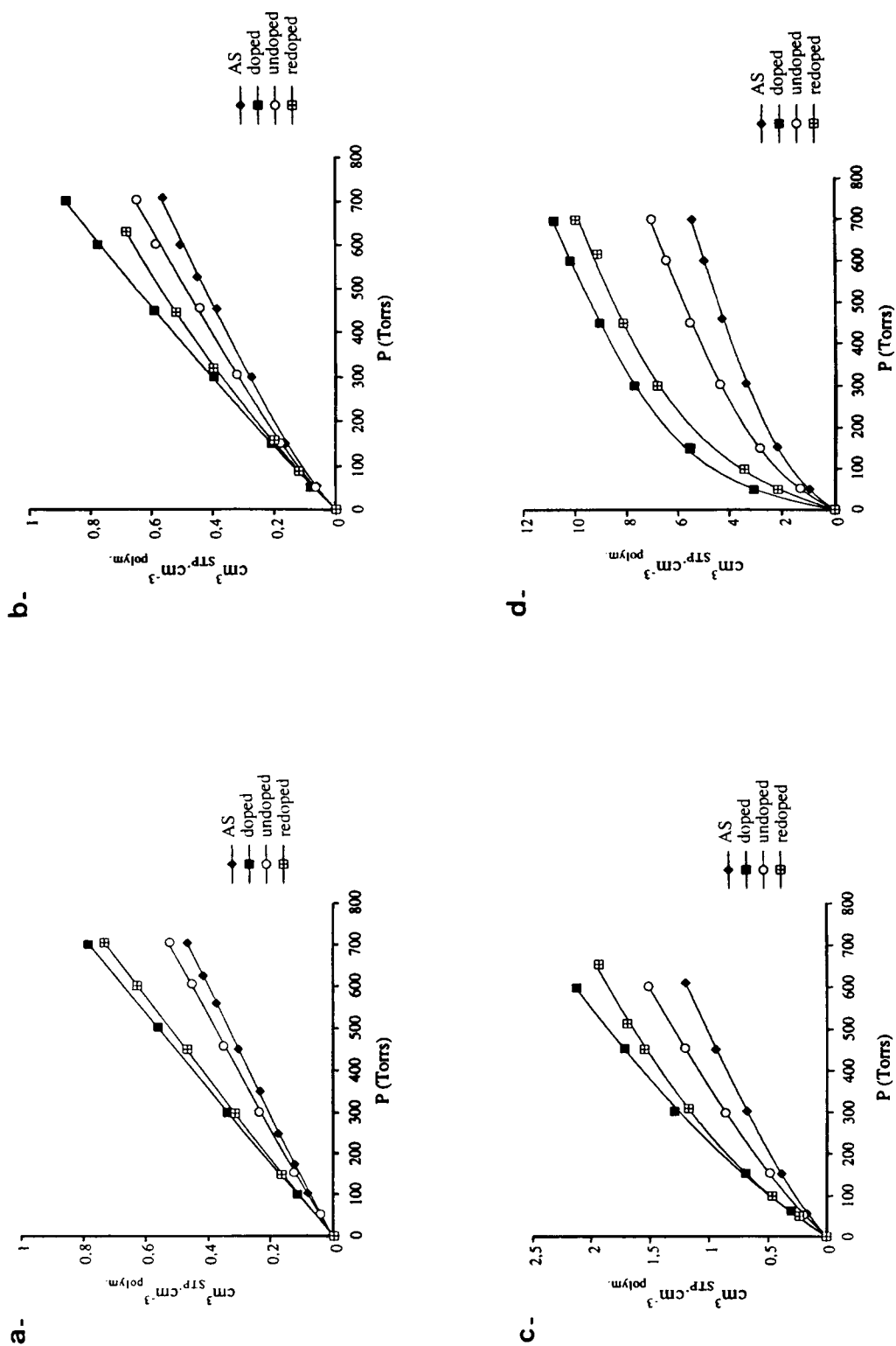
Isotherms of the redoped powder are rather close to the ones of the doped powder, even if the doping level is only the fifth (9–10 chloride ions per 100 ring nitrogens for the redoped powder against 50 for the doped powder). Therefore even a small concentration of doping agent involves a significant variation in the sorption isotherms.

### Fits of Isotherms

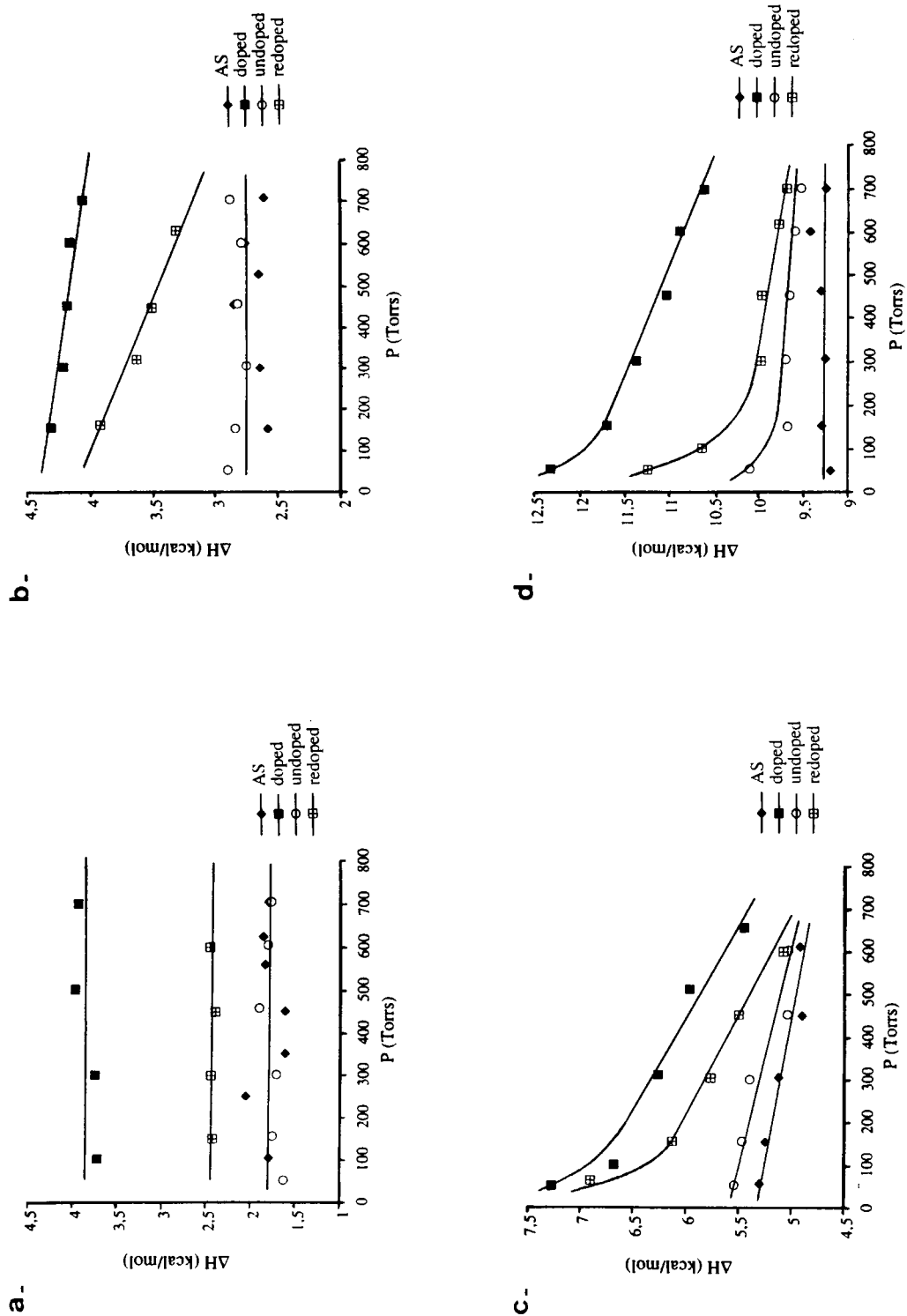
Sorption isotherms are linear for  $N_2$ , which means this gas is dissolved following Henry's law in the pressure range examined. On the other hand, sorption isotherms of  $O_2$ ,  $CH_4$ , and  $CO_2$  are concave to the time axis and seem to obey a dual-mode mechanism. Experimental data were fitted by Henry's law for  $N_2$  and by the dual-mode equation for  $O_2$ ,  $CH_4$ , and  $CO_2$ . The results are listed in Table I.

As a general point of view, the Henry's constant  $k_D$  significantly increases with the level of doping although the redoped powder presents a low contribution of Henry's type for  $CH_4$  and  $CO_2$ .

The hole saturation constant  $C'_H$  clearly increases with the level of doping, which demonstrates that the protonated functions  $N^+Cl^-$  represent preferential sites for a Langmuir type sorption. However, the hole affinity constant  $b$  decreases when the doping level increases, which is rather surprising. Let us remember that  $b$  represents the ratio of rate constants of gas absorption and desorption. A decrease in  $b$  means the kinetic equilibrium between sorbed and mobile molecules is enhanced. As a consequence the doping level increases the number of sites likely to sorb gas molecules following a Langmuir isotherm, but it decreases the duration that molecules are trapped in such sites. As  $C'_H$  and  $b$  vary in the opposite direction, it is not possible to determine whether this evolves the Langmuir contribution during the doping treatment. From the calculated parameters of the dual-mode equation, we have estimated the Langmuir contribution to the overall



**Figure 3** Sorption isotherms for as-synthesized (AS), HCl 4M doped,  $\text{NH}_4\text{OH}$  1M undoped, and HCl  $10^{-2}M$  redoped polyaniline powders for: (a)  $\text{N}_2$ ; (b)  $\text{O}_2$ ; (c)  $\text{CH}_4$ ; and (d)  $\text{CO}_2$ . The fits were drawn from numerical calculation.



**Figure 4** Enthalpic measurements of the gas molecules dissolution in as-synthesized (AS), HCl 4M doped,  $NH_4OH$  1M undoped, and HCl  $10^{-2}M$  redoped polyaniline powders: (a)  $N_2$ ; (b)  $O_2$ ; (c)  $CH_4$ ; and (d)  $CO_2$ .

**Table I Sorption Parameters Calculated from Fits of Isotherms**

Gas	Powder	$k_D \left( \frac{\text{cm}^3_{\text{STP}}}{\text{cm}^3_{\text{polym. atm}}} \right)$	$C'_H \left( \frac{\text{cm}^3_{\text{STP}}}{\text{cm}^3_{\text{polym.}}} \right)$	$b \text{ (atm}^{-1}\text{)}$
N <sub>2</sub>	AS	0.509	—	—
	Doped	0.855	—	—
	Undoped	0.573	—	—
	Redoped	0.796	—	—
O <sub>2</sub>	AS	0.486	0.159	3.457
	Doped	0.792	0.306	1.18
	Undoped	0.58	0.161	3.449
	Redoped	0.589	0.352	1.674
CH <sub>4</sub>	AS	1.084	0.504	2.656
	Doped	1.363	2.131	1.308
	Undoped	1.372	0.696	2.281
	Redoped	0.935	1.987	1.692
CO <sub>2</sub>	AS	3.176	3.156	4.906
	Doped	4.319	7.809	8.308
	Undoped	3.832	4.351	4.839
	Redoped	2.889	9.116	4.076

concentration for three different gas pressures. Results are listed in Table II.

The doped and redoped powders present significantly higher Langmuir contributions than the unprotonated samples, showing that the Langmuir sorption is enhanced by the doping treatment. For every gas and for every pressure, the Langmuir contribution is higher for the redoped sample: the doping, undoping, and redoping process involves con-

siderable morphological changes within the polymer because it favors the creation of microcavities able to trap molecules following a Langmuir isotherm.

From Table II, we can observe the Langmuir contribution is proportionally higher at low pressures. This observation is confirmed by enthalpimetric measurements (Fig. 4). Indeed the sorption energies of CH<sub>4</sub> and CO<sub>2</sub> are markedly increased at low pressures for the doped and redoped powders. This result is consistent with a predominant Langmuir sorption. This last corresponds to a more exothermic phenomenon than Henry sorption because the process of filling preexisting microcavities requires less energy than the ordinary dissolution in Henry's law state. If Langmuir sorption and Henry dissolution can be considered as competitive processes, the Langmuir sorption is energetically favored at low pressures and disfavored at high pressures when the number of available sorption sites has strongly decreased.

**Table II Percentages of Langmuir Contribution to Overall Gas Concentration**

Gas	Powder	$\frac{C_H}{C_D + C_H} \text{ (%)}$		
		0.1 bar	1 bar	3 bar
O <sub>2</sub>	AS	49	25	12
	Doped	64	47	30
	Undoped	49	26	13
	Redoped	76	57	37
CH <sub>4</sub>	AS	45	20	9
	Doped	29	17	9
	Undoped	42	18	8
	Redoped	46	27	14
CO <sub>2</sub>	AS	77	45	24
	Doped	89	62	37
	Undoped	79	49	26
	Redoped	90	72	50

Values calculated from the parameters of Table I for three different gas pressures.

### Discussion of Specific Interactions

From sorption isotherms and enthalpimetric measurements, a dual-mode mechanism has been evidenced for O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>. It might be interesting to find an interpretation of the specific interactions responsible for a Langmuir type affinity.

- Concerning O<sub>2</sub>, which is a paramagnetic gas in the triplet state, we supposed a paramagnetic

interaction may occur between O<sub>2</sub> and the free radicals of PANi in the doped state and especially in the polaronic form (cf. Fig. 1). Electron spin resonance (ESR) experiments that were previously described,<sup>19</sup> have shown that a paramagnetic interaction exists between PANi and O<sub>2</sub> because the ESR signal of doped PANi vanishes when the polymer is in contact with O<sub>2</sub>. Recent studies have supported these results: magnetic susceptibility measurements by SQUID have demonstrated that the decrease in the spin number of PANi is only apparent because the real number of spins keeps constant.

- It seems difficult to find a specific interaction between PANi and CH<sub>4</sub>, which is a chemically inert gas. Among the gases we have studied, CH<sub>4</sub> is the one that presents the larger kinetic diameter ( $\phi = 3.8 \text{ \AA}$ ). As a consequence the partial molar volume theory developed by Kirchheim<sup>18,20</sup> could explain the curvature of the isotherms and the variation in the dissolution enthalpies with pressure.
- Sorption isotherms of CO<sub>2</sub> present an important dual-mode effect that cannot be satisfactorily explained by the partial molar volume theory of Kirchheim: the isotherm curvature is more pronounced for CO<sub>2</sub> than for CH<sub>4</sub> (or in other terms the Langmuir contribution to the overall concentration is more important for CO<sub>2</sub> than for CH<sub>4</sub>, cf. Table II), and the CO<sub>2</sub> kinetic diameter is smaller than the CH<sub>4</sub> one. An additional interaction occurs between PANi and CO<sub>2</sub>. As CO<sub>2</sub> is an anhydrid acid (because it leads to carbonic acid in contact with water), an acid–base type interaction may take place between CO<sub>2</sub> molecules and the neutral amine or imine functions of PANi. To explain that the Langmuir sorption is enhanced in the doped state (which corresponds to a 50% protonation of the nitrogen functions), we suggest the acid–base interaction is strengthened by the Langmuir type sorption in the N<sup>+</sup>Cl<sup>-</sup> sites.

### Gas Permeation Results

Gas permeation experiments were carried out by varying the upstream pressure  $P_1$  and the redoped film was used because gas sorption measurements have brought to the fore that the Langmuir contribution (and therefore the dual-mode effect) is more important for the redoped sample than for the others.

Permeation curves are presented in Figure 5 for O<sub>2</sub> and CO<sub>2</sub>. The slope of the curves tend to increase when  $P_1$  increases, but it does not mean the permeability coefficient increases. Indeed the calculation of  $Pe$  needs to take into account the differential pressure across the membrane ( $\Delta P \cong P_1$ ) according to the equation:

$$Pe = \frac{a}{P_1} \times e \times \frac{dP_2}{dt} \quad (6)$$

where  $a = 847.4$  if the upstream pressure  $P_1$ , the thickness  $e$ , and the slope  $dP_2/dt$  are, respectively, expressed in cm Hg, in  $\mu\text{m}$ , and in  $\text{torr min}^{-1}$ . When both  $P_1$  and  $dP_2/dt$  increase,  $Pe$  can either increase or decrease.

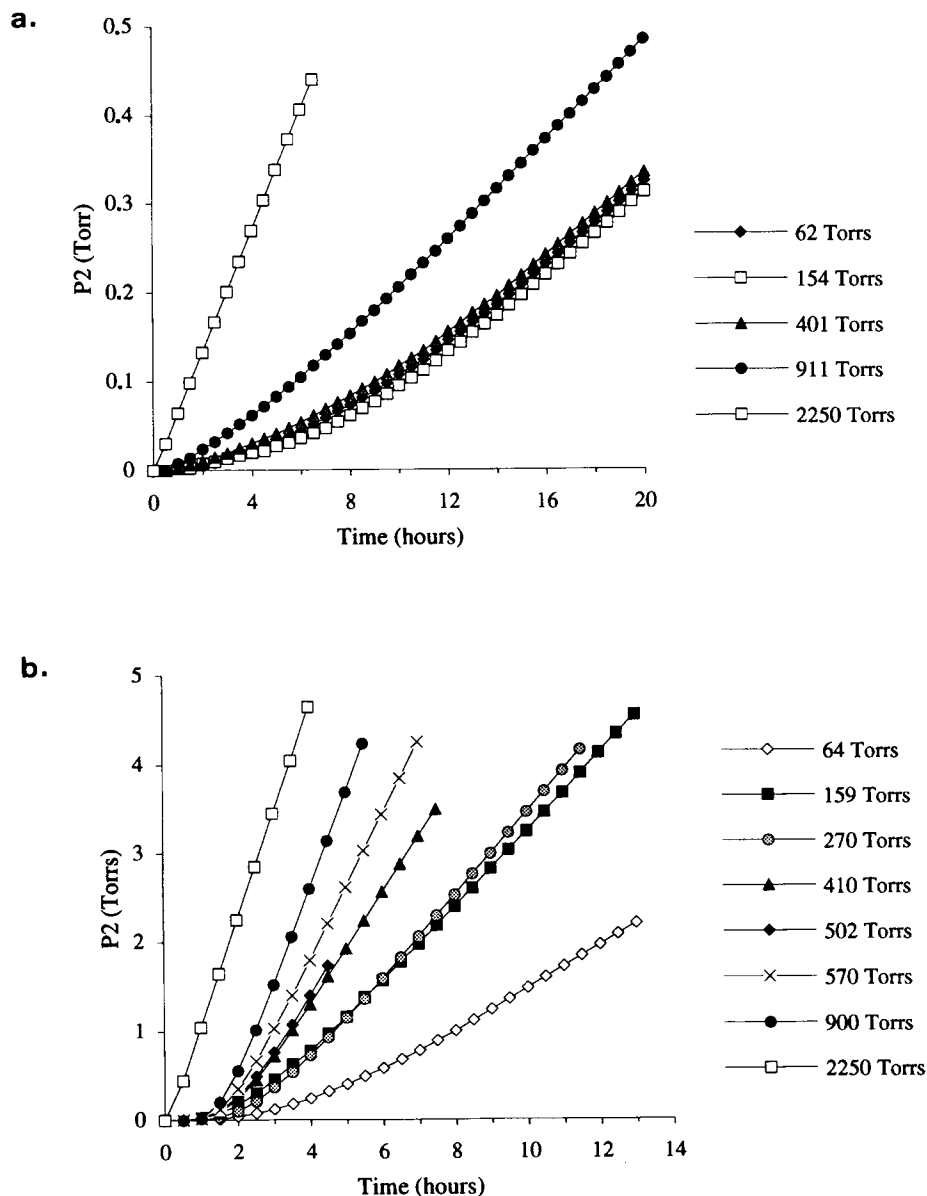
Permeability and apparent diffusion coefficients have been calculated from permeation experiments and are listed in Table III.

The permeability coefficients of O<sub>2</sub> and CO<sub>2</sub> considerably decrease when  $P_1$  increases, which is consistent with the dual-mode mechanism observed by sorption measurements [cf. eq. (5)]. The apparent diffusion coefficients of O<sub>2</sub> and CO<sub>2</sub> increase when  $P_1$  increases, which is logical because the gas diffusivity is mainly due to the molecules sorbed following a Henry's law and the Henry contribution to the overall concentration increases with  $P_1$  (cf. Table II). On the other hand, the  $Pe$  and  $D_{\text{app}}$  coefficients of N<sub>2</sub> do not present significant variations with the upstream pressure, consistent with the ordinary dissolution in Henry's law state observed by sorption experiments.

The  $Pe = f(P_1)$  curves have been fitted by the Paul and Koros model (Fig. 6). There is a very good agreement between experimental data and the calculated fits because an error inferior to 0.01% was reached. The diffusion coefficients of the Henry contribution ( $D_D$ ) and the Langmuir contribution ( $D_H$ ) have been determined from the fits and the mobile fraction  $F (=D_H/D_D)$  has been calculated. Results are listed in Table IV.

The  $D_D$  and  $D_H$  diffusion coefficients are extreme values in comparison with the apparent diffusion coefficients measured from permeation experiments (cf. Table III). The mobility of the molecules sorbed according to a Langmuir isotherm is smaller for CO<sub>2</sub> than for O<sub>2</sub>, which means CO<sub>2</sub> molecules are more strongly held in Langmuir sites than O<sub>2</sub> molecules. This result is consistent with enthalpimetric measurements because the dissolution enthalpies of CO<sub>2</sub> are significantly higher than those of O<sub>2</sub>.





**Figure 5** Gas permeation experiments through the redoped film obtained with different upstream pressures for (a) O<sub>2</sub> and (b) CO<sub>2</sub>.

### Gas Solubilities

Gas solubility coefficients were calculated for N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> from the parameters of Table I according to eq. (2). The results are presented in Table V for three different gas pressures (0.1, 1, and 3 bar).

To estimate the solubility coefficients of N<sub>2</sub> we have supposed the gas sorption does not present a dual-mode effect above the atmospheric pressure. Therefore the solubility coefficient is pressure independent.

Concerning O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>, gas solubilities decrease when the pressure increases because the Langmuir influence is less and less pronounced. If we compare the solubility factors of O<sub>2</sub> and N<sub>2</sub>, these are quite equivalent at 3 bar whereas they present a significant difference at 0.1 bar. To improve the separation of these gases from a difference in solubilities, it might be interesting to work at very low pressures. Concerning the gas permeation experiments performed at 40 psi ( $\approx 2.76$  bar) by Anderson et al.,<sup>11-13</sup> we can clearly establish that the exceptional separation factors ( $> 30$ ) observed for the O<sub>2</sub>/

**Table III Permeability and Apparent Diffusion Coefficients**

Gas	$P_1$ (torrs)	$P_e$ (Barrer)	$D_{app}$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )
O <sub>2</sub>	62	0.503	109
	154	0.264	120
	401	0.184	129
	911	0.156	136
	2250	0.152	140
CO <sub>2</sub>	64	6.93	15
	159	4.84	22.5
	270	3.043	25.4
	410	2.404	34.2
	502	2.12	35.5
	570	1.95	36.6
	900	1.452	41.1
	2250	0.88	47
	N <sub>2</sub>	150	0.021
2250		0.014	7

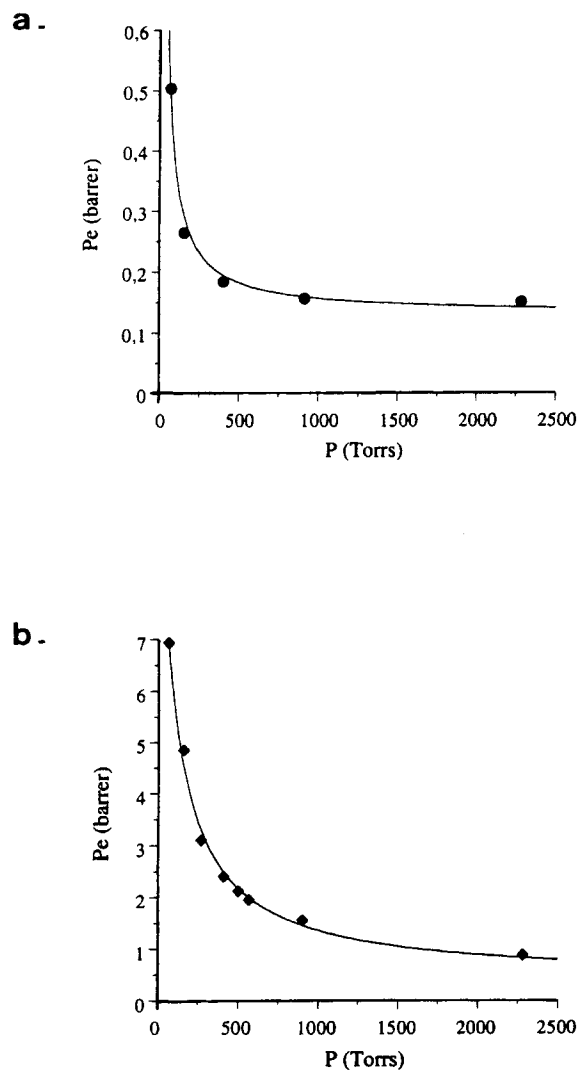
Values calculated from permeation curves obtained with different upstream pressures.

N<sub>2</sub> gas pair undoubtedly do not come from a difference in solubility factors.

## CONCLUSION

Sorption of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were carried out on as-synthesized, HCl 4M doped, NH<sub>4</sub>OH 1M undoped, and HCl 10<sup>-2</sup>M redoped polyemeraldine powders. Below atmospheric pressure, sorption isotherms are linear for N<sub>2</sub> and these are concave to the time axis for O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>. Isotherms were fitted by Henry's law for N<sub>2</sub> and by the dual-mode equation for O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>. A very good agreement was reached for each fit.

The doping treatment multiplies the gas solubilities by a factor of 2 and it increases the molar dissolution enthalpies of 2–3 kcal mol<sup>-1</sup>. This result can be explained by a Debye type interaction: indeed the N<sup>+</sup>Cl<sup>-</sup> sites produced by the protonation represent permanent dipoles that can induce a polarization of gas molecules. The doping treatment also increases the Langmuir contribution of O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> to the overall concentration. Moreover the doping–undoping–redoping cycle favors the creation of microcavities able to trap molecules following a Langmuir isotherm. Specific interactions between PANi and O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were discussed: the Langmuir sorption is attributed to a paramagnetic interaction for O<sub>2</sub>, it is attributed to the partial molar volume theory developed by Kirchheim for CH<sub>4</sub>, and



**Figure 6**  $P_e = f(P_1)$  curves obtained from gas permeation experiments for (a) O<sub>2</sub> and (b) CO<sub>2</sub>. The fits were calculated from the Paul and Koros model.<sup>4,5</sup>

it might come from an acid–base type interaction for CO<sub>2</sub>. Gas permeation experiments confirm the dual-mode mechanism for O<sub>2</sub> and CO<sub>2</sub> and the Henry's dissolution observed with N<sub>2</sub>.

Gas solubilities of N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were calculated from sorption isotherm parameters and

**Table IV Diffusion Coefficients of Henry ( $D_D$ ) and Langmuir ( $D_H$ ) Populations and Calculation of Mobile Fraction  $F$**

Gas	$D_D$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )	$D_H$ ( $\times 10^{-11}$ cm <sup>2</sup> s <sup>-1</sup> )	$F = \frac{D_H}{D_D}$
CO <sub>2</sub>	86	8.4	0.1
O <sub>2</sub>	192	42	0.22

**Table V Solubility of N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> Calculated from Parameters of Table I for Three Gas Pressures**

Gas	Powder	$S \left( \times 10^{-3} \frac{\text{cm}_{\text{STP}}^3}{\text{cm}_{\text{polym.}}^3 \text{ cm Hg}} \right)$		
		0.1 bar	1 bar	3 bar
N <sub>2</sub>	AS	7	7	7
	Doped	11	11	11
	Undoped	7	7	7
	Redoped	10	10	10
O <sub>2</sub>	AS	12	8	7
	Doped	15	13	11
	Undoped	13	9	8
	Redoped	14	11	9
CH <sub>4</sub>	AS	28	19	16
	Doped	50	34	25
	Undoped	35	24	21
	Redoped	50	29	19
CO <sub>2</sub>	AS	177	76	54
	Doped	519	148	89
	Undoped	235	97	68
	Redoped	382	134	74

it appears the high selectivity values observed by Anderson for the O<sub>2</sub>/N<sub>2</sub> gas pair absolutely cannot come from a difference in solubility factors.

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