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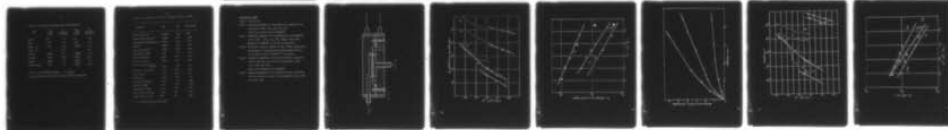
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THE BARRIER PROPERTIES OF POLYACRYLONITRILE,

by

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INTRODUCTION

Abstract

The permeabilities and time lags ^{diffusivities} have been determined in machine cast polyacrylonitrile films for helium, neon, argon, krypton, oxygen, nitrogen and carbon dioxide. Removing the last traces of residual solvent caused a slight reduction in the values, but the activation energies were unchanged. Separate high pressure sorption measurements showed that dual mode sorption was taking place.

The permeabilities were remarkably low. The ratios of the permeabilities of helium to the other gases is remarkably high. This, coupled with the rather low activation energies, suggests that one important reason for the excellent barrier properties of polyacrylonitrile is the very small size of the fluctuating free volume elements in this polymer.

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INTRODUCTION

Polyacrylonitrile (PAN) film, under normal service conditions as a gas barrier, probably exhibits the lowest permeability to gases of any hydrophobic polymer.¹ Highly hydrogen bonded hydrophilic polymers such as polyvinyl alcohol and regenerated cellulose have even better barrier properties when bone dry, but deteriorate rapidly, in this respect, at elevated humidity. The permeability of polyacrylonitrile to gases, however, increases only by 10-20% at high humidities, although PAN is very polar and the nitrile groups offer hydrogen bonding sites for strong interaction with water. Some comparative permeability values for oxygen, carbon dioxide, and water vapor in a number of different polymers are presented in Table I. The highly polar nature of PAN does, however, lead to high water sorption and water vapor permeability. This limits its potential application as a high barrier packaging film, although high acrylonitrile copolymers have been successfully developed for plastic carbonated beverage bottles.^{1,2}

The reasons for the extremely low gas permeabilities are not clear. Certainly, the combination of high cohesive energy density and chain stiffness is a contributor to the observed barrier properties. In addition, although the detailed description of the morphology of polyacrylonitrile films is still controversial, it does have a highly ordered quasi-crystalline structure which, undoubtedly, further adds to the barrier properties of PAN, but confounds a simplistic interpretation of structure-property relationships.

The very low gas permeabilities and diffusivities make gas transport studies extremely difficult and time consuming. With carbon dioxide, for example, time lags of more than two days can be encountered for 0.5 mil films. This paper will present what is believed to be the first comprehensive and reliable data on gas transport in pure polyacrylonitrile films. Hopefully, this work, together with a systematic investigation of acrylonitrile copolymers including high pressure sorption studies, which are currently in progress, will contribute to the understanding of the rather unique barrier properties of these materials.

EXPERIMENTAL

Initial attempts to cast films without orientation, even from high molecular weight PAN, resulted in fragile films, in which pinholes were easily formed, and this approach was discarded. The polyacrylonitrile (PAN) films used were 0.5 mils thick and were lightly oriented machine made solvent cast films, kindly supplied by the Sohio Co., Cleveland, Ohio.

The films were known to contain 2-3% of tenaciously held residual solvent. It was found, following a lead by Carr et al.³, that the solvent could be effectively removed from the Sohio films by boiling in distilled water for ten hours. This treatment resulted in a systematic reduction of only 20% in the permeability constants, but the time lags increased ^{by} a factor of two. The temperature dependencies of the permeabilities and time lags were identical for both the extracted and original films. Since the PAN films were glassy, the time lags are not simply related to the diffusivities. Unequivocal determination of diffusivities were, therefore, not available and since the differences in the permeabilities between the unextracted and ex-

tracted films were modest, unextracted films were used for the bulk of the measurements reported in this paper.

The gases used were all at least 99.9% pure and were obtained from the Matheson Company (O_2 , Ar, and Kr) and the Air Products Company, (He, Ne, N_2 , and CO_2).

The permeabilities and time lags were measured, using the Barrer high vacuum technique^{4,5}. Two separate installations, each with two permeability cells, were used. The downstream pressures were monitored for three cells with an MKS Baratron capacitance type pressure transducer, the fourth cell was monitored with a McLeod Gage.

The cells used were somewhat different from those employed previously. The new design, which proved quite satisfactory, is illustrated in Figure 1. The membranes were supported by force fitted sintered stainless steel discs.⁶ The cells were heated and cooled by circulating a suitable heat transfer fluid through narrow channels in the top and bottom sections. The cells were insulated by substantial asbestos jackets. Temperatures were insulated by substantial asbestos jackets. Temperatures were continuously monitored by a thermocouple, embedded in the cell block close to the vacuum chamber.

The cells were sealed to the glass vacuum system with standard kovar seals and flexible metal bellows; this made the membrane replacement very simple, requiring only that the upstream glass connection be broken and resealed.⁶

RESULTS AND DISCUSSION

Permeabilities

The permeability constants for He, Ne, Ar, Kr, N_2 , O_2 and CO_2 are presented in the form of Arrhenius plots in Figures 2 and 3. Most of the

measurements were made in the temperature range 25°C-70°C, which is below the glass temperature of the PAN. In the case of argon, however, measurements were continued up to 135°C. A break in the Arrhenius plot for Argon is apparent at 72°C; presumably the glass transition temperature. Dilatometry measurements⁷ made on similar film samples suggested a glass temperature of 70°C. These values are close to those reported in the literature for the T_g for PAN⁸.

Included in Figure 2 are the permeability data of Nakagawa et al⁹ for He, Ne and Ar in a 93:7 acrylonitrile-vinyl acetate film. In the case of Ne and Ar, as would be expected, the permeabilities are somewhat higher for the more disordered copolymer film. In the case of helium, however, the values are slightly lower for the copolymer. The helium permeability in PAN will be discussed later in this paper. The Arrhenius plots, describing the temperature dependence of the permeability for the copolymer, show a clear break at 96°C. Dilatometry measurements⁷ with similar copolymer films showed two glass transitions at 70°C and 137°C. The reasons for the difference between the temperatures of the apparent transitions, suggested by the permeability and dilatometry measurement for the copolymer, is not clear. One possible explanation could be that the films used by Nakagawa for the permeability measurements contained residual solvent and, therefore, both transitions were reduced. This plasticization could easily reduce the upper temperature to 96°C and reduce the lower transition temperature (observed by dilatometry) below 60°C, which was the lowest experimental temperature.

The permeability values obtained by Salame¹ for O₂ and CO₂ in similar films are also included in Figure 2. These permeabilities are about a

factor of two lower than those obtained in the present work. The agreement is reasonable, since different films were used and the experimental requirements were quite demanding, since the time lags were about 8 hours and 2 days for O_2 and CO_2 , respectively. This would necessitate protracted measurements to insure that the steady state is actually reached.

The activation energies for permeation and related pre-exponential factors are presented in Table III. The activation energies are surprisingly low for such very low permeability films. For example, with polyvinylidene chloride, another high barrier polymer, the activation energy is 16.8 K-cal/mole for nitrogen, compared with 10.6 K-cal per mole for PAN films. Presumably, the low value for PAN is due to the relatively small size of the segments contributing to the cooperative motion, in the glassy state, involved in the diffusive transport. Indeed, the permeability of argon, the only gas measured both below and above the glass transition temperature for PAN, has an activation energy of 10.6 below T_g and 20.1 Kcal/mole above the glass transition temperature. This behavior is rather common and has been discussed in some detail by Meares¹⁰ and by Stannett¹¹.

Diffusivities and Solubilities

Since PAN is in the glassy state for most of the measurements reported in this paper, dual mode sorption was suspected. High pressure sorption measurements, shown in Figure 4, confirmed that this was indeed the case. Consequently, the diffusivities calculated from the time lag data require substantial qualification. The treatment of Paul et al^{12,13} describes a general relationship between the observed time lag and the true value of the

penetrant diffusivity. The Paul model accounts for the so-called dual mode sorption however, the model does not require that the Langmuirian population of species is completely immobilized. The resulting relationship for the true diffusivity offered by Paul, for permeation at asymptotically low pressures is:

$$D_{\text{true}} = \frac{\ell^2(1+K)}{6\tau(1 + KF)}$$

where ℓ is the film thickness, τ the observed time lag, F is the fraction of Langmuirian species which are mobile, or alternatively the relative mobility of these species compared with the species dissolved by normal Henry's law solution, and $K = \frac{C_H' b}{Kd}$

where Kd is the normal Henry's law constant, C_H' is the hole saturation constant and b the hole affinity constant. An excellent review of the dual mode sorption theory has recently been published by Vieth et al.¹⁴ When all the Langmuirian species are mobile, $F=1$ and the equation reverts to the normal time lag expression $D = \ell^2/6\tau$. Alternatively, if the species dissolved in pre-existing holes are completely immobile, $F=0$ and $D = \frac{\ell^2}{6\tau} (1 + \frac{C_H' b}{Kd})$.

The permeabilities are in fact pressure independent for such idealized dual mode sorption, i.e. with complete immobilization. When the species are partly mobile, however, the permeability coefficients become pressure dependent and $\underline{P} = Dkd \left[1 + \frac{FK}{1 + b_p} \right]$

Both high pressure sorption and permeability measurements are necessary to evaluate F , as shown by Paul et al^{12,13} and these experiments will be conducted in these laboratories, together with more extensive high pressure sorption data. However, until this work is complete, the diffusion coefficients have been calculated in the normal way. In any event, the values are

more familiar than simple time lags and can be compared with other literature values for glassy polymers. These time lag diffusivities are shown in the form of Arrhenius plots in Figures 5 and 6; the associated activation energies are included in Table III. In the case of argon, a break in the Arrhenius plot at 70°C is apparent. This result is consistent with the permeability data.

In view of the dual mode sorption, there seems little point in calculating the solubilities. A discussion of this aspect of the work must be deferred until the high pressure sorption isotherms are determined.

The permeability of PAN film to helium is unusually high compared with the permeability of other polymers as shown, for example, in Table IV. Thus, the ratio of the permeabilities to helium and oxygen at 25°C is 1770 compared to less than 60 for all the polymers, where reliable values for both gases are known as shown in Table IV. This is a most important observation and indicates that the fluctuating free volume elements responsible for successful diffusive transport, must be very small in PAN compared with other polymers, even though the overall free volume could be of similar magnitude. With copolymerization, the remarkable ratio of permeability to He versus O₂ drops dramatically as can be seen from the results of Nakagawa⁹ and from other work¹⁵. Presumably, the extremely small and hence highly selective size of the zones of diffusion, suggested by the low activation energy for permeation, as well as the remarkable permeability ratios, results in the unusually high barrier properties of PAN towards most gases. This limited molecular motion probably derives from the extremely high cohesive energy density of the PAN which, plus the small size of the nitrile group, in turn, results in rather well developed order in the glassy polymer.

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Table 1. The permeability of Various Polymers to Oxygen, Water and Carbon Dioxide at 30°C.

Material	P _{O₂}	P _{CO₂}	Ratio (CO ₂ /O ₂)	P _{H₂O}
Polyacrylonitrile	0.0003	0.0018	6.0	300
Polymethacrylonitrile	0.0012	0.0032	2.7	410
Lopac (Monsanto Co.)*	0.0035	0.0108	3.1	340
Polyvinylidene Chloride	0.0053	0.029	5.5	1.0
Barex (Sohio Co.)*	0.0054	0.061	3.4	660
Polyethylene Terephthalate	0.035	0.017	4.9	175
Nylon 6	0.038	0.016	3.6	275
Polyvinyl Chloride (unplast.)	0.045	0.016	3.6	275
Polyethylene (dens.0.964)	0.40	1.80	4.5	12
Cellulose Acetate (unplast.)	0.80	2.40	3.0	6,800
Butyl Rubber	1.30	5.18	4.0	120
Polycarbonate	1.40	8.0	5.7	1,400
Polypropylene (dens.0.907)	2.20	9.2	4.2	65
Polystyrene	2.63	10.5	3.8	1,200
Polyethylene (dens.922)	6.90	28.0	4.0	90
Neoprene	4.0	25.8	6.5	910
Teflon	4.9	12.7	2.6	33.0
Poly (2,6 dimethyl penylene oxide)	15.8	75.7	4.8	4,060
Natural Rubber	23.3	153	6.6	2,600
Poly 4,methyl pentene-1	32.3	92.6	2.9	-
Poly dimethyl siloxane	605	3,240	5.3	40,000

*High acrylonitrile copolymers

Units: CCS. (S.T.P/cm²/cm/sec/cm. Hg x 10¹⁰)

Table II. Carbon Dioxide Transport in Polyacrylonitrile Films.

<u>Temp.</u> (°C)	<u>Original Film</u>		<u>Water Extracted Film*</u>	
	<u>$\bar{P}$</u> (cm(STP)cm/sec cm cmHg)	<u>θ</u> (min)	<u>$\bar{P}$</u> (cm (STP)cm/sec cm cmHg)	<u>θ</u> (min)
70	1.10×10^{-12}	340	0.89×10^{-12}	690
55	6.36×10^{-13}	690	5.04×10^{-14}	1.410
40	3.50×10^{-13}	1.530	2.68×10^{-13}	3.160

*2.7% loss on extraction to constant weight.

Table III. Gas Transport Parameters for Polyacrylonitrile.

<u>Gas</u>	$P_{25^{\circ}\text{C}}$ $\times 10^{12}$	E_p <u>Kcals/mole</u>	$D_{25^{\circ}\text{C}}$ $\times 10^9$	E_d <u>Kcals/mole</u>
Helium	53.0	5.3	19.1	6.4
Neon	1.67	7.4	9.85	6.6
Argon T_g	0.01	10.6	0.0023	11.0
Argon T_g	-	20.1	-	13.7
Krypton	0.003	11.1	0.00023	11.0
Nitrogen	0.016	10.6	0.0021	12.7
Oxygen	0.028	11.9	0.0082	9.7
Carbon Dioxide	0.18	8.1	0.0013	10.8

Units $P = \text{ecs} \cdot \text{STP} / \text{cm}^2 / \text{cm} / \text{cm Hg} / \text{sec}$. $D = \text{cm}^2 / \text{sec}$.

P_0 and D_0 for Argon above T_g are 0.32 and 4.54×10^{-4} respectively.

Table IV. Permeability of Polymers to Oxygen and Helium at 25°C.

Material	P _{O₂}	P _{He}	Ratio He/O ₂
Polyacrylonitrile	0.0003	0.53	1770
Polyvinylidene Chloride	0.0053	0.31	58.5
Polyethylene Terephthalate	0.035	1.32	37.7
Nylon-6	0.038	0.53	13.2
Polyvinyl Chloride	0.045	2.05	45.6
Polyethylene 0.964	0.40	1.14	2.15
Polyvinyl Acetate	0.50	12.6	25.2
Cellulose Acetate	0.80	16.0	20.0
Butadiene-Acrylonitrile (61-39)	0.96	6.81	7.1
Polyethyl methacrylate	1.28	18.0	14.0
Polypropylene	2.20	38.0	17.3
Polystyrene	2.63	18.7	7.11
Polyethylene (0.914)	2.90	4.9	1.68
Hydropol (0.894)	11.3	15.7	1.38
Polyphenylene oxide	15.8	78.1	4.9
Poly 4-methyl pentene-1	32.3	101	3.13
Polydimethyl siloxane	605	233	0.39

P = ccs STP/cm²/cm/sec/cm. Hg X 10¹⁰

CAPTIONS FOR FIGURES

Figure 1 Diffusion Cell

Figure 2 Temperature dependence of the permeability constants for the noble gases in PAN. $\circ$ He, $\triangle$ Ne, $\circ$ Ar, $\square$ Kr
dotted lines represent data of Nakagawa⁹.

Figure 3 Temperature dependence of the permeability of the atmospheric gases in PAN. $\triangle$ CO₂, $\circ$ O₂, $\square$ N₂. $\blacktriangle$ CO₂, solvent free
 $\blacktriangle$, $\bullet$ results of Salame¹ for CO₂ and O₂ respectively.

Figure 4 Equilibrium sorption isotherms for CO₂ in PAN $\square$, polystyrene $\circ$, polycarbonate $\triangle$ the polystyrene and polycarbonate data are for the work of Vieth¹⁴ and Paul^{12,13} respectively.

Figure 5 Temperature dependence of the diffusion constants (calculated from the time lags, see text) for the noble gases in PAN
 $\circ$ He, $\triangle$ Ne, $\circ$ Ar, $\square$ Kr.
dotted lines represent data of Nakagawa⁹.

Figure 6 Temperature dependence of the diffusion constants (calculated from the time lags, see text) of the atmospheric gases in PAN
 $\circ$ O₂, $\square$ N₂, $\triangle$ CO₂.

