

# The Effect of Casting Solvent and Water on Gas Permeability of Poly( $\gamma$ -methyl *L*-Glutamate) Membrane

NORIIHIKO MINOURA, *Industrial Products Research Institute, Yatabe-machi Higashi, Tsukuba-gun, Ibaraki 305, Japan*

## Synopsis

Gas permeability of poly( $\gamma$ -methyl *L*-glutamate) (PMLG) membranes prepared by using dichloroethane, trifluoroacetic acid, and formic acid as solvents was studied. The membranes prepared by casting dichloroethane and trifluoroacetic acid solutions of the polymer, designated as PMLG—DCE and PMLG—TFA, respectively, had  $\alpha$ -helical structures according to infrared absorption spectra, while the membranes prepared by allowing the PMLG—TFA membranes to swell in formic acid, designated as PMLG—FA, had mainly a  $\beta$ -sheet structure. The diffusion coefficients of each gas studied for PMLG—DCE, PMLG—TFA, and PMLG—FA decreased in that order, and the apparent activation energies of diffusion increased in that order. The apparent heats of solution for Ne, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were negative in PMLG—FA. These results were discussed in connection with the molecular conformations of PMLG in the membranes. It is suggested that the diffusion of gases in PMLG—DCE takes place in the side-chain regions between helices, while in PMLG—FA the diffusion occurs across the polymer main chain whose mobility is depressed by the intermolecular hydrogen bonds. The effect of water on oxygen permeability of PMLG—DCE was small; on the contrary that of PMLG—FA was very large. Furthermore, it is assumed that the random-coil conformation partly exists in PMLG—TFA.

## INTRODUCTION

It is known that when polypeptide membranes are formed by casting from solutions, different chain conformations result in the membranes obtained, depending on the kind of solvent, temperature, casting velocity, etc. Nakajima et al.<sup>1</sup> reported that poly( $\gamma$ -methyl *L*-glutamate) exists in the  $\alpha$ -helix form in membranes cast from trifluoroacetic acid solutions but in the  $\beta$ -chain form in membranes swollen in formic acid.

The writer has studied the effect of casting solvent on the sorption and diffusion of water vapor in the poly( $\gamma$ -methyl *L*-glutamate) membranes cast from 1,2-dichloroethane (helical solvent) and trifluoroacetic acid (random-coil solvent) and swollen in formic acid.<sup>2</sup> The sorption and diffusion behavior in the membranes cast from 1,2-dichloroethane solutions was hydrophobic, while the behavior in the membranes swollen in formic acid was hydrophilic. Furthermore, from the sorption and diffusion experiments, it is assumed that the molecular chains in the membranes cast from trifluoroacetic acid solutions are mainly in  $\alpha$ -helical and partly random-coil conformations.

The purpose of this study is to elucidate the relationship between gas permeability of the membranes described above and the molecular conformations of the membranes. Further, the effect of water on oxygen permeability of the membranes is investigated.

## EXPERIMENTAL

## Materials

Poly( $\gamma$ -methyl *L*-glutamate) (PMLG) supplied by Kyowa Hakko K. K. (Japan) was prepared by the polymerization of *N*-carboxy amino acid anhydride. The viscosity-average molecular weight is about 60,000, which was determined by the intrinsic viscosity of dichloroacetic acid solution at 25°C.

The solvents used were 1,2-dichloroethane, trifluoroacetic acid, and formic acid of extrapure grade, and they were used without further purification.

Membranes were prepared as follows: The membranes designated as PMLG—DCE (0.200–0.300 mm thick) were prepared by casting the dichloroethane solution of the polymer on a glass plate at 20°C. The membranes designated as PMLG—TFA (0.080–0.130 mm thick) were prepared by casting the trifluoroacetic acid solution by the identical technique as PMLG—DCE. The membranes designated as PMLG—FA (0.020–0.030 mm thick) were prepared from PMLG—TFA by allowing the PMLG—TFA membranes to swell in formic acid at room temperature for 1 month and then drying the swollen membranes under reduced pressure at about 13°C. All membranes were dried under vacuum at 80°C for a few days to remove completely the casting solvents.

Infrared absorption spectra of these membranes were reported in detail.<sup>2</sup> The result shows that the PMLG—DCE and PMLG—TFA membranes have  $\alpha$ -helical structures, while the PMLG—FA membranes have mainly  $\beta$ -sheet structures.

Wide-angle X-ray diffraction profiles were obtained with a Rigaku Denki Model D-3F diffractometer. Figure 1 shows the X-ray intensity profiles of PMLG—DCE, PMLG—TFA, and PMLG—FA. The patterns observed depend on the casting solvent, and support the respective conclusions derived from the infrared spectra. The crystallinity of the PMLG—TFA membranes is higher, while that of the PMLG—FA membranes is lower. In PMLG—DCE and PMLG—TFA the first main reflection corresponds to an intermolecular spacing of the  $\alpha$ -helical chains, and the spacing of the PMLG—TFA membranes is narrower than that of the PMLG—DCE membranes.

The degree of hydration of the membrane is the volume fraction of water in the water-swollen membrane, and it was determined as follows: The membrane

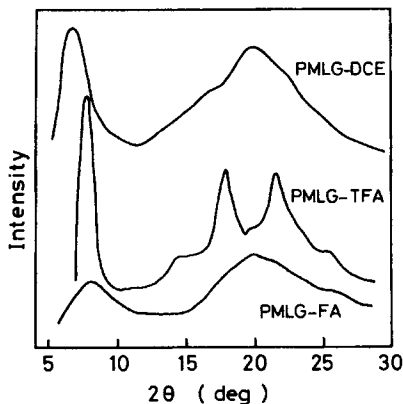
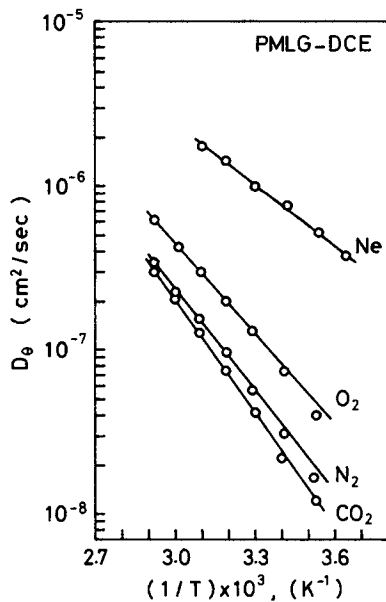


Fig. 1. Wide-angle X-ray intensity profiles.

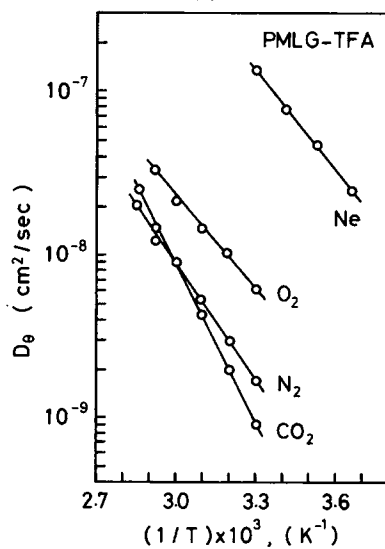
was swollen, blotted, and weighed repeatedly until constant weight of the swollen membrane was obtained within experimental error at 20°C. The membrane was then dried to constant weight under vacuum at 80°C.

### Permeation Experiment of Gases

The general theory of gas transport in polymers and detailed discussions of the methods of measurement and calculation of the permeability, diffusion, and solubility coefficients,  $P$ ,  $D_\theta$ , and  $S$ , respectively, have been published elsewhere.<sup>3</sup> The experimental method used in this study was an adaptation of the high-



(a)



(b)

Fig. 2. Temperature dependence of diffusion coefficients.

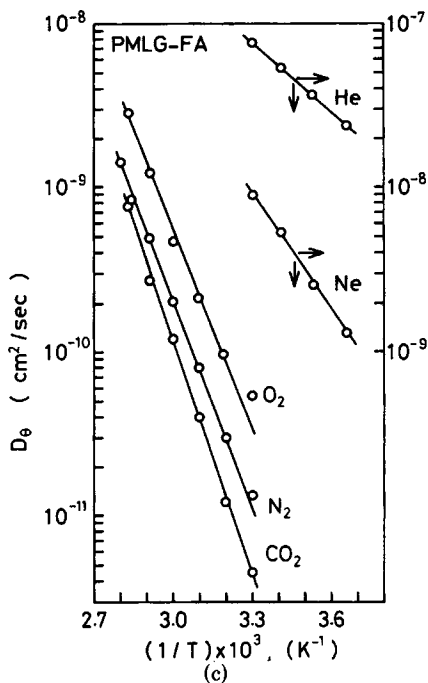


Fig. 2. (Continued from previous page.)

vacuum gas transmission technique described by Stannet and co-workers.<sup>4</sup> A time-lag method was used for the calculation of diffusion coefficients. Solubility coefficients were calculated by  $S = P/D_\theta$ . He, Ne, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> were used as penetrants.

### Permeation Experiment of Oxygen Dissolved in Water

The permeation measurement of dissolved oxygen through the membranes was done by means of an oxygen electrode. The experimental method has been reported in detail.<sup>5</sup> The membranes were laminated to polystyrene membranes to avoid membrane degradation during the measurement, as described previously. The permeability coefficients were calculated from the steady-state current of the permeation curve.

TABLE I  
Apparent Activation Energy of Permeation  $E_P$ , Diffusion  $E_D$ , and Apparent Heat of Solution  $\Delta H_S$

(kcal/mol)		He	Ne	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
$E_P$	PMLG—DCE	5.63	7.24	8.33	9.83	5.93
	PMLG—TFA		7.16	10.3	13.1	10.5
	PMLG—FA	6.54	7.64	12.1	15.5	10.4
$E_D$	PMLG—DCE		5.68	8.31	9.47	10.7
	PMLG—TFA		8.91	8.58	10.8	14.9
	PMLG—FA	6.27	10.7	18.8	18.4	21.8
$\Delta H_S$	PMLG—DCE		1.6	0.02	0.36	-4.8
	PMLG—TFA		-1.8	1.7	2.3	-4.4
	PMLG—FA	0.27	-3.1	-6.7	-2.9	-11.4

Prior to measurement, the membranes were immersed in distilled water for about 1 month. Sorption equilibrium with respect to water is assumed.

## RESULTS AND DISCUSSION

### Diffusivity of Gases

The diffusion coefficients  $D_\theta$  (cm<sup>2</sup>/s) of the PMLG—DCE, PMLG—TFA, and PMLG—FA membranes are plotted against the inverse temperature in Figure 2. The diffusion coefficients are strongly influenced by the casting solvent. In each gas the diffusion coefficients of PMLG—DCE, PMLG—TFA, and PMLG—FA decrease in that order. Since these Arrhenius plots are linear for all polymers measured, the apparent activation energies of diffusion  $E_D$  (kcal/mol) were calculated from Figure 2, and are summarized in Table I. The apparent activation energies of diffusion for PMLG—DCE, PMLG—TFA, and PMLG—FA increase in that order.

The vast difference in diffusion behavior observed among PMLG—DCE, PMLG—TFA, and PMLG—FA membranes can be attributed to difference in the molecular conformations, namely, the type of molecular interaction.

I have reported that the PMLG—DCE membranes have  $\alpha$ -helical structure and that the diffusion of small molecules in the membranes occurs through the side-chain region between helices.<sup>2,6</sup>

In the PMLG—TFA membranes the result of the sorption and diffusion experiments of water vapor suggested that the molecular chains in the membranes are mainly in  $\alpha$ -helical and partly random-coil conformation.<sup>2</sup> The formation of the random-coil part in the PMLG—TFA membranes is thought to be due to the fixation of a part of the polymer molecules in random-coil conformation during the evaporation process of trifluoroacetic acid, though the transition of the polymer molecules from random-coil conformation to helical conformation occurs during the process. The random-coil part exists in the amorphous region of the membrane. Since the diffusion of small molecules takes place in the amorphous region, the mobility of the polymer main chain in the random-coil part affects the diffusion property. The mobility of the polymer main chain in the random-coil part is supposed to be lower than that of the side chain in the other part. Accordingly, it is thought that because of not only the higher crystallinity but also the presence of the random-coil part the diffusion coefficients of the PMLG—TFA membrane are smaller than those of the PMLG—DCE membrane, and the activation energy of diffusion for the former membrane is larger than that of the latter membrane.

In the case of PMLG—FA, it has been reported that intermolecular hydrogen bonding produces sheet-type structures and that the plane of the sheet is parallel to the surface of the membrane.<sup>1</sup> Accordingly, the smaller diffusion coefficient and the larger activation energy of diffusion are attributed to the lower mobility of the polymer main chain, which is due to the formation of intermolecular hydrogen bonds.

A relationship between the activation energies for diffusion and the molecular diameters of the various penetrants is shown in Figure 3. According to the theory of Brandt,<sup>7</sup> activation energy for diffusion may be divided into one component related to the cohesive energy of the polymer and another related to chain

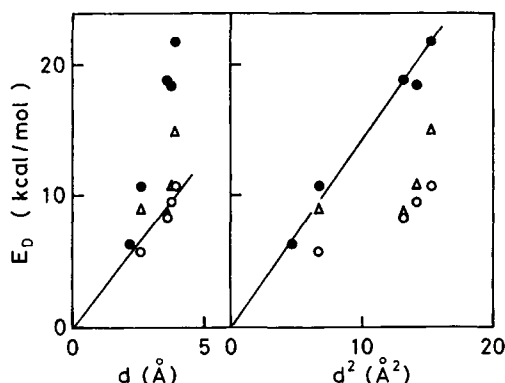


Fig. 3. Apparent activation energy for diffusion vs. gas diameter  $d$  and  $d^2$ . (○) PMLG—DCE; (△) PMLG—TFA; (●) PMLG—FA.

TABLE II  
Selectivity Ratios of Permeability Coefficients for Gas Pairs Indicated at 30°C

	He/N <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /O <sub>2</sub>
PMLG—DCE	27	3.5	10
PMLG—TFA		6.5	3.7
PMLG—FA	1100	6.2	1.8

TABLE III  
Comparison between Permeability of Dissolved Oxygen  $P_w$  and That of Gaseous Oxygen  $P_g$  at 30°C and between Activation Energy of Permeation of Dissolved Oxygen  $E_{P_w}$  and That of Gaseous Oxygen  $E_{P_g}$

	Degree of hydration	Permeability coefficient [cm <sup>3</sup> (STP)·cm/cm <sup>2</sup> ·s·cm Hg]		$P_w/P_g$	Activation energy (kcal/mol)	
		$P_w$	$P_g$		$E_{P_w}$	$E_{P_g}$
PMLG—DCE	0.109	$2.05 \times 10^{-10}$	$1.74 \times 10^{-10}$	1.2	8.3	8.33
PMLG—TFA	0.116	$3.00 \times 10^{-11}$	$7.77 \times 10^{-12}$	3.9	10.4	10.3
PMLG—FA	0.845	$3.20 \times 10^{-9}$	$2.59 \times 10^{-13}$	12,000	1.2	12.1

stiffness. The former is proportional to the molecular diameter of the penetrant and the latter to the square of the diameter. The activation energy was found to be proportional to the gas molecular diameter in rubbery polymers and to the square of the diameter in glassy polymers.<sup>8</sup> In the case of PMLG—DCE, the activation energy seems to be proportional to the gas molecular diameter, whereas with PMLG—FA the activation energy seems to be proportional to the square of the gas molecular diameter. This result suggests that the diffusion of gases in PMLG—DCE takes place in the side-chain regions between helices, while in PMLG—FA the diffusion occurs across the polymer main chain whose mobility is depressed by the intermolecular hydrogen bonds.

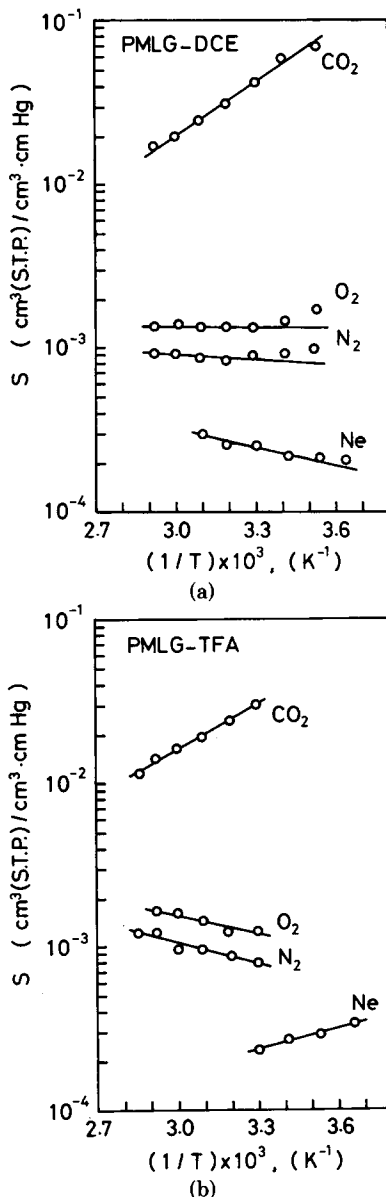


Fig. 4. Temperature dependence of solubility coefficients.

### Solubility of Gases

Figure 4 shows the temperature dependence of solubility coefficients  $S$  [ $\text{cm}^3(\text{STP})/\text{cm}^2\cdot\text{cm Hg}$ ] for PMLG—DCE, PMLG—TFA, and PMLG—FA. The solubility coefficients are less influenced by the casting solvent. However, the apparent heats of solution  $\Delta H_S$  (kcal/mol), obtained from Figure 4, are different (Table I). The apparent heats of solution in PMLG—DCE for Ne,  $\text{O}_2$ , and  $\text{N}_2$  are positive. I have reported that the sorption of small molecules onto polypeptide with  $\alpha$ -helical structure occurs in the side-chain region between helices.<sup>2,6</sup> On the contrary, in the case of PMLG—FA the apparent heats of solution for Ne,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2$  are small and negative. This means that the

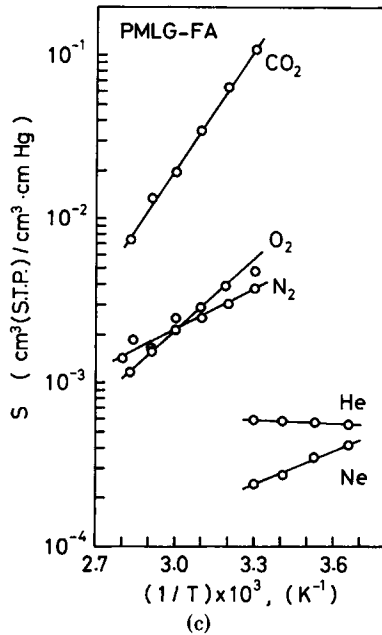


Fig. 4. (Continued from previous page.)

solution process for these gases in the PMLG—FA membrane is exothermic. Barrer et al.<sup>9</sup> suggested that a solution process may be considered to consist of two separate steps: (1) the formation of a hole or site and (2) the occupancy of this site by the solute molecule. Step (1) is endothermic, while step (2) is exothermic. I suppose that in PMLG—FA the mobility of the polymer main chain is very low because of the intermolecular hydrogen bonds, and the solution process may be mainly step (2). This behavior is well known to be characteristic of the solution process for gases into glassy polymers.

### Permeability of Gases

Figure 5 shows the Arrhenius plot of the permeability coefficients  $P$  [ $\text{cm}^3(\text{STP})\text{-cm}/\text{cm}^2\text{-s-cm Hg}$ ] for PMLG—DCE, PMLG—TFA, and PMLG—FA. The permeability coefficients are extremely influenced by the casting solvent. In each gas the permeability coefficients of PMLG—DCE, PMLG—TFA, and PMLG—FA decrease in that order. The vast difference in permeation behavior observed among PMLG—DCE, PMLG—TFA, and PMLG—FA reflects the difference in diffusion behavior, namely the difference in the molecular conformations as discussed above.

The selectivity ratios of the permeability coefficients for the gas pairs indicated at 30°C are listed in Table II. The selectivity ratios are also influenced by the casting solvent. It is noteworthy that in PMLG—FA the selectivity of He to N $_2$  is very large.



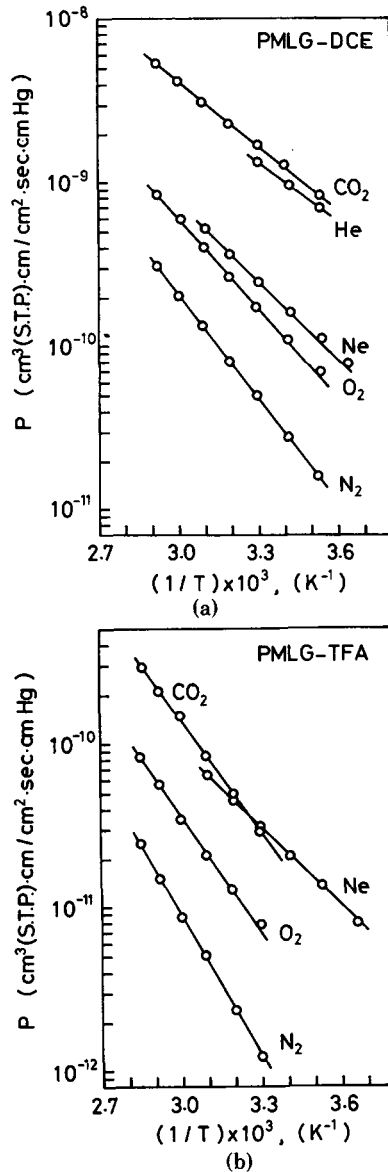
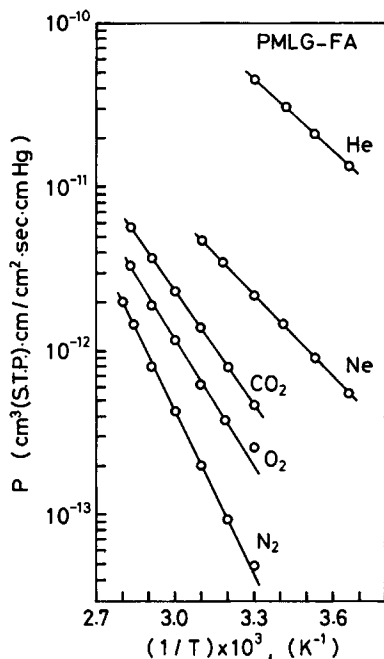


Fig. 5. Temperature dependence of permeability coefficients.

### Effect of Water on Oxygen Permeability

It is very interesting to elucidate the effect of water on oxygen permeability of the PMLG—DCE, PMLG—TFA, and PMLG—FA membranes which have the different molecular conformations as discussed above. The permeability coefficients of the PMLG—DCE, PMLG—TFA, and PMLG—FA membranes to dissolved oxygen are plotted against the inverse temperature in Figure 6. The permeability coefficients of the PMLG—FA membranes are larger than those of the PMLG—DCE and PMLG—TFA membranes.

In order to express the effect of water on oxygen permeability quantitatively, the permeability coefficients of dissolved oxygen,  $P_w$  (water-membrane-water system), are compared with those of gaseous oxygen,  $P_g$  (gas-membrane-gas



(c)  
Fig. 5. (Continued from previous page.)

system), obtained above by the high-vacuum method; these are given in Table III. From the ratio of  $P_w$  and  $P_g$ , the influence of water on oxygen permeation can be observed. The activation energies of permeation of dissolved oxygen,  $E_{P_w}$ , were calculated from Figure 6, since temperature dependences of permeability coefficients are linear. These are also given in Table III with the activation energies of permeation of gaseous oxygen,  $E_{P_g}$ , obtained above by the high-vacuum method.

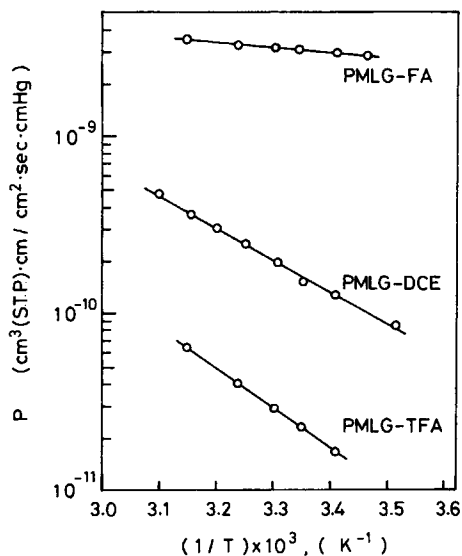


Fig. 6. Temperature dependence of permeability coefficients of oxygen dissolved in water.

In PMLG—DCE which has intramolecular hydrogen bonds, the  $P_w/P_g$  ratio is near 1.0 and  $E_{P_w}$  is nearly the same as  $E_{P_g}$ . The effect of water on oxygen permeability is small. The  $P_w/P_g$  ratio in PMLG—TFA is larger compared with PMLG—DCE. This result suggests that, as discussed above, the random-coil part exists in the PMLG—TFA membranes and polar groups which do not take part in the formation of intramolecular hydrogen bonds are accessible to water. In the case of PMLG—FA the  $P_w/P_g$  ratio is very large and the difference between  $E_{P_w}$  and  $E_{P_g}$  is also large. The PMLG—FA membrane has a  $\beta$ -sheet structure and is highly swollen by water (Table III). The intermolecular hydrogen bonds are broken by water molecules, so that oxygen can easily permeate through the membrane.

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