

## A Simple Method for Prediction of Gas Permeability of Polymers from Their Molecular Structure

Lianda JIA and Jiping XU

*Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,  
109 Stalin Avenue, Changchun, 130022, PR China*

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**ABSTRACT:** A method for the prediction of gas permeabilities ( $P$ ) through polymers from their chemical structure has been developed on the basis of the ratio of molar free volume to molar cohesive energy,  $V_f/E_{coh}$ . The permeation of small gas molecules through polymer membranes is dependent on the chain packing density measured by  $V_f$  and segmental motion of polymer chains measured by  $E_{coh}$ . But no simple relationship between  $P$  and  $V_f$  or  $E_{coh}$  alone was found. The permeability data of more than 60 polymers covering 7 orders of magnitude for six gases have been treated with linear regression analysis. All plots of  $\log P$  vs.  $V_f/E_{coh}$  gave good straight lines. It is also found that a linear relationship holds when plotting both the intercepts and slopes of  $\log P$  vs.  $V_f/E_{coh}$  lines against square of the diameters of gas molecules. Therefore, the permeabilities of all the non-swelling gases through a great variety of polymers can be estimated using two correlations above. Moreover, this method is more accurate than others in the literature and may found useful for the selection of gas separation or barrier membrane materials.

**KEY WORDS** Polymer Membranes / Gas Permeability / Free Volume / Cohesive Energy / Gas Separation / Barrier /

Permeation of small molecules through polymer membranes is very important for many applications, including separation processes, barrier packaging and controlled release devices for medicine and agriculture. It is significant to have a simple method for predicting what chemical structures will provide permeabilities in the range desired for a particular use.

In an attempt to relate the penetrant to the polymer, Lee<sup>1</sup> put forward a prediction technique for gas permeability from polymer structure on the basis of a specific free volume (SFV) diffusive theory. Recently, Salame<sup>2</sup> suggested so called "Permachor" approach to predict gas permeability in polymers and he found that there is a good linear relationship between the logarithm of gas permeability and a polymer structure parameter Permachor ( $\pi$ ), which can be calculated from both the cohesive energy density (CED) and fractional free volume ( $V_f$ ) of the polymer.

However, it is clear from the discussion later that the linear relationship between  $\log P$  and  $\pi$  is not so good as mentioned above. Furthermore, only 20 individual segmental values ( $\pi$ ) of the backbones and side groups of polymers are available for the calculation of polymer Permachor. So, the permachor values of many polymers can not be calculated easily.

The object of the present study is to relate gas permeability with gas molecule diameters and two polymer molecular structure parameters i.e. cohesive energy ( $E_{coh}$ ) and free volume ( $V_f$ ) without taking into account such factors as crystallinity, orientation and rubbery or glassy state. These parameters can be obtained easily from group contributions. Therefore, the advent of this method simplified greatly the selection of membrane materials for different kinds of applications.

#### FOUNDATION AND APPROACH

The permeability of non-swelling gas through polymer is given by:

$$P = D S \quad (1)$$

where  $P$  is the permeability,  $D$  -- the diffusion coefficient and  $S$  -- the solubility of the penetrant in given polymer. The temperature dependence of diffusion coefficient and solubility over small temperature range can be represented by:

$$D = D_0 \exp(-E_d/RT) \quad (2)$$

$$S = S_0 \exp(-\Delta H_s/RT) \quad (3)$$

where  $E_d$  is the apparent activation energy for the diffusion process and  $\Delta H_s$  -- the heat of solution which may be expressed by the molar heat of condensation  $\Delta H_{cond}$  and the partial molar heat of mixing  $\Delta H_1$ :

$$\Delta H_s = \Delta H_{cond} + \Delta H_1 \quad (4)$$

The value of  $\Delta H_1$  can be estimated from the cohesive energy density (CED) of the penetrant and the polymer by means of the Hildebrand equation<sup>3</sup>:

$$\Delta H_1 \approx \Delta E_1 = v_1(\delta_1 - \delta_2)^2 \phi_2^2 \quad (5)$$

The solubility parameters  $\delta_1$  and  $\delta_2$  are the square roots of the CED of the penetrant and polymer respectively,  $v_1$  -- the partial molar volume of the penetrant and  $\phi_2$  -- the volume fraction of polymer in the mixture. For gases well above their critical point (e.g.  $H_2$ , He,  $O_2$ ,  $N_2$  at room temperature) the hypothetical value of  $\Delta H_{cond}$  would be very small and  $\Delta H_s$  is governed by  $\Delta H_1$ . Utilization of the Flory-Huggins equation<sup>4</sup> leads to an expression for the solubility coefficients:

$$S = f_2 / [f_1 p_1^0 \exp(1 + \chi_1)] \quad (6)$$

where  $p_1^0$  is the saturated vapor pressure of penetrant,  $\chi_1$  is the Flory-Huggins interaction parameter and  $f_1$ ,  $f_2$  are the fractional free volume of penetrant and polymer respectively.

As for  $E_d$ , Meares<sup>5</sup> derived the expression:

$$E_d = (1/4) \pi d^2 N \lambda (\text{CED}) \quad (7)$$

where  $d$  is the collision diameter of the penetrant molecule,  $N$  -- the Avogadro's number and  $\lambda$  -- the jump distance.

From an expression similar to the Doolittle equation as modified for diffusion:

$$D = RT A_d \exp(-B_d/f) \quad (8)$$

where  $A_d$  is a parameter which is dependent on the size and shape of the penetrant and  $B_d$  is a parameter characterizing the "efficiency" of using the available free volume fraction,  $f$ , in the diffusion processes.

Table 1. Gas Permeabilities at 25°C and Polymer Structural Parameters

Material	$V_f/E_{coh}$ $\times 10^4$	$\log V_f, E_{coh}$	$\pi$	1/SFV (g/cc)	P (barrer)						Ref.
					O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	
Poly[1-(trimethylsilyl)-1-propyne]	10.46	-2.980	-	3.565	3000	1800	2200	5200	19000	4300	15
Poly(tert-butylacetylene)	8.10	-3.092	-	3.603	130	43	180	300	560	85	15
Poly(1-n-heptyl-propyne)	7.20	-3.143	-	4.413	35	14	48	76	130	40	15
Poly[o-(trimethylsilyl)phenylacetylene]	6.81	-3.167	-	5.022	78	24	170	290	290	38	15
Poly(1-chloro-2-n-butylacetylene)	6.31	-3.200	-	5.324	35	10	59	100	180	30	15
Poly(1-chloro-2-n-hexylacetylene)	6.26	-3.203	-	5.357	32	11	41	66	130	33	15
Poly(1-chloro-2-n-octylacetylene)	6.24	-3.205	-	5.38	47	16	43	76	170	46	15
Poly[o-(trifluoromethyl)phenylacetylene]	6.06	-3.218	-	7.420	25	7.3	130	140	130	6.6	15
Poly(1-n-hexyl-2-phenylacetylene)	5.90	-3.229	-	5.165	14	5.5	30	45	48	14	15
Poly(1-ethyl-2-phenylacetylene)	5.83	-3.234	-	5.035	12	4.5	40	57	40	4.4	15
Poly(1-phenyl-1-propyne)	5.80	-3.237	-	4.987	6.3	2.2	30	43	25	2.8	15
Poly(o-methyl phenylacetylene)	4.92	-3.308	-	5.959	8.1	3.0	29	39	15	3.0	15
Poly(1-chloro-2-phenylacetylene)	4.87	-3.312	-	6.448	5.1	1.0	23	29	23	1.3	15
Poly(oxydimethylsilylene)	9.50	-3.022	-23#	4.437	600	280	340	650	3230	940	14
Hydrogenated Polybutadiene	5.70	-3.244	15	5.874	11.3	3.98	15.7	--	48.2	13	13
Poly(1,3-butadiene)	6.50	-3.187	6#	4.471	19	6.42	32.6	41.9	138	--	13
Polyisoprene (NR)	6.03	-3.220	-	4.939	24	8.1	31	49	131	30	14
Polychloroprene	6.40	-3.194	-	4.343	3.95	1.17	13	13.57	25.74	3.27	14
Polydimethylbutadiene	5.73	-3.242	-	5.276	2.1	0.472	14.4	17	7.47	0.79	13
Rubber hydrochloride	5.00	-3.301	38.3	6.568	0.43	0.106	--	1.6	1.02	--	11
Polysulfide (Thiokol Rubber)	4.39	-3.358	-	8.763	7.7	--	--	--	10.63	--	12
LD Polyethylene	4.76	-3.322	25#	7.03	2.88	0.969	4.9	8.7*	12.6	2.88	14
HD Polyethylene	2.86	-3.544	39#	11.688	0.40	0.143	1.14	6	0.36	0.39	13
Polypropylene	4.80	-3.319	31#	6.101	0.88	0.219	6.22	5.98	2.89	--	13
Poly(vinyl chloride)	3.80	-3.420	61#	9.328	0.045	0.012	2.05	1.70	0.157	0.029	13
Polystyrene	4.86	-3.313	27	6.017	2.63	0.788	18.7	23.3	10.5	0.84	13
Poly(vinyl alcohol)	0.81	-4.092	157#	18.375	0.009	0.0005	--	--	0.01	--	13
Poly(vinyl acetate)	4.57	-3.340	--	6.830	0.384	0.06	10.8	7.25	--	0.05	13
Poly(vinyl toluene)	4.44	-3.353	--	6.754	3.5	0.46	--	--	10.81	--	12
Poly(vinylidene chloride)	1.83	-3.738	86#	21.6	0.0084	0.001	0.248	0.109	0.0196	--	13
Poly(vinyl fluoride)	1.87	-3.728	59#	27.08	0.02	0.0042	0.970	0.35	0.09	0.0057	12
Poly(vinylidene fluoride)	1.39	-3.857	67.5	60.99	0.04	--	--	0.41	0.36	--	11
Poly(trifluorochloroethylene)	4.95	-3.305	64	15.43	0.486	0.119	34.08*	4.56	1.82	0.0348	13
Poly(tetrafluoroethylene)	5.50	-3.260	30	27.03	4.2	1.4	25*	9.8	11.7	--	13

Prediction of Permeability from  $V_f/E_{coh}$

Table 1. Gas Permeabilities at 25°C and Polymer Structural Parameters(Continued)

Material	$V_f/E_{coh}$ $\times 10^4$	$\log V_f/E_{coh}$	$\pi$	1/SFV (g/cc)	P (barrer)						Ref.
					O <sub>2</sub>	N <sub>2</sub>	He	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	
Poly(ethylene oxide)	4.90	-3.310	33	6.067	0.46	--	--	--	--	--	11
Poly(methylmethacrylate)	3.80	-3.420	--	8.342	0.102	0.023	--	--	--	--	11
Poly(ethylmethacrylate)	4.45	-3.352	--	7.222	1.4	0.25	15	--	5.0	--	11
Poly(4-methylpentene-1)	6.50	-3.187	7#	4.527	32.3	7.83	101	136	92.6	--	13
Poly(2,6-dimethylphenyl oxide)	5.68	-3.246	13	5.427	15.8	3.81	78.1	112.8	75.7	4.3	13
Poly(oxymethylene)	3.00	-3.523	42.5	9.677	0.09	0.024	--	--	0.45	--	11
Poly-p-xylene	4.30	-3.367	30	7.35	0.47	0.132	--	3.54	2.64	--	12
Poly(chloro-p-xylene)	3.14	-3.503	66	10.845	0.03	0.004	--	--	0.07	--	11
Nylon 6	1.50	-3.824	80#	9.203	0.006	0.0015	0.53	0.54	0.021	--	11
Nylon 11	1.58	-3.801	41.7	10.976	0.12	0.03	1.95*	1.78*	0.06	--	11, 13
Nylon 6,6	1.34	-3.873	73#	10.343	0.034	0.008	--	1.0	0.17	--	14
Nylon 6,10	1.10	-3.959	52	14.27	0.02	--	--	--	0.074	--	11
Nylon 6,9	1.82	-3.740	54.2	8.358	0.035	--	--	--	--	--	11
Nylon 8	1.90	-3.721	51.8	8.115	0.058	--	--	--	--	--	11
Nylon 12	2.60	-3.585	39.5	7.16	0.36	--	--	--	--	--	11
Bisphenol-A-Polycarbonate**	4.5	-3.347	31#	6.75	1.484	0.289	15.0	13.6	6.0	0.257	16
Hexafluorobisphenol-A-Polycarbonate**	6.01	-3.221	58.5	7.53	6.9+	1.7+	60.0++	--	24++	1.05++	18
Tetramethylhexafluorobisphenol-A-Polycarbonate**	7.39	-3.131	--	5.949	32+	7.7+	206++	--	111++	4.7++	18
Tetramethylbisphenol-A-Polycarbonate**	5.20	-3.284	-21	6.027	5.59	1.09	46.2	--	17.58	0.80	16
Tetrabromobisphenol-A-Polycarbonate**	4.25	-3.372	--	10.975	1.36	0.182	17.6	--	4.23	0.126	16
Tetrachlorobisphenol-A-Polycarbonate**	4.43	-3.354	72	7.896	2.29	0.36	27.4	--	6.66	0.224	16
Tetramethylbisphenol-A-Polysulfone**	4.54	-3.343	--	6.56	--	--	47.1	--	33.0	1.34	17
Bisphenol-A-Polysulfone	3.66	-3.437	--	7.93	1.3	0.25	9.6**	10.8	5.7	0.16**	11, 17
Polyepichlorohydrin (Hydrin 100)	3.83	-3.417	45	8.607	0.42	--	--	--	--	--	11
Polyisobutylene	5.51	-3.259	-2.5	5.687	9.0	--	--	--	--	--	11
Poly(ethylene terephthalate)	2.70	-3.569	65	11.648	0.059	0.013	3.28	0.6	0.30	0.009	13
Poly-4,4'-diphenylether pyromellitimide (Kapton, H-film)	2.70	-3.569	--	12.773	0.15	0.036	--	1.5	0.27	--	11

\*: at 30° C; \*\*: at 35° C; +: at 2 atm.; ++: at 10 atm.; #: from ref. [2].

It is clear from the equations (2)-(8) that both the diffusion and solution, and thus the permeation of given gas molecule through polymer membranes is predominantly dependent on free volume ( $V_f$ ) and cohesive energy ( $E_{coh}$ ). The  $V_f$  term can be considered as a measure of chain packing density or the "tightness" of the polymer structure. The  $E_{coh}$  term can be considered as a measure of interaction of polymer chains and mainly determined the ability in segmental motion of polymer chains. The larger the  $V_f$  or the smaller the  $E_{coh}$ , the larger the  $P$  will be. But no simple relationship between permeability ( $P$ ) and  $V_f$  or  $E_{coh}$  of polymer was found<sup>6</sup>. It was found from the data of over 60 different polymers that there is a simple linear relationship between  $\log P$  and the ratio of  $V_f/E_{coh}$  for a given gas (Fig. 1), i.e. the following equation exists:

$$\log P = a_1 + b_1(V_f/E_{coh}) \quad (9)$$

where  $a_1$  and  $b_1$  are constants for a given penetrant and different from penetrant to penetrant. The molar free volume  $V_f$ , is defined as:

$$V_f = V_t - V_o \quad (10)$$

where  $V_t$  and  $V_o$  are the molar volume of polymer at  $t$  (usually 298K) and at 0 K respectively. A good approximation to  $V_o$  is<sup>8</sup>:

$$V_o = 1.3 V_w \quad (11)$$

where  $V_w$ , the van der Waals volume can be obtained through group contribution consideration<sup>8</sup>. If no experimental data on  $V_t$  are available, the values of  $V_w$  or  $V_f$  estimated by group contribution<sup>7</sup> was adopted. Thus, the gas permeability of other existing or new polymer can be estimated by calculating  $V_f$  and  $E_{coh}$  from group contribution<sup>7</sup> and interpolating the ratio of  $V_f/E_{coh}$  on Figure 1. Furthermore, it was found also that a linear relationship holds when plotting the values of both intercept( $a_1$ ) and slope( $b_1$ ) of the lines on the  $\log P$  vs.  $V_f/E_{coh}$  plots against the square of diameter  $d^2$  of penetrant molecules (Figure 2). Therefore, the plots of  $\log P$  vs.  $V_f/E_{coh}$  for other gases can be drawn from the values of intercept and slope found by interpolating their molecular diameters on Figure 2. This simple method for predicting gas permeability may found useful for the selection of gas separation and barrier membrane materials.

## RESULTS AND DISCUSSION

The permeability data of about sixty homopolymers covering 7 orders of magnitude for six common gases i.e.  $O_2$ ,  $N_2$ ,  $H_2$ , He,  $CO_2$  and  $CH_4$  from different sources are listed in Table 1. Almost all of the homopolymers published in the literature to date no matter whether it is in rubbery or glassy state, amorphous or partially crystalline are included in the table. The temperature and pressure at which the permeability was measured are not quite the same, although most of the data were measured at 25 °C.

In order to compare with Lee's and Salame's technique,  $1/SFV$ ,  $\pi$  value and  $\log(V_f/E_{coh})$  are also included in Table 1. According to Lee<sup>1</sup>, the specific free volume, SFV, is defined as:

$$SFV = V_f / M \quad (12)$$

where  $M$  is the molecular weight of repeating structural unit in Dalton  $V_f$  is given in eq.(10). At a given temperature Lee's expression became:

$$\log P = a_2 + b_2/SFV \quad (13)$$

if  $S$  is assumed to be not strongly SFV dependent as Lee did.

Here  $a_2$  and  $b_2$  are constants.

From Salame's equation<sup>2</sup>

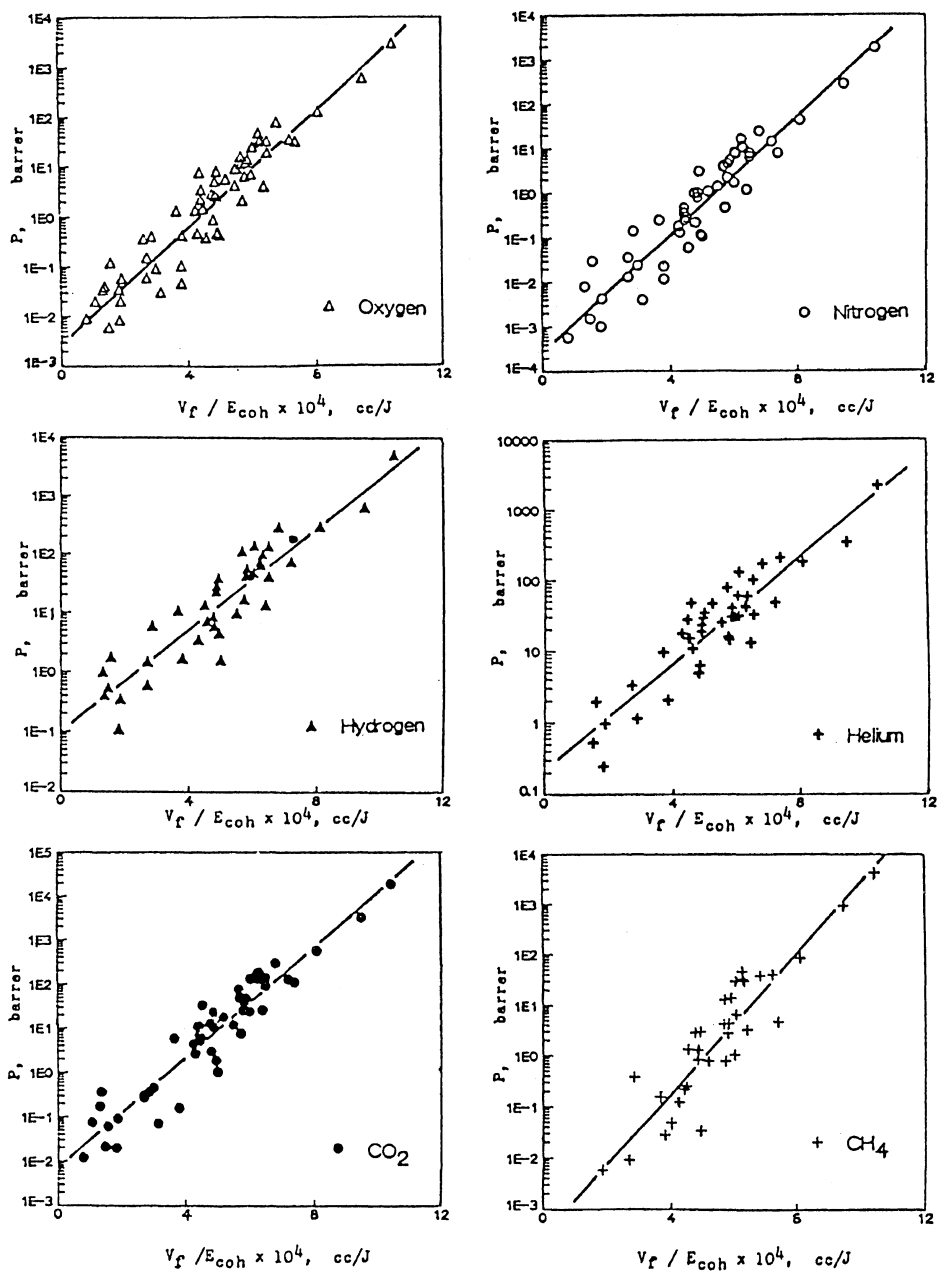


Figure 1. Plots of Permeabilities for Six Gases vs. Their  $V_f/E_{coh}$

$$P = A \exp[-s \pi] \quad (14)$$

the following expression can also be obtained:

$$\log P = \log A - s \pi = a_3 + b_3 \pi \quad (15)$$

where  $a_3 = \log A$  and  $b_3 = -s$

$$s = (1/RT - B')v + \beta \quad (16)$$

and  $s$  is in direct proportion to the square of gas molecule diameter.

Because<sup>9</sup>  $\pi = 57 \ln(CED/f_v) - 325$

where  $CED = E_{coh}/V_t$ ,  $f_v = (V_t - V_o) / V_t = V_f/V_t$

Salame's eq.(14) can be rewritten as:

$$\log P = a_4 + b_4 \log(V_f/E_{coh}) \quad (17)$$

where  $a_4$  and  $b_4$  are constants and  $a_4 = \log A + 141s$ ,  $b_4 = 57s$ .

All the data were treated with linear regression analysis and the results are listed in Table 2. It is evident that the eq. (9) has the highest linear correlation coefficient( $r$ ) among all of the four equations (13), (15), (17) and (9) for all the six gases studied. In other words, the method of predicting gas permeabilities from the ratio of molar free volume to molar cohesive energy of polymers is more accurate than others. It is also simpler and easier in use. However, it is clear from those plots in Figure 1 that the scattering of gas permeability data is still considerable, in fact, there is a correlation band instead of a single line between  $\log P$  and  $V_f/E_{coh}$ . The possible reason for this is the variety of the sources of permeability data. If the conditions at which the permeabilities were measured were kept just the same, a better correlation between  $\log P$  and  $V_f/E_{coh}$  would result, the authors believe. Even though, this correlation in its present form will work satisfactorily for predicting the molecular structure dependence of gas permeability of polymers and lend itself as a useful criteria for gas separation and barrier material selections.

Furthermore, it can be seen from Figure 2 that the intercepts of lines in Figure 1 were decreased linearly with increasing gas molecule diameters, while the slopes were increased linearly. It indicated that the larger the gas molecules, the smaller the permeability through polymer membranes and the gas permeabilities varied more rapidly with the ratios of  $V_f/E_{coh}$  of polymers. This is conformable with actual situation.

Although similar relationship also existed between  $a_4$ ,  $b_4$  and  $d^2$ , it is clear from Table 2 that the linear correlation of equation (17) is much less than that of equation (9). As to other two equations (13) and (15), such correlation was absent either between  $a_3$  (or  $a_2$ ) and  $d^2$ , or between  $b_3$  (or  $b_2$ ) and  $d^2$ .

Having above correlations we can estimate the permeabilities of all the non-swelling gases through a great variety of polymer membranes from gas diameters and the ratios of  $V_f/E_{coh}$  of polymers.

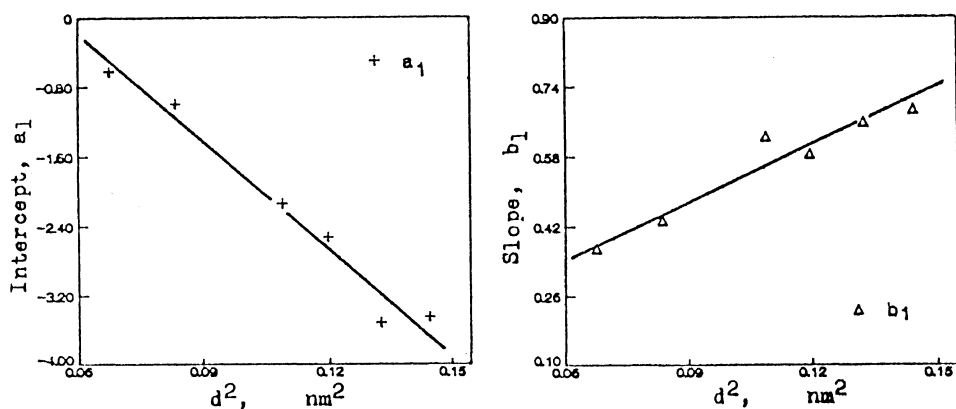
## CONCLUSION

The good linear relationship between  $\log P$  and the ratio of  $V_f/E_{coh}$  of polymers suggested that in a first order approximation, the permeabilities of a given gas through polymer membranes were governed by the ratio of molar free volume to molar cohesive energy  $V_f/E_{coh}$  of polymers. And there is also a good linear relationship between both the intercepts and the slopes of the lines on the  $\log P$  vs.  $V_f/E_{coh}$  plots and the square of gas molecule diameters. Therefore, the permeabilities of all non-swelling gases through almost all the polymer membranes can be estimated

Table 2. Comparison of linear regression analysis of gas permeability data among Eqs. (9), (17), (15) and (13)

		He	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
	d(nm)*	0.260	0.289	0.33	0.346	0.364	0.380
Eq. (9)	n	43	40	53	60	51	35
	a <sub>1</sub>	-0.6186	-0.9975	-2.1381	-2.5229	-3.5123	-3.4446
	b <sub>1</sub>	0.3702	0.4345	0.6261	0.5857	0.6590	0.6870
	r	0.9128	0.9220	0.9475	0.9417	0.9439	0.9012
Eq. (17)	n	43	40	53	60	51	35
	a <sub>4</sub>	13.3096	13.9338	17.8195	16.1515	18.1503	26.2167
	b <sub>4</sub>	3.6191	3.8078	5.0302	4.7095	5.4903	7.8865
	r	0.8927	0.8753	0.8958	0.8912	0.8891	0.8734
Eq. (15)	n	21	21	29	34	27	14
	a <sub>3</sub>	1.6623	1.9841	1.5313	0.8842	0.546	0.9086
	b <sub>3</sub>	-0.0184	-0.0322	-0.0287	-0.0285	-0.0304	-0.0343
	r	-0.6854	-0.9296	-0.7828	-0.7925	-0.8123	-0.7784
Eq. (13)	n	43	40	53	60	51	35
	a <sub>2</sub>	1.9810	1.6965	1.5808	0.9065	1.1186	1.9078
	b <sub>2</sub>	-0.0821	-0.0547	-0.0770	-0.0804	-0.1661	-0.2137
	r	-0.5832	-0.5518	-0.5017	-0.5112	-0.6291	-0.6948

\* from ref.10.

Figure 2. Plots of Intercept  $a_1$  and Slope  $b_1$  in Eq. (9) from Figure 1 vs.  $d^2$  of Gases



from the relationships mentioned above. Moreover, this method is more accurate and simpler than others in the literature, thus should serve as a useful tool for the selection of gas separation membrane and barrier materials from polymer structures for industrial applications.

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#### REFERENCES

1. W.M. Lee, *Polym. Eng. Sci.*, 20, 6 (1980).
2. M. Salame, *Polym. Eng. Sci.*, 26, 154 (1986).
3. J.H. Hildebrand and R.L. Scott, "The Solubility of Nonelectrolytes" 3rd Ed., Reinhold, New York, 1950.
4. A. Peterlin, *J. Macromol. Sci.*, B11, 57 (1975).
5. P. Meares, *J. Am. Chem. Soc.*, 76, 3415 (1954).
6. J. Hao, L. Jia and J. Xu, *Functional Polym.*, 1, 54 (1988) (China).
7. Van Krevelen, et.al., "Properties of Polymers" 2nd Edn. Elsevier, New York, 1976.
8. A. Bondi "Physical Properties of Molecular Crystals, Liquids and Gases", Chap. 3 and 4, Wiley, New York, 1968.
9. M. Salame, personal communication, 1988.
10. D.W. Breck, "Zeolite Molecular Sieves", p.636, Wiley, New York, 1974.
11. H.J. Bixler and O.J. Sweeting, in "Science and Technology of Polymer Films", vol 2, ed. O.J. Sweeting, Wiley, New York, 1971.
12. S.T. Hwang, C.K. Choi and K. Kammermeyer, *Sep. Sci.*, 9, 461 (1974).
13. H. Yasuda and V. Stannett, in "Polymer Handbook", 2nd ed., eds. J. Brand and E.H. Immergut, Wiley, New York, 1975.
14. V.T. Stannett, W.J. Koros, D.R. Paul, H.K. Lonsdale and R.W. Baker, *Adv. Polym. Sci.*, 32, 69 (1979).
15. T. Masuda, Y. Iguchi, B. Tang and T. Higashimura, *Polymer*, 29, 2041 (1988)
16. N. Muruganandam, W.J. Koros and D.R. Paul, *J. Polym. Sci. Polym. Phys. ed.*, 25, 1999 (1987).
17. M.B. Mae, W.J. Koros and D.R. Paul, *J. Polym. Sci. Polym. Phys. ed.*, 26, 1931 (1988).
18. M.W. Hellums, W.J. Koros, G.R. Husk and D.R. Paul, *J. Membrane Sci.*, 46, 93 (1989).