

AN EXTENSION OF THE METHOD FOR PREDICTING PERMEABILITY THROUGH POLYMER MEMBRANES FROM SIMPLE GASES TO WATER VAPOR*

FU Hongyong(付洪勇) JIA Lianda**(贾连达)
and XU Jiping(徐纪平)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022)

ABSTRACT

It is found that there is a linear relationship between $\log P_w$ and the parameter term $V_f/0.5 E_{coh} [1 + (\delta_w - \delta_p)^2/\delta_p^2]$, from the water permeability (P_w) data of 21 polymers covering 4 orders of magnitude. This correlation may be useful in choosing membrane materials for dehumidification of gases.

In a previous paper^[1] we reported a prediction method for gas permeability from polymer structure on the basis of the ratio of free volume to molar cohesive energy V_f/E_{coh} in the condition that there is no strong interaction between molecules of the gases and the polymers. Because the interaction between water molecules and polymer molecules is rather complicated, there have been no report on the method for predicting water vapor permeability up to now. To present such a prediction method is obviously important for the selection of membrane materials for dehumidification of gases.

In order to extend the prediction method for permeability from simple gases to water vapor, the strong interaction between the molecules of water and a polymer must be taken into account. To describe the interaction between the molecules of water and the polymer, $(\delta_w - \delta_p)^2/\delta_p^2$ is used based on the following fact: the heat of mixing of two substances is dependent on

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** To whom all correspondence should be addressed

$(\delta_1 - \delta_2)^2$ ^[5]. Here, δ_w and δ_p are the solubility parameters of water vapor and polymers respectively. If the heat of mixing is not so large as to prevent mixing, then $(\delta_1 - \delta_2)^2$ is relatively small. As the value of $(\delta_1 - \delta_2)^2$ approaches zero, the two substances will be miscible. This means that the interaction between the molecules of the two substances is stronger than that between the same molecules. Thus the difference in δ of two substances can be considered as a measure of the interaction between the molecules of two substances, and $(\delta_w - \delta_p)^2 / \delta_p^2$ as a parameter describing the magnitude of the interaction between molecules of water and polymers. The smaller the value of the parameter, the stronger the interaction between the molecules of water and polymer, thereby the larger the solubility, S , thus the larger the permeability P . The reason is that the value of S/P is much larger than that of D/P for transport of water vapor in polymers as seen in Ref. [2], in other words, the contribution of S to P for water is considerably larger than that of D to P . We found that the permeability of water vapor in polymers, P_w , changed statistically with the parameter term $V_f / 0.5E_{\text{coh}} [1 + (\delta_w - \delta_p)^2 / \delta_p^2]$, into which the parameters V_f / E_{coh} and $(\delta_w - \delta_p)^2 / \delta_p^2$, describing respectively the nature of polymers and the interaction between molecules of water and polymers were combined. For simple gases δ is nearly zero, the above term reduced to original form V_f / E_{coh} which is used to predict the gas permeability^[1].

The molar free volume V_f (cm³/mol) is defined as:

$$V_f = V_t - V_0$$

where V_t and V_0 are molar volumes of the repeating unit of polymers at temperature t (usually 298 K) and at 0 K, respectively. V_t can be obtained from the density of polymers at t . A good approximation to V_0 ^[3] is

$$V_0 = 1.3V_w$$

where V_w , the van der Waals volume, can be obtained through group contribution consideration^[4]. The cohesive energy can also be obtained through group contribution^[4]. The values of δ_p for various polymers can be found from a handbook^[5]. If no δ_p data is available for a certain polymer, it can be calculated by:

$$\delta_p = \left(\frac{E_{\text{coh}}}{V_t} \right)^{1/2}$$

The values of V_f , E_{coh} , δ_p and P_w for 21 polymers found in literature are collected in Table 1. P_w ranges from 10^0 to 10^4 barrer covering 4 orders of magnitude. The plot of $\log P_w$ against the parameter $V_f / 0.5E_{\text{coh}} [1 +$

$(\delta_w - \delta_p)^2 / \delta_p^2]$ is roughly a straight line (Fig. 1) with a linear correlation coefficient of 0.873. That is to say, this method for estimating the water vapor permeabilities for polymers is practical.

Table 1 Water vapor permeability P_w and structure parameters of polymers

No.	Polymer	V_f (cm ³ /mol)	E_{coh} (J/mol)	δ_p (J/cm ³) ^{1/2}	$A \times 10^5$ * (cm ³ /J)	P_w (barrer) **	T (°C)	Ref.
1	Polydimethylsiloxane	16.70	17700	14.9	31.80	43067	35	2
2	Polytrifluoropropylsiloxane	33.30	30740	13.6	29.28	21400	25	6
3	Polyphenylene oxide	22.13	38990	19.0	34.10	4060	25	2
4	Polyethyl methacrylate	15.80	34160	18.3	25.46	3173	25	2
5	Polyisoprene (NR)	12.68	19575	16.2	26.68	2290	25	6
6	Polycarbonate (Lexan)	34.82	83680	20.3	29.08	1400	25	6
7	Polyoxymethylene (POM)	3.03	10697	20.9	21.12	911	25	2
8	Polychloroprene	11.20	20635	17.0	25.10	911	25	2
9	Polystyrene	17.44	32839	17.4	25.96	865	25	6
10	Polyvinyl butyral	26.96	32270	15.5	30.96	811	25	6
11	Polymethyl methacrylate	10.54	40375	22.0	21.78	640	23	2
12	Polymethacrylonitrile	4.87	43020	26.9	14.02	413	25	2
13	Polyethylene terephthalate	9.24	63138	19.8	9.66	151	25	6
14	Polyvinyl chloride	4.34	20630	19.2	12.94	120	25	6
15	LD polyethylene	4.04	7869	15.8	19.92	91	25	2
16	Polypropylene	6.52	14250	16.6	19.98	68	30	2
17	HD polyethylene	2.57	7462	15.8	13.37	56	25	6
18	Polyvinyl fluoride	1.70	9080	16.9	8.54	14	25	2
19	Polyvinylidene chloride	2.67	32544	20.3	5.74	9	25	2
20	Polytetrafluoroethylene	3.70	7013	12.7	12.10	8	38	6
21	Polyvinyl alcohol	2.40	29640	25.8	9.30	7	25	7

* $A = V_f / 0.5 E_{coh} [1 + (\delta_w - \delta_p)^2 / \delta_p^2]$ and $\delta_w = 47.9$ (J/cm³)^{1/2} [5]

** 1 barrer = 1×10^{-10} cm³ (STP) - cm/cm² · s · cmHg

The possible reason for scattering of the data is the variety of the sources of permeability data, the temperature and the relative humidity at which the permeability was measured were not quite the same. The temperature ranges from 25°C to 38°C, and relative humidity has great effect on P_w . Even though, this correlation in its present form will be useful for predicting the water vapor permeabilities of new polymers and hence for selecting dehumidification membrane materials according to the chemical

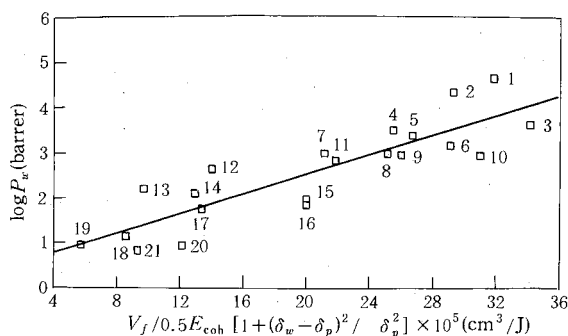


Fig. 1 Relationship between $\log P_w$ of 21 polymers from Ref. [2,6,7] and the parameter term $V_f/0.5E_{coh}[1+(\delta_w-\delta_p)^2/\delta_p^2] \times 10^5 (\text{cm}^3/\text{J})$

structure of polymers.

Keywords:

Polymer membranes; Water vapor permeability; Dehumidification; Prediction method

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