Macromolecules **2000,** *33,* 3111−3119

Volumetric Properties and Interaction Parameters of Dissolved Gases in Poly(dimethylsiloxane) and Polyethylene

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Received September 9, 1999; Revised Manuscript Received January 4, 2000

ABSTRACT: Henry's law coefficients and partial molar volumes of 34 penetrants (5 inert gases, 6 inorganic gases, 17 hydrocarbon gases, 5 fluorinated gases, and CCl_4 vapor) dissolved in poly(dimethylsiloxane) and low-density polyethylene were determined at 25 °C by measuring sorption of the gases and the concomitant dilation of the polymers. From the Henry's law coefficients and the partial molar volumes, Flory−Huggins parameters for polymer/gas interactions were estimated. The partial molar volumes were correlated with critical molar volumes of gases, and the interaction parameters were found to depend on the partial molar volumes. These relationships for the fluorinated gases were clearly different from those of all other gases. For CO_2 and CH_4 in poly(dimethylsiloxane), partial molar volumes and interaction parameters were obtained as a function of temperature over a range −30 to 95 °C. Thermal expansivities of these dissolved molecules were estimated to be 2×10^{-3} °C^{-1} from the temperature dependence of partial molar volumes.

Introduction

The knowledge of the thermodynamic state, in particular, the partial molar volume of dissolved gas molecules, is essential to elucidate mechanisms of sorption, diffusion, and permeation of gases in polymers and also to understand thermodynamic interactions between polymers and gases. The partial molar volume of dissolved gas in polymer can be determined from measurements of the sorption of gas and the concomitant dilation of the polymer. For a lot of gases in a few rubbery polymers, partial molar volumes have been reported.[1−3] However, there is no data on the molar volume except for CO_2 and a few other gases in the most practical polymers such as poly(dimethylsiloxane) and polyethylene.[4−7] The volumetric properties of gas molecules dissolved in these polymers will serve as the fundamental information for investigating equilibrium and kinetics of polymer/gas systems, mechanism of gas separation by polymer membranes, and so on.

In this study, we developed a new method using a linear variable differential transformer as displacement sensor in order to measure small changes in length of a polymer film due to gas sorption. Partial molar volumes of 34 penetrants (33 gases and a vapor) dissolved in the rubbery polymers, poly(dimethylsiloxane) and low-density polyethylene, are determined from sorption isotherms obtained gravimetrically and length-elongation data by the developed method. For CO_2 and CH_4 in poly(dimethylsiloxane), partial molar volumes are obtained as a function of temperature, and thermal expansivities of these dissolved molecules are evaluated. On the basis of experimental results, thermodynamic interactions between polymers and gases are investigated according to Flory−Huggins dissolution theory.

Experimental Section

Materials. The rubbery polymers tested are poly(dimethylsiloxane) (PDMS) and low-density polyethylene (LDPE). The PDMS sheet, 0.50 mm thick, is a nonreinforced medical grade silicone rubber, which is manufactured by Dow Corning Ltd. and sold under the commercial name Silastic 500. No information on filler content in the PDMS sheet has not been given by the supplier. The LDPE sheet, about 0.24 mm thick, was prepared by pressing resin pellets at 180 °C and 10 kg/cm^2 for 3 min and then cooling to 30 °C for 9 min, whose resin is manufactured by Japan Polychem. Corp. and sold under the commercial name of NOVATEC-LD.

The gases tested are He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, O_2, CO_2, N_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, cyclo-C_3H_6, C_3H_8, 1,3-C_4H_6 (99.0%), 1-C_4H_8 (99.0%), *cis*-2-C_4H_8 (99.0%), *trans*-2-C_4H_8 (99.0%), iso-C_4H_8 (99.0%), *n*-C_4H_{10}, iso-C_4H_{10}, *n*-C_5H_{12}, neo-C_5H_{12} (98.8%), iso-C_5H_{12}, CHF_3, CF_4, C_2F_6, C_3F_8, and SF_6. Purities of all gases are higher than 99.5% except for the gases having their purities in parentheses. A vapor of CCl_4 used is obtained from vaporization of the 99.8% pure liquid.

Measurements. Sorption isotherms for gases in polymers were determined gravimetrically using an electronic microbalance (Sartorius S3D-P), whose two chambers for a polymer specimen and a counterbalance were inserted into a water bath thermostated at −30 to 95 °C. This sorption apparatus is an improvement upon the previously reported one by changing the air bath to a constant-temperature water bath and adding a dilation cell described below.[8]

Weight changes indicated by the microbalance, whose sensitivity was ±1 μg, were monitored by a recorder during sorption experiments. The sorption data of every gas were corrected for buoyancy changes due to sorptive dilation using elongation data. The buoyancy changes were regarded as equivalent to the weights of gases that would be accommodated in volume increments of polymer dilation. This buoyancy contribution to concentration, for example, went up to −13% and 13% at about 60 atm for He and C_2H_4, respectively. Moreover, background corrections for zero-point drift of the microbalance due to pressurization were necessary to be made on sorption measurements of sparingly soluble gases such as He, H_2, and D_2, because the drifts of 0.3−0.6 μg/atm observed in blank tests of the microbalance, on both sides of whose beam

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10.1021/ma991536b CCC: $19.00

Table 1. Density, Thermal Expansion, and Compressibility of Polymers

		PDMS	LDPE
density (g/cm^3)	25.0 °C	1.161	0.914
crystallinity (vol %)		0	42
cubic thermal expansion (1/°C)			
elongation measurement	−30 to 95 °C	$3 \times 2.6 \times 10^{-4}$	
	−10 to 35 °C		$3 \times 2.2 \times 10^{-4}$
density measurement	15−45 °C	7.5×10^{-4}	
mercury dilatometer	10−90 °C	7.7×10^{-4}	6.7×10^{-4}
compressibility (1/atm)	5−60 atm, 25 °C	9.9×10^{-5}	4.4×10^{-5}

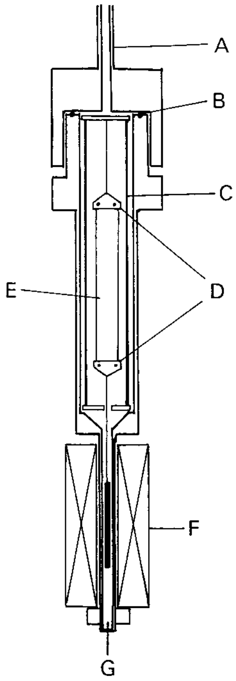

Figure 1. Schematic diagram of dilatometer based on linear variable differential transformer: A, gas inlet; B, O-ring seal; C, sample holder; D, film cramp; E, film specimen; F, differential transformer; G, thermocouple.

aluminum wires with the same size (0.26 cm^3) were suspended, could not be neglected in determining concentrations of these gases. More soluble gases (N_2, Ar, CH_4, CO_2, and so on) showed also similar or negatively large drifts of zero point, which however were negligible compared to weight changes due to their sorption. The magnitude of errors in gas concentrations obtained by the sorption experiments usually did not exceed ±2%.

Sorptive dilation of the polymers was investigated by measuring changes in the length of a rectangular sheet specimen (ca. 70 mm long and ca. 9 mm wide) during the sorption of gases. The length change was monitored by a displacement sensor based on a linear variable differential transformer (Shinko Electric Co., Ltd.). A mobile core of the differential transformer, about 2.4 g in weight, was attached to the end of the sheet specimen. The sensor could operate with a precision of ±1 μm in the range of length change ±5 mm at experimental conditions of this study. A schematic diagram of the dilation cell is shown in Figure 1.

Sorption and dilation experiments were stepwise conducted up to and down from the maximum pressures at 25.0 °C for all gases and at temperatures −30 to 90 °C for CH_4 and CO_2. Sorption isotherms and also dilation isotherms obtained by increasing and decreasing of pressure well accorded and were reproducible within experimental errors on repeated runs.

Densities of the polymers were determined by the flotation method with a density meter (Anton Paar, DMA60) and salt or alcohol aqueous solutions containing a slight amount of surface active substance. Thermal expansion of the polymers was measured with three methods: a conventional dilatometer using mercury (the length of capillary tube, 80 mm; the diameter of capillary, 0.96 mm; the total volume of dilatometer, 4.3 cm^3) (10−90 °C); length-elongation measurements (−30 to 95 °C); density measurements (15−45 °C). Compressibilities of the polymers were measured, in the pressure range 5−60 atm at 10−90 °C, by the above-mentioned mercury dilatometer which was placed in a pressure glass cell.

Results and Discussion

Volumetric Properties of Polymers. To compute concentration and partial molar volume of a gas penetrant dissolved in a polymer from gravimetric sorption and length-elongation data, it is essential to know volumetric properties of the polymer such as density, thermal expansion coefficient, and compressibility. The volumetric properties of PDMS and LDPE were measured using the methods described in the Experimental Section. Results are presented in Table 1. These volumetric properties are nearly equal to those estimated from data reported by Zoller and Walsh.[9]

As can be seen in the table, the cubic expansion coefficients of the sheet specimen obtained by the two methods of the mercury dilatometer and the density measurement are almost equal to 3 times the linear coefficients determined by the length-elongation method. This means that the thermal expansion of polymer sheets is isotropic at least in the range of volume dilation below 6% for PDMS and below 3% for LDPE.

Isothermal compressibilities of the polymers were determined at 10−90 °C. These temperature dependencies are expressed as

$$\beta_{T0} = 8.19 \times 10^{-5} + 6.89 \times 10^{-7}t \quad \text{for PDMS}$$

$$\beta_{T0} = 3.16 \times 10^{-5} + 5.02 \times 10^{-7}t \quad \text{for LDPE}$$

where t is temperature in °C. The values at 25 °C are presented in Table 1.

The cross-link density of the PDMS sheet was estimated by measuring both the swelling of a rectangular sheet of known sizes in liquid cyclohexane and the amount of liquid cyclohexane sorbed by the dry rectangular sheet of known weight according to Flory's equation for network polymer systems using χ value of 0.436 measured by Kuwahara et al. for un-cross-linked poly(dimethylsiloxane) in cyclohexane.[4,10] The obtained value of the effective cross-link density (ν_e/V_0) was 3×10^{-4} mol/cm^3.

Sorption. Sorption isotherms for 32 gases and a vapor in PDMS and for 33 gases in LDPE were measured at 25.0 °C. The isotherms of slightly soluble gases were linear in the investigated range of pressure and followed by Henry's law, whereas the isotherms for soluble gases were convex toward the pressure axis and were well described by Flory−Huggins theory of dissolution. The Flory−Huggins theory for gas dissolution in rubbery polymers is usually described as

$$\ln \frac{p}{p_0} = \ln \nu_1{}^* + (1 - \nu_1{}^*) + \chi(1 - \nu_1{}^*)^2 \qquad (1)$$

where p and p_0 are respectively the pressure of gas and the vapor pressure of the liquefied gas at the temperature of experiment, χ is the Flory–Huggins interaction parameter, and $\nu_1{}^*$ is the volume fraction of dissolved gas based on the amorphous region of the pure polymer. The volume fraction is given by

$$\nu_1{}^* = C\bar{V}/(\phi_a V_S + C\bar{V})$$

where ϕ_a is the volume fraction of amorphous region, C is the concentration in cm^3 (STP)/cm^3 (polymer), $\bar{V}$ is the partial molar volume in cm^3/mol, and V_S is the volume of a mole of ideal gas at 0 °C and 1 atm (22 410 cm^3/mol). To analyze the sorption isotherms, however, a simplified equation of the Flory–Huggins dissolution was used in this study.[11]

$$C = [k_D \exp(\sigma C)]p \qquad (2)$$

where $\sigma = 2(1 + \chi)\bar{V}/V_S$, and k_D is the solubility coefficient in the Henry's law limit, i.e., Henry's law coefficient. When $\sigma C \cong 0$, eq 2 is the so-called Henry's law of dissolution. Henry's law coefficients for every gas and dissolution parameters σ for highly soluble gases were determined by fitting eq 2 to the data. All results are presented, together with the maximum pressures investigated, in Tables 2 and 3. The relative errors in the obtained values of Henry's law coefficients for most of the examined gases were estimated to be within ±1%. The values of Henry's law coefficients are in fair agreement with the literature data.[12−14]

Henry's law coefficients of gases in a rubbery polymer are usually correlated to a scaling factor such as critical temperature, boiling temperature, or Lennard-Jones force constant.[13,15−18] The critical temperature, the boiling temperature, and the Lennard-Jones force constant, however, are interrelated so that the correlations of Henry's law coefficients with these are considered equivalent.[28] In this study the correlation with critical temperature was examined. As shown in Figure 2, logarithms of Henry's law coefficients plotted versus critical temperatures for all gases in the polymers exhibited two linear relationships; one is for fluorinated gases, and the other is for all the gases except for the former gases. The relationships of the latter gases are in fairly good agreement with those in the literature.[13,15−18] Slopes of these linear relation, d log k_D/dT_C, were 0.0076 for PDMS and 0.0078 for LDPE, whereas van Amerongen found it to be 0.0074 for 12 gases in a natural rubber,[15] Barrer and Chio obtained 0.007 for eight gases in a silicone rubber,[16] and Merkel et al. obtained 0.0065 for six gases in a silicone rubber.[18] It is noted here that, as well as solubility data of van Amerongen,[15] Henry's law coefficients of the lightest gases H_2 and D_2 deviate positively from the linear relationship in both cases of PDMS and LDPE (Figure 2).

As can be seen in Figure 2, the fluorinated gases are much less soluble than other gases with similar critical temperatures. Results analogous to these have recently been reported for a few fluorinated gases in rubbery polymers such as silicone rubber by Merkel et al.[18] and Hirayama et al.[19] It has also been found previously by Michaels and Bixler that SF_6 is much less soluble in polyethylene than CO_2 with similar Lennard-Jones force constant.[13]

Table 2. Saturated Vapor Pressures, Maximum Pressures Studied, Dissolution Parameters, Partial Molar Volumes, and Interaction Parameters for PDMS at 25 °C[a]

gas	p_0	p_{max}	k_D	σ	$\bar{V}$	χ
He	34^b	60	0.028		26	5.8
Ne	2300^b	37	0.042		28	1.1
Ar	654^b	68	0.225		47	0.18
Kr	261^b	40	0.586		51	0.05
Xe	67^b	6	1.92		59	0.09
H_2	318^b	60	0.071		34	2.4
D_2	660^b	20	0.084		31	1.6
N_2	823^b	72	0.111		54	0.51
O_2	717^b	50	0.205		46	0.20
CO_2	63.3	27	1.35	0.0043	50	0.65
N_2O	55.8	25	1.91	0.0041	49	0.47
CHF_3	45.9	20	1.00	0.0041	67	1.0
CF_4	158^b	33	0.166		87	1.3
C_2F_6	36^b	20	0.382		119	1.6
C_3F_8	8.62	5	0.803	0.033	149	2.1
SF_6	24.0	15	0.759	0.014	103	1.5
CCl_4	0.15	0.05	311	0.010	101	0.58
CH_4	319^b	30	0.436		54	0.09
C_2H_2	47.8	1.1	1.75		54	0.61
C_2H_4	67^b	55	1.74	0.0024	63	0.11
C_2H_6	41.2	8	2.34	0.0046	70	0.21
C_3H_6	11.4	8	6.75	0.0062	78	0.31
$(CH_2)_3$	7.98	2.5	12.6	0.0056	68	0.18
C_3H_8	9.32	8	7.52	0.0064	85	0.33
1,3-C_4H_6	2.76	1.2	21.3	0.0089	89	0.45
1-C_4H_8	2.92	1.2	20.1	0.0092	96	0.39
cis-2-C_4H_8	2.10	0.7	28.9	0.0088	92	0.39
trans-2-C_4H_8	2.30	1.0	25.0	0.0093	94	0.42
iso-C_4H_8	3.03	1.2	20.1	0.0086	96	0.35
n-C_4H_{10}	2.39	0.8	21.9	0.011	101	0.45
iso-C_4H_{10}	3.47	1.2	15.0	0.011	104	0.42
n-C_5H_{12}	0.67	0.2	64.4	0.014	118	0.48
neo-C_5H_{12}	1.69	0.5	24.3	0.012	123	0.49
iso-C_5H_{12}	0.90					

[a] Units: p_0 [saturated pressure], atm; p_{max} [maximum pressure used], atm; k_D, cm^3 (STP)/cm^3 (polymer) atm; σ, cm^3 (polymer) /cm^3 (STP); $\bar{V}$, cm^3/mol; χ, dimensionless. [b] Hypothetical values, since T_C is lower than 25 °C.

Sorptive Dilation and Partial Molar Volumes. Dilation of the polymers due to the sorption of gases was measured at 25.0 °C as length elongation of the sheet specimen, $l_s = (L - L_0)/L_0$, where L and L_0 are the lengths at p and $p = 0$ (or C and $C = 0$), respectively. Dilation isotherms of length elongation for all the gases in PDMS and LDPE, as well as their corresponding isotherms of sorption, were linear or convex toward the pressure axis.

If sorptive dilation is isotropic, a volume of gas-dissolved polymer can be described as $V = V_0(1 + l_s)^3$, where V_0 is the volume of pure polymer. Since the gas-dissolved polymer is compressed under an equilibrium pressure of gas, the volume dilation caused exclusively by the sorption of gas has to be corrected for the compression of polymer, that is,

$$(V/V_0)_{p\to 0} = (1 + l_s)^3(1 + \beta_{T0}p) \qquad (3)$$

where the compressibility of gas-dissolved polymer is approximated by that of pure polymer, β_{T0}. Values of volume dilation were computed from each set of l_s–p data with the value of β_{T0}. Dilation isotherms plotted versus concentration for all the gases were linear at low concentrations and became concave as the concentration increased over 30 cm^3 (STP)/cm^3 (polymer), which

Table 3. Maximum Pressures Studied, Dissolution Parameters, Partial Molar Volumes, and Interaction Parameters for LDPE at 25 °C

gas	p_{max}	k_D	σ	$\bar{V}$	χ
He	74	0.0039		37	6.9
Ne	50	0.0072		33	2.2
Ar	52	0.0513		42	1.2
Kr	22	0.165		47	0.87
Xe	3.3	0.746		55	0.56
H_2	70	0.013		34	3.5
D_2	13	0.013		37	2.7
N_2	56	0.0213		48	1.7
O_2	29	0.0433		43	1.3
CO_2	44	0.284		52	1.6
N_2O	23	0.519		51	1.2
CHF_3	15	0.0940		68	2.8
CF_4	41	0.0174		78	3.1
C_2F_6	20	0.0260		108	3.9
C_3F_8	5	0.0540		132	4.4
SF_6	10	0.0852		100	3.2
CCl_4					
CH_4	43	0.105		50	1.0
C_2H_2	1	0.302		58	1.7
C_2H_4	23	0.469		64	0.87
C_2H_6	6.6	0.698		68	0.89
C_3H_6	5.1	1.90		81	1.0
$(CH_2)_3$	1.1	4.51		73	0.60
C_3H_8	5	2.14		89	1.0
1,3-C_4H_6	1.6	8.21	0.012	87	0.89
1-C_4H_8	1.3	6.53	0.019	95	0.97
cis-2-C_4H_8	1.4	9.75	0.019	93	0.92
trans-2-C_4H_8	1.4	8.92	0.018	95	0.90
iso-C_4H_8	1.2	6.32	0.023	96	0.95
n-C_4H_{10}	1.5	7.69	0.020	101	0.95
iso-C_4H_{10}	1.3	4.66	0.022	98	1.1
n-C_5H_{12}	0.4	24.9	0.021	113	0.94
neo-C_5H_{12}	0.8	7.49	0.022	112	1.2
iso-C_5H_{12}	0.5	16.0	0.024	107	1.1

corresponds to a volume increment of about 10%, i.e., $(V/V_0)_{p\to 0} = 1.1$. Representative dilation isotherms are shown in Figure 3.

Since the polymer sheets used here are not oriented, this concavity of dilation isotherms, i.e., the negative deviation from the linearity, may result from an anisotropy in dilation of the sheets at high concentrations. That is, the elongation in planar directions will become less than the fractional change in thickness when the polymers dilate above 10 vol %. Such behavior was observed only for highly soluble gases in PDMS but not for any gases in LDPE. Under experimental conditions of this study, the maximum gas concentrations in LDPE were far below 30 cm^3 (STP)/cm^3 (polymer).

Consequently, partial molar volumes of dissolved gases in the polymers were estimated, from slopes of the linear parts of dilation isotherms, according to the relation[20]

$$\bar{V} \equiv \left(\frac{\partial V}{\partial n}\right)_{T,p\cong 0,N} = \frac{V_S\, \mathrm{d}[(1 + l_s)^3(1 + \beta_{T0}p)]}{\mathrm{d}C} \qquad (4)$$

where N is moles of polymer and n is moles of gas. All partial molar volumes (25 °C) obtained in this study are presented in Tables 2 and 3. The relative errors in these values of partial molar volumes for most of the examined gases were estimated to be within ±2%.

It has been found that there is a linear relationship between partial molar volumes and van der Waals volumes for various gases dissolved in a few rubbery polymers.[21,22] Recently Wong et al. pointed out that partial molar volumes correlate linearly with critical molar volumes of gases, which are more available in the literature than van der Waals volumes.[23] In this study, the critical molar volume was adopted as a scaling factor according to their finding. In Figure 4, partial molar volumes of all the gases in PDMS and LDPE were plotted versus critical molar volumes. As can be seen in the figure, there are two linear relationships; one is for fluorinated gases, and the other is for all the gases except for the former. The correlation lines for the fluorinated gases are larger in slope than those for another group of gases. In the figure, the extrapolation of the molar volumes (20 °C) of liquid C_4-C_{16} *n*-alkanes is drawn by a dotted line,[24] which accords well with the correlation between partial molar volumes and critical molar volumes for all the gases except for the fluorinated gases. The same accordance has been confirmed for several organic and inert gases in syndiotactic 1,2-polybutadiene and poly(ethylene-*co*-vinyl acetate).[2,3] From these facts, it is concluded that partial molar volumes of ordinary gases dissolved in rubbery polymers can be generally given as

$$\bar{V} = 26.3 + 0.28V_C, \quad \mathrm{cm^3/mol}$$

This result allows us to infer that these gas molecules dissolved in rubbery polymers are in the same thermodynamic state as molecules of liquids in themselves are.

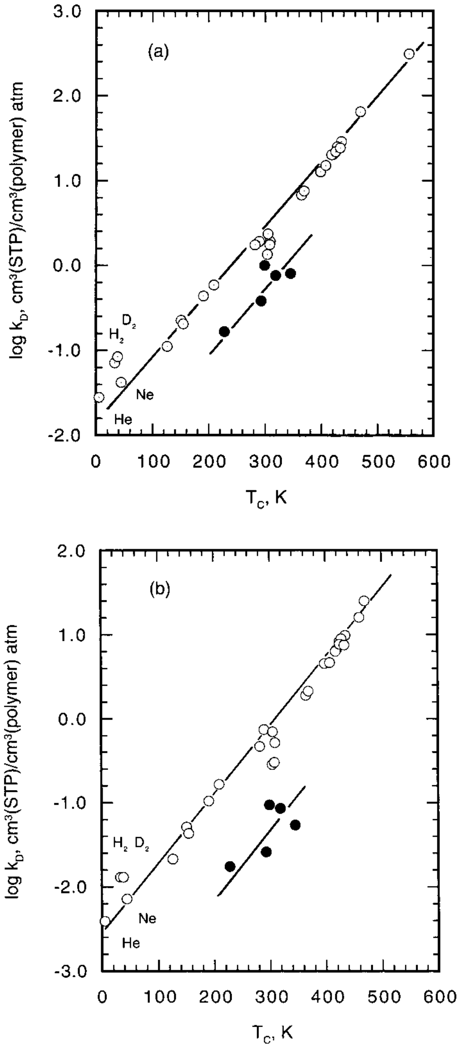

Figure 2. Correlation between Henry's law coefficients (25 °C) and critical temperatures: (a) 32 gases and a vapor in PDMS; **(b)** 33 gases in LDPE. Solid and open symbols correspond to fluorinated gases and other gases, respectively.

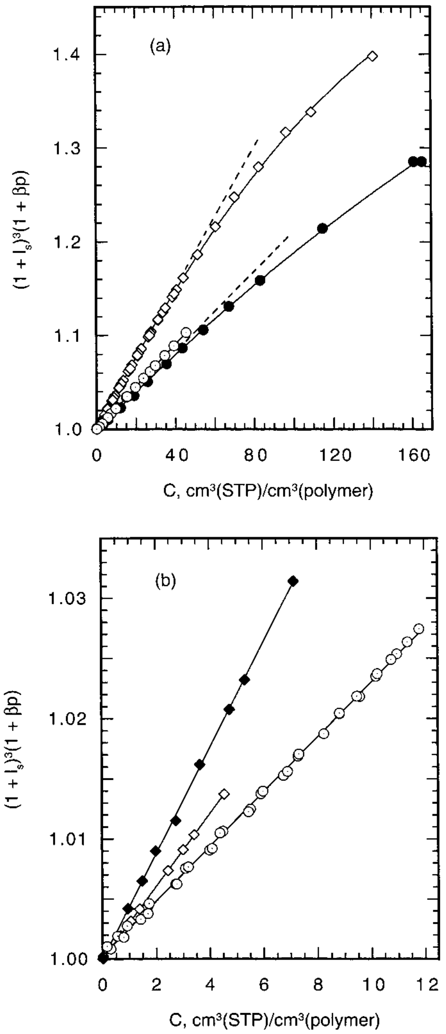

Figure 3. Volume dilation isotherms plotted versus concentration: (**a**) (□) C_3H_8 and (○) CO_2 at 25 °C and (●) CO_2 at −15 °C in PDMS; (**b**) (■) iso-C_4H_{10}, (□) C_2H_6, and (○) CO_2 in LDPE at 25 °C.

In the case of the fluorinated gases except CHF_3, on the other hand, the partial molar volumes can roughly be described by

$$V \cong 26.3 + 0.4V_C, \quad \text{cm}^3/\text{mol}$$

though there are only four points of data, and the relation is given as a straight line in Figure 4. This relation representing large partial molar volumes may reflect weaker intermolecular interactions for the fluorinated gases in the polymers than those for all other gases, because the correlation of molar volume with critical volume for perfluorocarbons (C_2−C_7) and SF_6 is linear and almost coincides with that of *n*-alkanes mentioned above.[24]

It is noted here that partial molar volumes of the quantum gases He, Ne, H_2, and D_2 especially in PDMS are much less than the extrapolation of the linear relationships (Figure 4). This may be related to the fact that these gases have relatively large Henry's law coefficients (Figure 2).

The partial molar volumes obtained here will be compared with literature data. Because the sorptive dilation of polymers has most frequently been studied for CO_2, its partial molar volume is the best for comparison. In this study we got as its value 50 cm^3/mol in PDMS and 52 cm^3/mol in LDPE at 25 °C (Tables 2 and 3). For poly(dimethylsiloxane), Fleming and Koros reported 46.2 cm^3/mol in the rubbery state at 35 °C (the corrected value, 48 cm^3/mol)[4] and Kamiya et al. also 48 cm^3/mol in the liquid state at 25 °C.[1] Hirose et al. obtained 44.5 cm^3/mol for the gas in low-density polyethylene at 25 °C (the corrected value, 49 cm^3/mol).[5] In the early studies of sorptive dilation, the compression of polymers by the pressure of penetrant gas was neglected in estimating its partial molar volume.[4,5] The compression effect on partial molar volume can be approximated by a quantity of $V_S\beta_{T0}/k_D$ according to eq 4. The partial molar volumes compensated for the compression effect by such a way are the values in parentheses described above. The CO_2 partial molar volumes obtained here are slightly greater than the values reported so far.

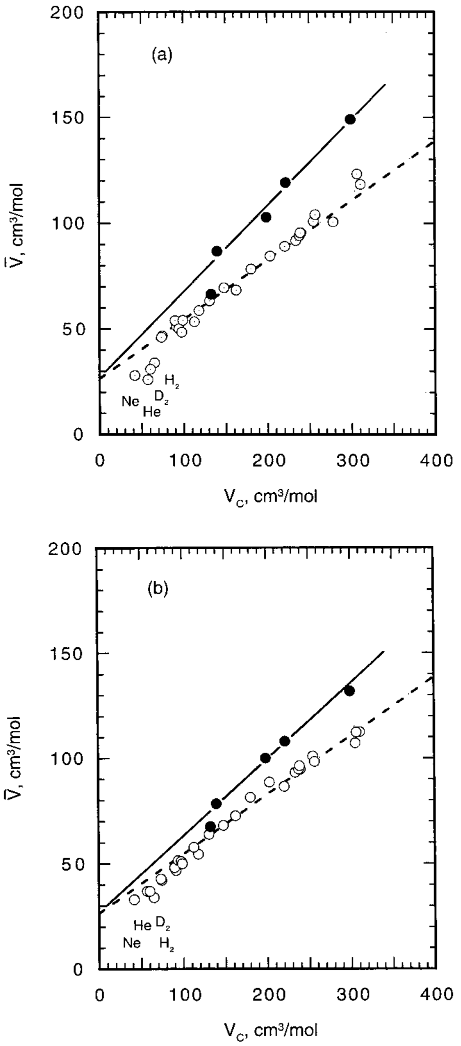

Figure 4. Correlation between partial molar volumes (25 °C) and critical molar volumes: (**a**) 32 gases and a vapor in PDMS; (**b**) 33 gases in LDPE. A dotted line is the extrapolation of molar volumes (20 °C) plotted versus critical molar volumes for liquid C_4−C_{16} *n*-alkanes. Symbols are the same as in Figure 2.

During the preparation of this paper, we received a private communication that sorption and dilation isotherms for a few fluorocarbons in poly(dimethylsiloxane) were measured, and their partial molar volumes were a little less than twice those of hydrocarbon analogues.[25] These are much the same as the present results mentioned above.

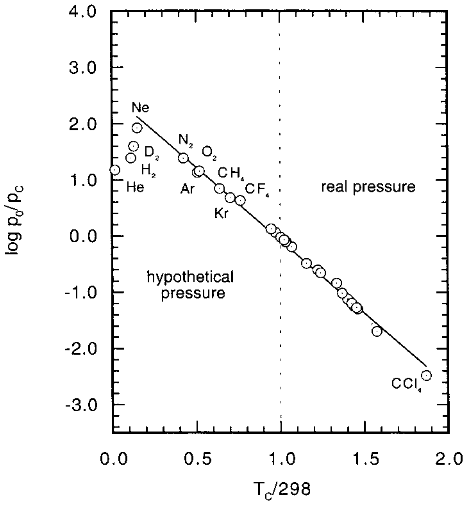

Figure 5. Corresponding-states correlation of real and hypothetical vapor pressures versus critical temperatures for 33 gases and a vapor.

Flory–Huggins Interaction Parameters. One of the fundamental factors governing the equilibrium sorption of a gas in a polymer is an intermolecular interaction between the gas and the polymer. To characterize it, Flory–Huggins interaction parameter χ is most convenient. There are a few methods to determine the interaction parameter for polymer/gas systems.[26] In this study, values of χ for polymer/gas systems infinitely dilute with respect to dissolved gases are calculated from Henry's law coefficients and partial molar volumes by use of the relation

$$\left(\frac{C}{p}\right)_{p\cong 0} = k_D = \frac{\phi_a V_S}{\bar{V} p_0} \exp(-1 - \chi) \qquad (5)$$

which is derived from the Flory–Huggins theory.[15,27]

In the evaluation of χ by this equation, saturation vapor pressures p_0 of gases at the relevant temperature are essential. The p_0 values of gases, whose critical temperatures are higher than experimental temperatures (in the most cases, 25 °C), were calculated using the Frost–Kalkwarf vapor-pressure equation with Harlacher–Braun constants or the Lee–Kesler equation with previously published constants.[28] For gases with critical temperatures lower than 25 °C, there do not exist their liquefied phases and hence saturated vapor pressures at 25 °C. Accordingly, the hypothetical vapor pressures for such gases were estimated by extrapolating of the linear relation ln p_0 versus $1/T$ to above the critical point. The real and hypothetical vapor pressures used in this study are presented in Table 2. Prior to the calculating of χ, the hypothetical vapor pressures are compared with the real vapor pressures based on the two-parameter corresponding-states correlation of the Clausius–Clapeyron equation.[28] Figure 5 shows plots of logarithms of p_0/p_C versus $T_C/298$ for all the gases investigated. A linear relationship, except for the quantum gases, passes through a point of $T_C/298 = 1$. This suggests that the use of the hypothetical values in calculating χ is reasonable for gases other than the quantum gases.

All χ values estimated are presented in Tables 2 and 3. The error limits for these χ values are estimated to vary from ±0.1 for gases uncondensable at 25 °C to ±0.02 for condensable gases by assuming relative errors of ±10% in hypothetical vapor pressures and of ±1% in calculated vapor pressures. However, the error limits for the quantum gases are possibly much more than ±0.1, because the errors in their hypothetical vapor pressures are thought far beyond ±10% as shown in Figure 5.

In Figure 6, the dependence of χ upon partial molar volume is shown. There are two linear relationships between interaction parameter and partial molar volume; one is for the fluorinated gases, and the other is for the hydrocarbon gases. A similar correlation has previously been reported for a series of organic gases in rubbery polymers, although the method used for computing χ was not always appropriate because of a poor approximation of the σ–χ relation given in eq 2.[21,26,29] Such molecular size dependency of interaction parameter agrees with an expectation of χ varying in proportion to molecular size in a homologous series of penetrants. The expectation is deduced from the definition of interaction parameter that the quantity of χ multiplied by the Boltzmann constant and absolute temperature is equivalent to the difference in energy of a penetrant molecule immersed in the pure polymer compared with one in its own liquid.[27] This energy difference must be proportional to the number of repeating units of penetrants.

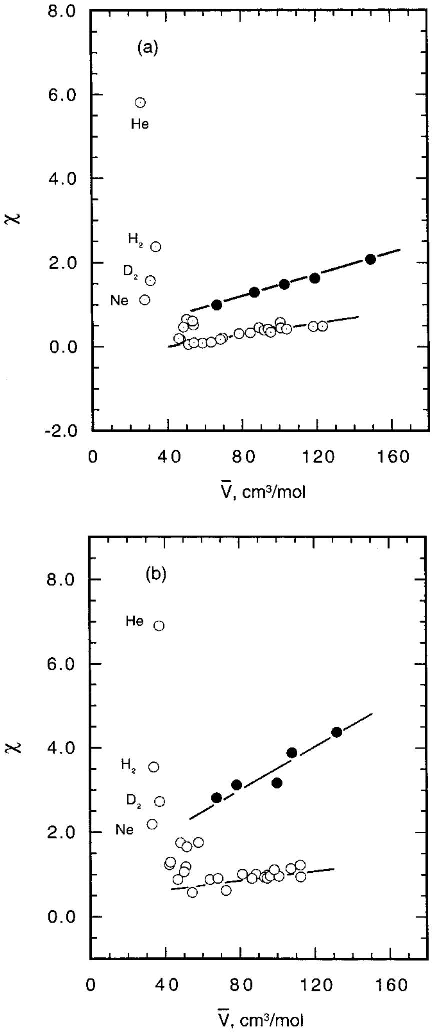

Figure 6. Correlation between interaction parameters and partial molar volumes at 25 °C: (**a**) 32 gases and a vapor in PDMS; (**b**) 33 gases in LDPE. Symbols are the same as in Figure 2.

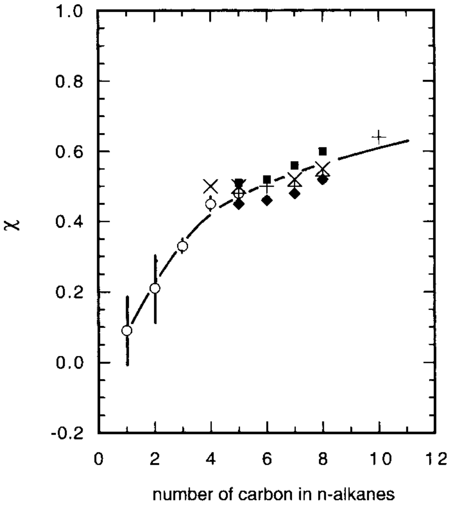

Figure 7. Flory−Huggins parameters plotted versus the number of carbon for *n*-alkanes in PDMS: (○) present data (25 °C); (◆) data from ref 30 (25 °C); (×) data from ref 31 (0−25 °C); (+) data from ref 32 (20 °C); (■) data from ref 33 (25 °C). Bars on data points indicate their error limits.

Interaction parameters estimated in this study will be compared with literature data. The interaction parameters, 0.65 and 1.7, for CO_2 in PDMS and LDPE are much the same as those reported previously.[4,29] For *n*-alkane vapors in PDMS, thermodynamic interactions have been evaluated by several authors.[30−33] Their results are plotted, together with the present data, versus the number of carbon in *n*-alkane in Figure 7. Such a comparison, however, cannot be performed for LDPE, because there are no χ data of gases and few data of organic vapors comparable with the present results.[34,35] As shown in Figure 7, the present data of C_4H_{10} and C_5H_{12} are in good agreement with the literature values, and there is a tendency for the interaction parameter to increase with increasing number of carbons. It is noted here that the correlation between χ and carbon number inflects between C_3H_8 and C_4H_{10}, even if the error limits in χ values have been taken into account. The reason for the inflection is not known at present.

During the preparation of this paper, we received a private communication that interaction parameters of CF_4, C_2F_6, and C_3F_8 in poly(dimethylsiloxane) have been estimated and found to increase linearly with increasing van der Waals volumes.[36] Those are much the same as the present results shown in Figure 6a.

Before closing this section, the effect of cross-linking on the interaction parameter for gases in PDMS should be noted. For network polymers with cross-linkages, the following equation is given instead of eq 1.[27]

$$\ln\left(\frac{p}{p_0}\right) = \ln \nu_1^* + (1-\nu_1^*) + \chi'(1-\nu_1^*)^2 + \bar{V}\left(\frac{\nu_e}{V_0}\right)\left[(1-\nu_1^*)^{1/3} - \frac{1-\nu_1^*}{2}\right] \qquad (1')$$

where ν_e/V_0 is the effective cross-link density. Accordingly, values of χ obtained by eq 1 or 5 for the network polymers are overestimated and greater than those computed using the above equation by $\Delta\chi = \chi - \chi' = \bar{V}(\nu_e/V_0)[(1-\nu_1^*)^{-5/3} - 0.5(1-\nu_1^*)^{-1}]$. As the effective cross-link density of the PDMS sheet used here is $\nu_e/V_0 = 3 \times 10^{-4}$ mol/cm^3, the magnitude of $\Delta\chi$ at $\nu_1^* \cong 0$ is estimated to be 0.005−0.02 dependent upon partial molar volumes. Consequently, χ values of PDMS presented in Table 2 will contain less than 5% errors due to neglecting of cross-linkage effects.

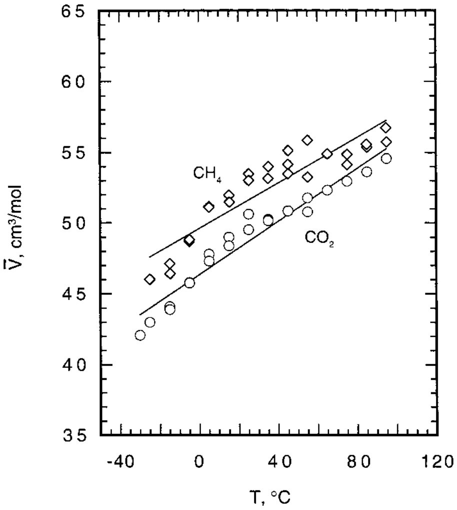

Figure 8. Temperature dependence of partial molar volume for (◇) CH_4 and (○) CO_2 in PDMS.

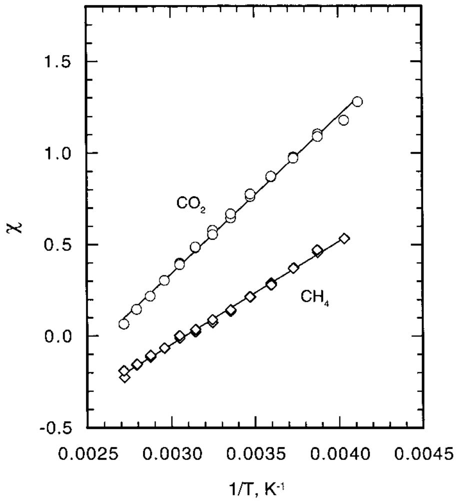

Figure 9. Temperature dependence of interaction parameter for (◇) CH_4 and (○) CO_2 in PDMS.

Temperature Dependence of Partial Molar Volume and Interaction Parameter. Sorption of CO_2 and CH_4 in PDMS and the concomitant dilation of the polymer were measured at −30 to 95 °C. From the results, Henry's law coefficients, partial molar volumes, and interaction parameters were determined as a function of temperature.

The Henry's law coefficient of each gas decreased with increasing temperature, and its van't Hoff plot was linear against $1/T$ axis. From slopes of the straight lines, the heats of sorption for CO_2 and CH_4 were estimated to be −2.59 and −1.21 kcal/mol, respectively.

The partial molar volumes increased almost linearly with increasing temperature as shown in Figure 8. From these temperature dependencies, the thermal expansion coefficient of dissolved molecules was estimated to be 1.9×10^{-3} °C^{-1} for CO_2 and 1.6×10^{-3} °C^{-1} for CH_4. These are much the same as those obtained previously in our laboratory: 2.4×10^{-3} °C^{-1} for CO_2 in poly(ethylene-*co*-vinyl acetate)[37] and 2×10^{-3} °C^{-1} for CO_2 in syndiotactic 1,2-polybutadiene and poly(ethyl methacrylate).[20]

By using Henry's law coefficients and partial molar volumes at various temperatures, the dependence of interaction parameters upon temperature for CO_2 and CH_4 in PDMS was determined. As shown in Figure 9, χ increases proportionately with the reciprocal of absolute temperature. Similar results have been reported for CO_2 in a few polymers[8,29] and for a few heavy organic vapors in a silicone rubber.[11] The values of χ for CH_4 above 50 °C became negative. The cause of the negative values is not clear, but it may be partly related to the fact that the sorption of gases studied here is not an isobaric process which is one of prerequisites for the Flory−Huggins dissolution theory.[2]

Conclusions

Henry's law coefficients and partial molar volumes of 33 gases and a vapor dissolved in poly(dimethylsiloxane) and low-density polyethylene were determined at 25 °C from measurements of the sorption of gases and the concomitant dilation of the polymers. From the Henry's law coefficients and the partial molar volumes, interaction parameters of these polymer/gas systems were estimated according to the Flory−Huggins dissolution theory. Partial molar volumes and interaction parameters for CO_2 and CH_4 in PDMS were obtained as a function of temperature in the region −30 to 95 °C.

In both cases of PDMS and LDPE, it was found that the partial molar volumes increase proportionately with the critical molar volumes of gases and there exist two linear relationships; one is for the fluorinated gases, and the other is for all the gases except for the former. The former gases exhibited partial molar volumes greater than the latter gases with similar critical volumes. The interaction parameters of gases except for the quantum gases and some others were also confirmed to correlate linearly with the partial molar volumes, and there existed two linear relationships belonging to the fluorinated gases and the hydrocarbon gases. These results indicate that in the two polymers intermolecular interactions for the fluorinated gases are weaker than those for the hydrocarbon gases with similar partial molar volumes. Such weak interactions will be responsible for the fluorinated gases having much less Henry's law coefficients than the other gases. It is noted that in both polymers CHF_3 has a fairly small partial molar volume compared with those of the other fluorinated gases, whereas its interaction parameter is in harmony with the correlation between χ and partial molar volumes for the fluorinated gases (Figures 4 and 6). The Henry's law coefficient, the partial molar volume, and the interaction parameter for CCl_4 in PDMS did not follow the trends for fluorinated gas data but those for hydrocarbon data, as shown in Figures 2a, 4a, and 6a. This will indicate that CCl_4, as well as all other gases, in the polymer has greater intermolecular interactions than the fluorinated gases.

Henry's law coefficients, partial molar volumes, and interaction parameters for the quantum gases He, H_2, D_2, and Ne in PDMS and LDPE showed somewhat different trends compared with those of the other gases (Figures 2, 4, and 6). The values of Henry's law coefficients for H_2 and D_2 in both polymers deviated appreciably from the linear correlations with critical temperature (Figure 2). The partial molar volumes of the quantum gases in especially PDMS were small compared with those of other gases (Figure 4). These unexpected events will not be caused only by the quantum effects on critical points (T_C and V_C), since the effects are not sufficient for compensating deviations from the linear correlations. That is, the quantum effects on critical temperature ($T_C^0 - T_C$) and critical volume ($V_C^0 - V_C$) are respectively 5.3 K and −19.6 cm^3/mol for He and 10.4 K and −13.7 cm^3/mol for H_2, where the superscript 0 designates the classical critical constants which are effective in the empirical equation of state at high temperatures.[38] The exceptionally great values of interaction parameters for the quantum gases in both polymers will result from their hypothetical vapor pressures being much less than the extrapolation of the linear relation between vapor pressures and critical temperatures (Figure 5).

From the temperature dependence of partial molar volumes, it was found that thermal expansivities of CO_2 and CH_4 molecules dissolved in PDMS are about 2×10^{-3} °C^{-1}. Since this is much the same as expansivities of van der Waals liquids such as hydrocarbons,[39] the gas molecules dissolved in the polymer seem to be in the liquidlike state. The interaction parameters of the two gases increase linearly with the reciprocal of absolute temperature. This suggests that supercritical fluids of these gases could act as a good solvent for PDMS at high temperatures, if polymer−gas interaction energies do not strongly depend on temperature.

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MA991536B