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Sorption and Partial Molar Volumes of Organic Gases in Rubbery Polymers

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ABSTRACT: Sorption of organic gases (C_2H_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, and n-C_5H_{12}) in two rubbery polymers, 1,2-polybutadiene and poly(ethylene-*co*-vinyl acetate), and dilation of the polymers due to sorption are measured as a function of gas pressure at 25 °C. Sorption isotherms for all the gases are well described as the Flory–Huggins dissolution. Dilation isotherms are similar in shape to the corresponding sorption isotherms. From sorption and dilation data, partial molar volumes $\bar{V}_R$ of the dissolved gases are determined. A linear relation is found between partial molar volume and van der Waals volume $\bar{V}_W$, i.e., $\bar{V}_R = 1.6\bar{V}_W + 18.5$ in cm^3/mol. This relation is almost the same as that between molar volume and $\bar{V}_W$ for liquid n-alkanes.

Introduction

The knowledge of the thermodynamic state, in particular, the partial molar volume of dissolved gas, has been essential to understand mechanisms of diffusion, sorption, and permeation of gases in polymers.[1] Recently, the experimental determination of the partial molar volume was done by a few workers.[2-6] They investigated sorption of several gases in polymers and dilation of the polymers due to the sorption, from whose data partial molar volumes of the dissolved gases were determined. However, no clear relationship between the partial molar volumes and the molecular properties of gases has yet been found, because sorption and dilation experiments have not been carried out for any homologous series of gases. To find the relationship is the purpose of the present paper.

In this study, we measure sorption and dilation isotherms for organic gases (five alkanes and two alkenes) in two rubbery polymers and determine the partial molar volumes of the dissolved gases. On the basis of the data obtained here and reported previously,[5,7] the dependence of partial molar volume on van der Waals volume is discussed and compared with volumetric properties of liquid n-alkanes.

Experimental Section

Materials. The rubbery polymers used are syndiotactic 1,2-polybutadiene (PB) (density 0.906 g/cm^3) and poly(ethylene-*co*-vinyl acetate) (EVAc) (density 0.935 g/cm^3, content of vinyl acetate 15 wt %), which are the same as those used previously.[5,7] PB films, ca. 200 μm thick, and EVAc films, ca. 300 μm thick, were employed in both sorption and dilation experiments.

Seven organic gases (C_2H_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, and n-C_5H_{12}) were tested. These gases, supplied by Takachiho Chemical Industry, were of at least 99.5% purity and were used without further purification.

Sorption and Dilation Measurements. Sorption amounts of gases in a polymer specimen of ca. 200 mg were measured gravimetrically with a microbalance (Cahn Model 2000) placed in a pressure chamber.[4,5] The microbalance could weigh to a precision of 1 μg under any ambient pressure employed. The magnitude of errors in sorption measurements was less than ±1% of the concentration for all the gases investigated.

Dilation isotherms were determined by observing changes in the length of two rectangular film strips (length ca. 60 mm and width ca. 3 mm) suspended in a glass pressure cell.[4,5] The two specimens cut in cross directions of the films gave no difference in length elongation within the accuracy of the experiments. For this observation a cathetometer with a precision of 0.01 mm was used, and hence relative errors in length measurements were estimated to be on the order of 2×10^{-4}.

Two pressure transducers were employed for pressure measurements. The low-pressure transducer has a range of 0–7 atm (±0.3% full scale) and the high-pressure one has a range of 0–75 atm (±1.0% full scale).

Sorption and dilation experiments were performed at 25.0 °C in an air bath controlled to ±0.5 °C.

Results and Discussion

Sorption Isotherms. Sorption isotherms for five gases (C_3H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, and n-C_5H_{12}) in the PB film were measured in this study. In the case of the EVAc film, sorption experiments were performed for all of the seven gases. Measurements on sorption and desorption runs for each gas were done stepwise up to the maximum pressure (0.4 to 40 atm) and then also stepwise down to vacuum (10^{-3} mmHg). The sorption and desorption equilibria for all the gases were reached within a few hours.

All sorption isotherms are presented in Figures 1 and 2. Some are depicted by solid curves without experimental points because of the simplicity of the figures, and only low-pressure parts of sorption isotherms are presented for gases with relatively low solubility. In the figures, sorption isotherms for C_2H_4 and C_2H_6 in PB and for CH_4 in EVAc, which were reported in previous papers,[5,7] are also shown.

The isotherms, which are convex with respect to the pressure axis, are analyzed using a simplified equation for the Flory–Huggins dissolution. According to a derivation by Suwandi and Stern,[8] concentration of a dissolved gas in a rubbery polymer is given by

$$C = k_D p \exp(\sigma C) \qquad (1)$$

where p, k_D, and σ are the pressure, the Henry's law parameter, and the constant related to the polymer–penetrant interaction, respectively. Dissolution parameters k_D and σ were estimated by fitting data using the equation $\ln (C/p) = \ln k_D + \sigma C$. The results are given in Tables I and II together with ranges of pressure used in the experiments. The dissolution parameters for CH_4, C_2H_4, and C_2H_6 in PB and for CH_4 in EVAc are cited in the tables, for comparison, from the previous papers. The magnitude of errors in concentration determination for CH_4 was in the range ±1% to ±4% and those for the others were less than ±1%.

Dilation Isotherms. Measurements of the length of the film, as well as sorption experiments, were performed stepwise up to the maximum pressure and then down to

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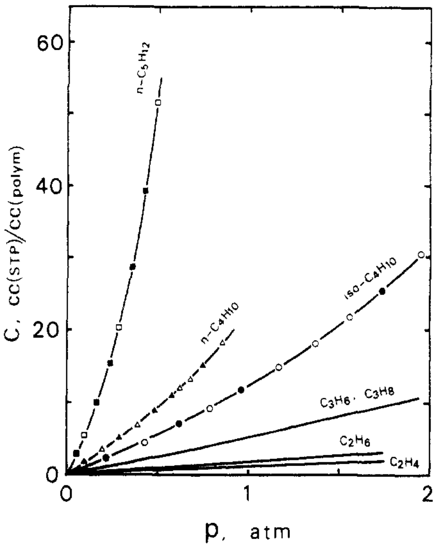

Figure 1. Sorption isotherms for organic gases in polybutadiene at 25.0 °C. C_2H_4 and C_2H_6 isotherms are earlier data.[5] Open and solid symbols correspond to sorption and desorption runs, respectively, throughout this paper.

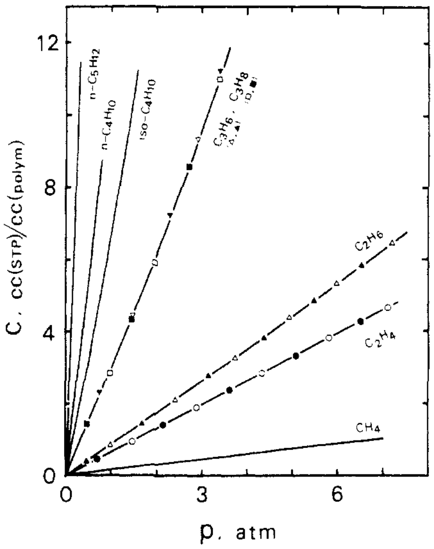

Figure 2. Sorption isotherms for organic gases in poly(ethylene-*co*-vinyl acetate) at 25 °C. CH_4 isotherm is earlier data.[7]

Table I
Dissolution Parameters and Partial Molar Volumes for Gases in Polybutadiene at 25 °C[a]

gas	range of pressure (atm)	k_D	$\sigma \times 10^3$	$\bar{V}_R$	ref
CH_4	50	0.226		44 ± 1	5
C_2H_4	40	1.18	3.1	52.0 ± 0.5	5
C_2H_6	20	1.82	3.6	57.0 ± 0.5	5
C_3H_6	7	5.09	8.0	71.8 ± 0.4	
C_3H_8	7	4.97	7.8	79.8 ± 1.2	
n-C_4H_{10}	0.9	16.52	12.8	95.2 ± 0.6	
iso-C_4H_{10}	2	10.31	13.6	96.1 ± 1.1	
n-C_5H_{12}	0.5	51.67	13.9	106.1 ± 1.5	

[a] Units: k_D, cm³(STP)/(cm³(polym) atm); σ, cm³(polym)/cm³(STP); $\bar{V}_R$, cm³/mol.

Table II
Dissolution Parameters and Partial Molar Volumes for Gases in Poly(ethylene-*co*-vinyl acetate) at 25 °C[a]

gas	range of pressure (atm)	k_D	$\sigma \times 10^3$	$\bar{V}_R$	ref
CH_4	50	0.145		46 ± 1	7
C_2H_4	7	0.634	8.5	61.0 ± 1.0	
C_2H_6	7	0.843	10.5	64.9 ± 0.6	
C_3H_6	5	2.86	12.7	73.7 ± 0.4	
C_3H_8	5	2.80	14.3	79.3 ± 0.4	
n-C_4H_{10}	0.8	9.32	19.7	93.8 ± 1.0	
iso-C_4H_{10}	1.5	5.78	19.7	102.1 ± 1.0	
n-C_5H_{12}	0.4	29.76	20.9	106.9 ± 0.9	

[a] See footnote *a* in Table I for units.

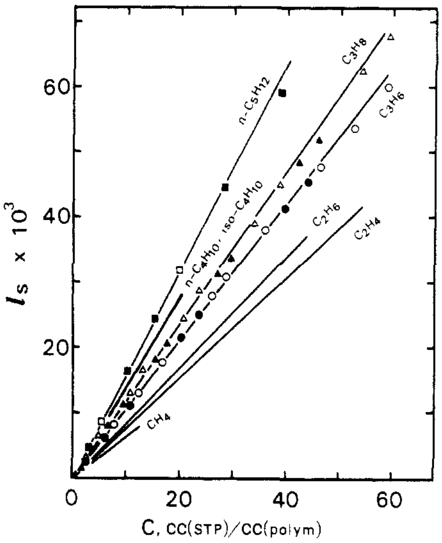

Figure 3. Elongation plotted versus concentration for organic gases in polybutadiene. CH_4, C_2H_4, and C_2H_6 isotherms are earlier data.[5]

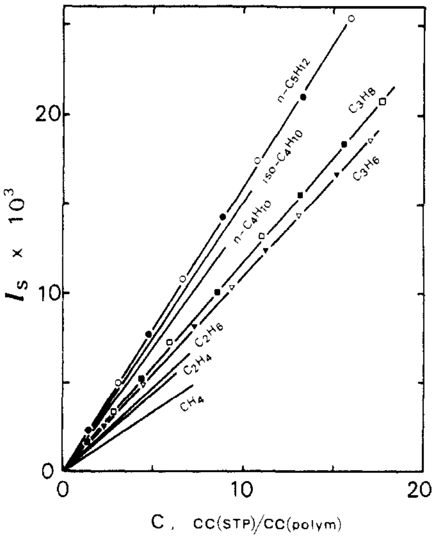

Figure 4. Elongation plotted versus concentration for gases in poly(ethylene-*co*-vinyl acetate). CH_4 isotherm is earlier data.[7]

vacuum. Dilation isotherms in the form of elongation versus pressure for the gases are very similar in shape to the corresponding sorption isotherms. The elongation is defined as $l_s = (L - L_0)/L_0$, where L is the length at $p(C)$ and L_0 the length at $p = 0$ $(C = 0)$. In Figures 3 and 4, the elongation data are plotted as a function of concentration. Earlier data for CH_4, C_2H_4, and C_2H_6 in PB and for CH_4 in EVAc are also shown in the figures.[5,7] Some data are depicted by solid curves without experimental points because of the simplicity of the figures. As shown in the figures, each plot is linear except for that of the PB film in the high-elongation region. The dilation isotherm obtained on the sorption run for every gas coincides with that on the desorption run. This indicates that creeping flow of the film specimen does not occur in dilation experiments. Hence the elongation data may be used as equilibrium values to characterize the total volume dilation.

Experimental points for the PB film deviate slightly and negatively from linearity at low concentration as the elongation exceeds ca. 4 × 10^{-2}. This elongation corresponds nearly to a volume dilation of 12 vol %. Considering that the partial molar volume must remain nearly constant in the small ranges of concentration studied here, such concavity of the l_s vs C plot at high concentrations may be due to a break in the isotropy of the film dilation; that is, length elongation in the plane directions of the film seems to become smaller than a fractional increase in its thickness when the polymer swells by more than 12 vol %. Pope et al., however, reported that a silicone rubber film undergoes an isotropic dilation up to an elongation of at least 9 × 10^{-2} during sorption of high pressure CO_2.[9] At the present time, no reasonable explanation can be offered for the difference between PB and silicone rubber films.

Partial Molar Volumes. The partial molar volume of a gas in a rubbery polymer can be obtained from sorption and elongation data, because the gas sorption is usually restricted to very low concentrations.[4,5] When the dilation is assumed to be isotropic and the compression of the polymer by a hydrostatic component of the gas pressure is negligible, the partial molar volume is given as

$$\bar{V}_R \equiv (\partial V/\partial n)_{T,p,N} \quad (2)$$

$$\cong 3 \times 22410(\mathrm{d}l_s/\mathrm{d}C) \quad (3)$$

where V is the volume of the polymer–gas mixture containing N moles of polymer and n moles of gas, and the volumetric concentration C is equal to $22410n/V$ cm^3(STP)/cm^3(polym).

As shown above, each dilation isotherm plotted in the form of elongation versus concentration exhibits a straight line except for the high-elongation region (Figures 3 and 4). From linear parts of the isotherms, partial molar volumes of the dissolved organic gases were calculated according to eq 3. Results are presented in Tables I and II together with earlier data.[5,7] Relative errors in the $\bar{V}_R$ determination by a least-squares method are within ±1.5% as listed in the tables.

In a case of a sparingly soluble gas (such as CH_4) whose value of k_D is much smaller than 1 (cm^3(STP)/cm^3(polym))/atm, the hydrostatic compression of the polymer by pressure of the gas is not negligibly small compared with the sorptive dilation. A partial molar volume of such a gas is approximately given by $\bar{V}_R = 22410\ \mathrm{d}[3l_s + \beta_T p]/\mathrm{d}C$, where β_T is the compressibility of the penetrant-free polymer.[5] The CH_4 data in Figures 3 and 4 are therefore plotted in the form of $(l_s + \beta_T p/3)$ versus concentration, where values of β_T are 4.75 × 10^{-5} atm^{-1} for PB and 3.9 × 10^{-5} atm^{-1} for EVAc. The partial molar volumes thus obtained are cited in Tables I and II from the earlier papers.

Relation between Partial Molar Volume and Molecular Size. Figure 5 shows partial molar volumes plotted versus van der Waals volumes $\bar{V}_W$ for the eight organic gases. The van der Waals volumes used here were calculated according to a group contribution method by Bondi.[10] The linear relationship found in the range of elongation below 4 × 10^{-2} or of concentration below 30–40 cm^3(STP)/cm^3(polym) is expressed as

$$\bar{V}_R = 1.6\bar{V}_W + 18.5\ \mathrm{cm^3/mol}$$

The relation agrees very closely with a relationship between molar volume and van der Waals volume for liquid n-alkanes (carbon number n = 5–24); $\bar{V} = 1.59\bar{V}_W + 21.41$ in cm^3/mol at 20 °C.[11] The latter is also shown as a dotted line in Figure 5.

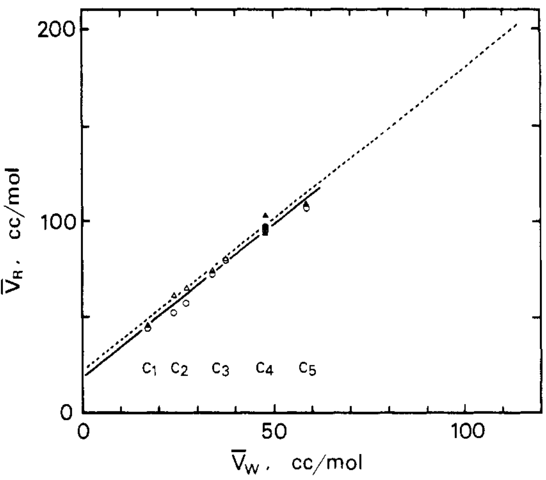

Figure 5. Correlations of partial molar volume with van der Waals volume for gases in (○) polybutadiene and (△) poly(ethylene-*co*-vinyl acetate), where solid symbols belong to iso-C_4H_{10}. Dotted line is molar volume plotted versus van der Waals volume for liquid n-alkanes (carbon number 5–24) at 20 °C.

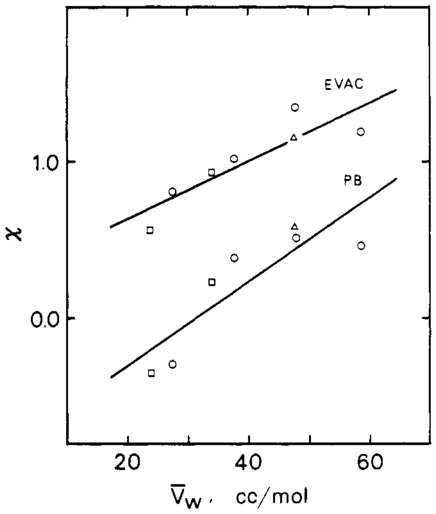

Figure 6. Flory–Huggins parameter plotted versus van der Waals volume: (○) n-alkanes; (△) iso-C_4H_{10}; (□) n-alkenes.

This result indicates that an additivity rule holds for the partial molar volumes of the dissolved gases, as well as for their van der Waals volumes.[10,12] We then tried to divide the partial molar volumes of the n-alkane gases into contributions of the methylene group $\bar{V}(CH_2)$ and methyl group $\bar{V}(CH_3)$ to itself and had the linear relation between the partial molar volume and carbon number n; $\bar{V}_R = (n-2)\bar{V}(CH_2) + 2\bar{V}(CH_3)$, where $\bar{V}(CH_2)$ = 16 cm^3/mol and $\bar{V}(CH_3)$ = 31 cm^3/mol. These contributions are almost the same as those for the molar volumes of the liquid n-alkanes, i.e., $\bar{V}(CH_2)$ = 16.3 cm^3/mol and $\bar{V}(CH_3)$ = 32.5 cm^3/mol. From the above results, it is inferred that gas molecules dissolved in the polymers are in almost the same thermodynamic state as molecules of liquid in itself are.

Interaction between Polymer and Gas. The Flory–Huggins parameter χ was estimated from the values of σ and $\bar{V}_R$ using the relation $\sigma = 2(1 + \chi)\bar{V}_R/22410$.[8] Results are presented as a function of van der Waals volume in Figure 6. According to the definition, the quantity of χ multiplied by the Boltzmann constant and temperature is equivalent to the difference in energy of a gas molecule inserted in the pure polymer compared with one in its own liquid.[13] The value of χ for a homologous series of organic gases is therefore expected to vary in proportion to molecular size or carbon number. The data shown in Figure

6 agree well with this expectation.

The values of χ for C_2H_4 and C_2H_6 in PB, however, became negative. The cause of the negative values is not clear, but it may be partly related to the fact that the dissolution studied here is not an isobaric process. That is, because the Flory–Huggins equation is a solution theory of a polymer–solvent system at constant temperature and pressure, it is not applicable to the gas dissolution of a polymer in which the effect of the hydrostatic component of the gas pressure on its solubility is not negligibly small. Therefore we compensated amounts of the dissolved gases for their decreases in solubility due to pressure using the relation $(\partial \ln L_s/\partial p)_T = \beta_T - \bar{V}_R/RT$, where L_s is the Ostwald coefficient of solubility.[14] The corrected amounts of the dissolved gases, which can be regarded as isobaric values at 1 atm, were again analyzed by the above-mentioned method. However, reestimated values of χ were still negative, but came close to zero; $\chi = -0.1$ for both C_2H_4 and C_2H_6. There will possibly be other causes to get χ negative such as thermal behavior of the dissolution and experimental errors in pressure measurements.

Comparison among the Two Polymers and Others. As shown in Tables I and II, the solubilities of PB to the organic gases are about twice those of EVAc, which are similar in magnitude to the solubilities of low-density polyethylene.[15] Since the degrees of crystallinity of the polymers are much the same (PB, 0.26; EVAc, 0.3), it is apparent that the organic gases have better affinities for PB molecules than EVAc molecules. This tendency is consistent with the result shown in Figure 6 that χ values of PB are much smaller than those of EVAc. For C_3H_8 and C_4H_{10}, the χ values of PB obtained in this study are comparable to those of natural rubber estimated by van Amerongen.[1]

The partial molar volumes of the organic gases in the two polymers are almost the same, as shown in Tables I and II and in Figure 5. By comparing these volumes with literature data for other polymers, it can be confirmed whether the linear relation between the partial molar volume and the van der Waals volume found in this study is accepted as a general rule. However, there are only a few data of $\bar{V}_R$ available for comparison: CH_4 41, C_2H_4 55.2, and C_2H_6 56.0 cm^3/mol in a poly(dimethylsiloxane) rubber at 25 °C;[16] C_2H_4 52, C_2H_6 65, and C_3H_8 77 cm^3/mol in poly(ethyl methacrylate) above the glass transition concentration at 15 °C;[17] CH_4 52.2, C_2H_2 50.4, C_2H_4 61.0, and C_2H_6 67.1 cm^3/mol on the average in five organic solvents (carbon tetrachloride, chlorobenzene, benzene, acetone, and methyl acetate) at 25 °C.[18] In spite of the large differences in solubilities, the partial molar volumes in these polymers and the organic solvents are very similar in magnitude to the values obtained here and have also a tendency to increase with size of the gas molecule. Furthermore, the linear relation found here is almost the same as that between the molar volume and the van der Waals volume for a series of liquid *n*-alkanes, as mentioned above. From these facts, it may be concluded that the linearity of partial molar volume versus van der Waals volume exists in nearly every system consisting of a rubbery polymer and a homologous series of organic gases.

Conclusions

Sorption isotherms for organic gases in two rubbery polymers, 1,2-polybutadiene and poly(ethylene-*co*-vinyl acetate), are well described as the Flory–Huggins dissolution. Dilation isotherms in the form of elongation versus pressure mimic the corresponding sorption isotherms. Plotting elongation versus concentration gives a linearity except for the high-concentration region.

Partial molar volumes of dissolved organic gases are determined from sorption and elongation data, and a linear relation is found between the volumes and the van der Waals volumes. The linear relation, which is similar to that between the molar volume and the van der Waals volume for liquid *n*-alkanes, will possibly exist in every rubbery polymer–organic gas system.

The present data at relatively low concentrations make it possible to conclude that the additivity rule of partial molar volume is obeyed by organic gases dissolved in rubbery polymers and that the dissolved molecules are in almost the same thermodynamic state as molecules of liquid in itself are. The results will give us the volumetric approach, one of the most fundamental approaches, to the understanding of every phenomenon or process relating to polymer–gas systems such as sorption, diffusion, and permeation of gases in rubbery polymers and plasticization of polymers due to sorption of gases.

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Registry No. C_2H_2, 74-85-1; C_2H_6, 74-84-0; C_3H_6, 115-07-1; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *iso*-C_4H_{10}, 75-28-5; *n*-C_5H_{12}, 109-66-0; (ethylene)(vinyl acetate) (copolymer), 24937-78-8.