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Measurements of the Solubility Coefficients of Gases and Vapors in Natural Rubber by Gas Chromatographic Technique

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The solubility coefficients of hydrocarbons in unvulcanized natural rubber at 25 °C were determined by gas-liquid chromatography. Natural rubber was used as a stationary liquid and nine kinds of lower olefins and paraffins as solutes. The retention volume for all the solutes did not vary with sample size. It was found that the correction for gas phase imperfection is negligible. Thus the solubility coefficient was readily obtained from the specific retention volume without any correction. The values obtained were in fairly good agreement with those determined by the volumetric method given in other works. Modified equations expressing the relationships between the solubility coefficient and the boiling temperature, the critical temperature, and the Lenard-Jones force constant, which might be applicable to a more extensive range of gaseous compounds, were presented.

Recently gas-liquid chromatography (GLC) has attracted attention as a means for determining thermodynamic properties of a solution consisting of stationary liquid and solute gas. Many investigations have been made since Porter *et al.*1) measured the partition coefficient and the heat of solution by GLC in 1956. The method is especially effective for a system of polymer and organic compounds. For example, the volatility of solvents in polymer coatings was measured by Newman and Prausnitz,2) and the solubility parameter of polyethylene glycol by Takamiya *et al.*3) and by Kawakami *et al.*4) In the present work GLC was employed to determine the solubility coefficients of some lower olefins and paraffins in unvulcanized natural rubber at 25 °C. The values obtained were in fairly good agreement with those determined by van Amerongen5) and Michaels and Bixler6) by means of the volumetric method. Modified empirical formulas were proposed on the relation between the solubility coefficient and other physicochemical properties of gases.

Theoretical

When the Henry law holds between stationary liquid and solute gas and the gas phase imperfection can be neglected, the net retention volume V_N is related to the partition coefficient K by7)

$$V_N = KV_L. \tag{1}$$

Here K is defined by

$$K = \frac{n_L/V_L}{n_G/V_G}, \tag{2}$$

where n_L and n_G are the numbers of moles of solute in the liquid phase and the gas phase with volumes of V_L and V_G, respectively.

The solubility coefficient S, on the other hand, is defined by

$$c = Sp, \tag{3}$$

where c is the concentration expressed in m^3(STP) of solute gas dissolved per m^3 of solvent and p is the equilibrium partial pressure of solute gas. Using the ideal gas equation, the concentrations in the liquid phase and the gas phase are respectively given by $n_L/V_L = cp^\circ/RT^\circ$ ($p^\circ = 1$ atm$=101325$ Pa, $T^\circ = 273.2$ K) and $n_G/V_G = p/RT$ where T is the column temperature. Thus the partition coefficient is expressed by

$$K = \frac{T}{T^\circ}\frac{p^\circ}{p}c = \frac{T}{T^\circ}p^\circ S, \tag{4}$$

and

$$S = \frac{T^\circ}{T}\frac{1}{p^\circ}\frac{V_N}{V_L}. \tag{5}$$

The simplified expression is obtained by using the specific retention volume V_g which denotes the net retention volume per unit weight of stationary liquid converted into 0 °C. We thus have

$$V_g = \frac{V_N}{w_L}\frac{T^\circ}{T}, \tag{6}$$

where w_L is the weight of stationary liquid. Substitution of Eq. 6 into Eq. 5 gives

$$S = \frac{1}{p^\circ}\rho_L V_g, \tag{7}$$

where ρ_L is the density of stationary liquid. The solubility coefficient can thus be calculated from the specific retention volume. The value of V_g can be obtained experimentally by the equation

$$V_g = \frac{t_R F}{w_L}\frac{T^\circ}{T_r}J_2^3, \tag{8}$$

where t_R is the peak maximum retention time, F is the flow rate of carrier gas at room temperature T_r.

$$J_n^m = \frac{n}{m}\left\{\frac{(p/p_o)^m - 1}{(p_i/p_o)^n - 1}\right\}, \tag{9}$$

where p_i and p_o are the column inlet and outlet pressures, respectively.

Correction is necessary when gas phase imperfection is not negligible.8) It was first proposed by Everett and Stoddart,9) and improved by Cruickshank *et al.*10) According to the latter, the net retention volume is related to the partition coefficient at zero total pressure K_0 by

$$V_N = K_0 V_L \exp(\beta p_o J_3^4). \tag{10}$$

Here

$$\beta = \frac{2B_m - v^\infty}{RT}, \tag{11}$$

where B_m is the second mixed virial coefficient between solute gas and carrier gas, and v^∞ the partial molar volume of solute at infinite dilution. The solubility coefficient at zero pressure S_0 is related to K_0 by Eq. 4. Thus

$$S_0 = \frac{1}{p^\circ}\rho_L V_g \exp(-\beta p_o J_3^4), \tag{12}$$

S_0 can be obtained when the values of B_m and v^∞ are known.

Experimental

Preparation of Column. A certain volume of 1 wt% benzene solution of the stationary liquid, unvulcanized natural rubber (smoked sheet) was added with stirring to a weighed amount of solid support, Uniport B (Gasukuro Kogyo Co.), and then air-dried. For each impregnation operation, the amount of benzene solution equal to the pore volume of solid support was used. The operation was repeated five times to reach the desired coverage ratio of the stationary liquid and finally dried in a vacuum. The coverage ratio measured with a Soxhlet extractor was 8.2 wt%. Since particles adhered to each other with increase in coverage ratio, it was impossible to increase it further. The coated support was packed into a copper tube of 3 mm i.d. and 3 m in length. The density of natural rubber was measured by the floatation method and found to be 910 kg/m³.

Solute. Nine kinds of commercial lower olefins and paraffins were used.

Apparatus and Procedure. A KOR-70 gas chromatograph (Gasukuro Kogyo Co.) was used. The mercury manometer was attached to the inlet of the column. Helium was used as a carrier gas, the flow rate of which being kept at 10^{-5} m³/min. The column temperature differed with sample gases in the range −10—25 °C. A solute gas was injected with a micrometer syringe in the range $(2—5) \times 10^{-9}$ m³ as a vapor.

Usually a gas hold-up can be determined from the retention volume of an inert gas. Nitrogen was used as the inert gas. The retention volume of nitrogen, however, has to be corrected, because of its slight solubility in natural rubber. The solubility coefficient of nitrogen determined by Michaels and Bixler⁶⁾ was used for the correction.

When the separation of solute gas and air brought within the sample is not sufficient due to lower solubility of the solute gas, the column temperature falls. In such a case the retention volume at 25 °C was estimated by interpolation using a linear relationship between log V_g and $1/T$.

Results and Discussion

Effect of Sample Size on Retention Volume. The retention volume did not vary with sample size. Thus the partition isotherms of all solute gases examined can be regarded as rectilinear under the experimetal conditions.

Correction for Gas Phase Imperfection. The magnitude of the correction term for gas phase imperfection was examined. v^∞ was taken to be equal to the molar volume of pure liquid v°. A negligible error will result from this approximation. The values of B_m, v° and the correction term at 25 °C are given in Table 1. The second mixed virial coefficient was estimated from the McGlashan-Porter reduced equation¹¹⁾ using Hudson-McCoubrey's combining rule.¹²⁾ The molar volume of pure liquid was estimated from the density using the expansion factor proposed by Watson.¹³⁾ It is clear from Table 1 that the contribution of the term of $\exp(-\beta p_o J_3^4)$ to the specific retention volume is insignificant. A considerable error may be incurred by the estimation of physical properties such as B_m and v°. Thus it is more reasonable to ignore this term than to make an uncertain correction.

*Comparison with Other Works.*¹⁴⁾ The results obtained by neglecting gas phase imperfection are given in Table 1. It can be seen that the solubility coefficient of propane is in good agreement with those obtained independently by van Amerongen⁵⁾ and Michaels and Bixler,⁶⁾ by means of the volumetric method. For propylene, on the other hand, the value obtained seems to differ somewhat from that presented by Michaels and Bixler. Although it is not clear which is accurate, both values do not differ too greatly from the correlations between the solubility coefficient and the physicochemical properties of gases, as described below.

From the assumption that the dissolution process involves condensation and mixing process, the solubility coefficient can be written as¹⁵⁾

$$2.303 \log S = \frac{L_b}{RT_b}\left(\frac{T_b}{T} - 1\right) + 2.303 \times \log \frac{22.4 \times 10^{-3}}{v^\circ} - 1 - \chi,$$

where L_b is the molar latent heat of condensation at boiling temperature T_b, and χ is the interaction parameter. When χ can be taken as constant, a linear relationship is valid between log S and T_b. Moreover,

TABLE 1. SECOND MIXED VIRIAL COEFFICIENTS, LIQUID MOLAR VOLUMES, CORRECTION TERMS, AND SOLUBILITY COEFFICIENTS AT 25 °C

	$10^6 B_m$ / m³ mol⁻¹	$10^6 v^\circ$ / m³ mol⁻¹	$\exp(-\beta p_o J_3^4)$	$10^5 S$/m³ (STP)m⁻³ Pa⁻¹	
				This work$^{a)}$	Other works
Ethylene	28	129	1.0038	0.93	
Ethane	30	97	1.0019	1.55	
Propylene	34	83	1.0008	6.01	5.2$^{b)}$
Propane	36	90	1.0009	6.19	6.1$^{b)}$ 6.4$^{c)}$
1-Butene	40	96	1.0008	19.3	
trans-2-Butene	40	94	1.0008	24.2	
cis-2-Butene	39	94	1.0008	28.1	
1-Pentene		110		56.1	
Pentane	46	116	1.0012	61.2	

a) Obtained by neglecting gas phase imperfection. b) A. S. Michaels and H. J. Bixler.⁶⁾ c) G. J. van Amerongen.⁵⁾

by applying the Guldberg rule, $T_b/T_c \approx 2/3$, a similar relationship between log S and critical temperature T_c can be derived. For solubility coefficients of gases in vulcanized natural rubber Barrer and Skirrow[16] proposed

$$\log S = -7.0 + 0.007\ T_c \quad (\text{at } 50\ ^\circ\text{C});$$

van Amerongen[5] proposed

$$\log S = -7.1 + 0.0074\ T_c \quad (\text{at } 25\ ^\circ\text{C})$$

and

$$\log S = -7.1 + 0.0123 T_b \quad (\text{at } 25^\circ\ \text{C}).$$

The results obtained are shown in Figs. 1 and 2 together with those by van Amerongen and Michaels and Bixler, the relation of van Amerongen being shown by broken lines. Although there exists a fairly good correlation between log S and T_c or T_b, a slight deviation from the broken lines is found when T_c ot T_b becomes higher. Therefore the relationships may be expressed better by the equations

$$\log S = -7.0 + 0.0030\ T_c^{1.15}$$

and

$$\log S = -7.0 + 0.0071\ T_b^{1.10},$$

which were calculated by least-squares treatment with all data in the figures, where the correlation coefficients are 0.994 and 0.992, respectively. These relations are shown in Figs. 1 and 2 by solid lines.

Michaels and Bixler,[6] on the other hand, proposed the use of the Lenard-Jones force constant ε/k instead of T_c or T_b. The plot is shown in Fig. 3. In this study ε/k determined from viscosity[17] was used.[18] The straight line was calculated by least-squares treatment with all data in the figure:

$$\log S = -7.05 + 0.0105\ (\varepsilon/k),$$

where the correlation coefficient is 0.970.

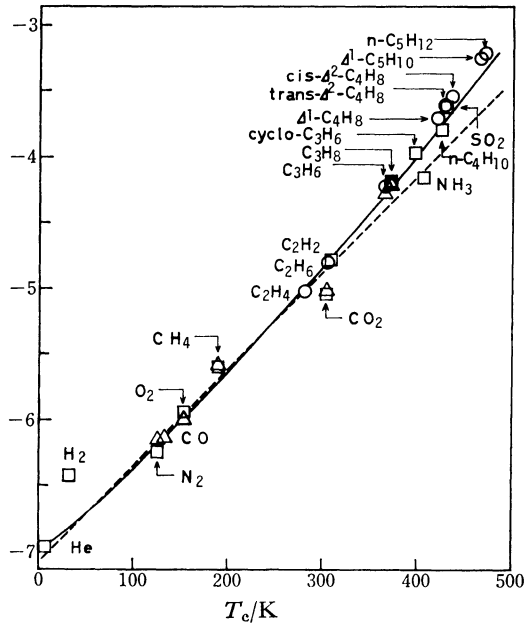

Fig. 1. The relationship between solubility coefficients and critical temperatures.
○: This work, □: Van Amerongen, △: Michaels and Bixler.

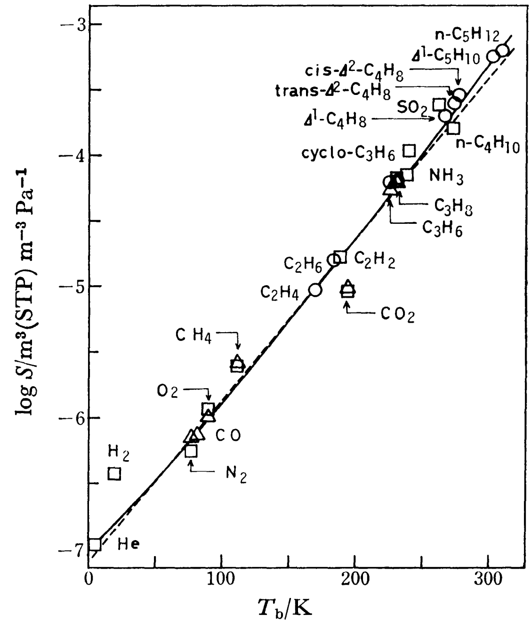

Fig. 2. The relationship between solubility coefficients and boiling temperatures.
○: This work, □: Van Amerongen, △: Michaels and Bixler.

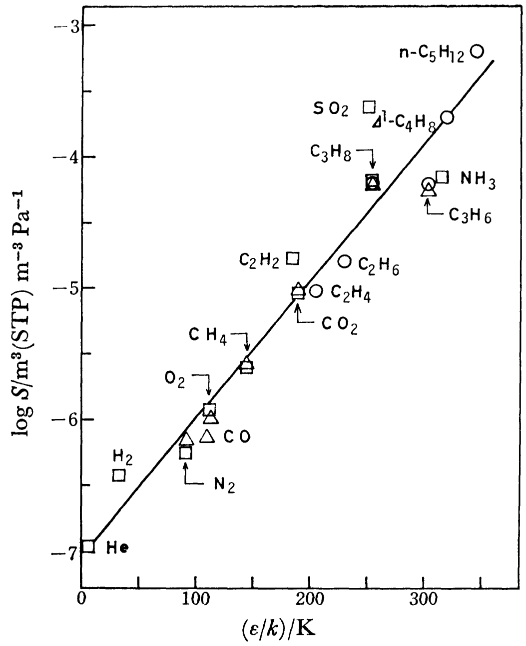

Fig. 3. The relationship between solubility coefficients and Lenard-Jones force constants.
○: This work, □: Van Amerongen, △: Michaels and Bixler.

Thus the values obtained here seem to be reasonable and the relationships are confirmed between log S and T_c, T_b or ε/k.

The solubility coefficients have been measured by the volumetric or gravimetric method. The gas chromatographic technique could be an alternative method, simpler and taking less time than the conventional ones.

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