

MEASUREMENT AND PREDICTION OF SOLUBILITIES OF HYDROCARBON VAPORS IN MOLTEN POLYMERS

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The solubilities of *m*-xylene and nonane vapors in polystyrene and of ethylbenzene and nonane vapors in polybutadiene were measured with a sorption apparatus in the temperature range from 130 to 175°C and 80 to 130°C, respectively.

A new expression for the free-volume term derived previously was coupled with UNIFAC to predict activities of hydrocarbons in polymer solutions. In this study, the UNIFAC-FV model has been reexamined and the parameters in the free volume term have been revised. The parameters in the UNIFAC-FV model can be calculated by the group contribution. The model was applied to predict solubilities, activities, or mass-fraction Henry constants for the systems studied here and published in the literature. From comparison of experiment with calculation it is found that the present UNIFAC-FV model can give fairly good predictions of such equilibrium properties of organic vapors in polymers on the basis of a knowledge of molecular structure alone.

Introduction

In the polymer industry, equipment is required to separate unreacted monomers and solvents from the polymer produced. To design such equipment, solubilities of hydrocarbon vapors in molten polymers along with a successful calculation method are needed.

Experimental techniques and data sources for vapor-liquid equilibria of concentrated polymer solutions have been reviewed by Bonner,⁵⁾ Iwai *et al.*,^{17,19)} and Murasige *et al.*²⁶⁾

The authors have measured the mass-fraction Henry constants of hydrocarbon vapors and gases in polystyrene, polypropylene, polybutadiene, styrene-butadiene copolymers, and acrylonitrile-butadiene copolymer^{12-14,16,28)} by a gas chromatographic method. Furthermore, the solubilities of ethylbenzene and octane vapors in polystyrene were measured by a sorption apparatus with quartz spring²¹⁾ and the data were compared with those measured by the gas chromatographic method. In this work, the solubilities of *m*-xylene and nonane in polystyrene and of ethylbenzene and nonane in polybutadiene were measured by sorption apparatus in the temperature range from 130 to 175°C and 80 to 130°C, respectively.

It is very helpful if the solubilities of vapors in polymers can be estimated by a predictive method. Correlation methods were reviewed by Bonner⁵⁾ and Murasige *et al.*²⁷⁾ A large number of theories have been proposed to correlate the thermodynamic properties of polymer solutions. These include the Flory-

Huggins lattice theory,^{7,11)} the Flory equation of state,⁸⁾ an equation of state proposed by Schotte,³³⁾ the Perturbed-Hard-Chain theory²⁹⁾ and the Analytical Solution of Groups Variable Size Parameter model.²⁵⁾ These theories have been successfully applied to correlate the solubilities of solutes in polymers. However, adjustable parameters are necessary to correlate the solubilities by these models. Oishi and Prausnitz³⁰⁾ proposed the UNIFAC-FV model, which is based on UNIFAC¹⁰⁾ with a free volume term. The UNIFAC-FV model has been shown to be a very useful correlation method.^{1,2,15,31)} However, it seems difficult to determine the unique value of external degrees of freedom for the same solute.¹⁵⁾ To avoid this disadvantage, the authors in a previous paper¹⁸⁾ proposed a new expression for the free volume term which was derived from a partition function and was applicable to polymer and low-molecular weight hydrocarbon mixtures. Further, an equation of state obtained from the partition function was shown to be useful in calculating volumes of low-molecular weight hydrocarbon liquids and molten polymers.²⁰⁾ The newly proposed UNIFAC-FV model was found to be successful in predicting the Henry constants of hydrocarbon vapors and gases in polystyrene, polypropylene, polyethylene, and polybutadiene^{12,18)} from the contributions of each group contained in the molecules. In this study, the UNIFAC-FV model has been reexamined and the parameters in the free volume term have been revised.

1. Experimental

1.1 Materials

The polystyrene used was obtained from Nakarai

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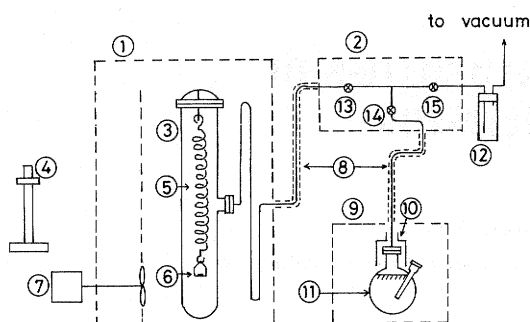


Fig. 1. Sorption apparatus. ① Air bath, ② Air bath, ③ Sorption column, ④ Cathetometer, ⑤ Quartz spring, ⑥ Polymer sample, ⑦ Motor, ⑧ Ribbon heater, ⑨ Ethylene glycol bath, ⑩ Heating cover, ⑪ Hydrocarbon vapor source, ⑫ Cold trap, ⑬–⑮ Valves

Chemicals, Ltd. The number-average molecular weight and weight-average molecular weight of polystyrene are 5.37×10^4 and 2.47×10^5 , respectively, and the glass transition temperature is 357 K. The polybutadiene used is obtained from Scientific Polymer Products, Inc. It is 98% *cis*-polybutadiene and the weight-average molecular weight is 2×10^5 – 3×10^5 . The glass transition temperature is 170 K.

All hydrocarbons used were reagent grade, obtained from Nakarai Chemical, Ltd., and were used without further purification. Their purities are believed to be more than 98%, 99%, and 99.7% for ethylbenzene, *m*-xylene, and nonane, respectively.

1.2 Apparatus

The solubilities of hydrocarbon vapors in polystyrene were measured by a sorption apparatus with quartz spring. **Figure 1** shows the apparatus used in the present work. Details of the experimental procedure have been reported in our previous papers.^{21,23)} In brief, a film of polystyrene coated on thin aluminum plate 6 was suspended by a sensitive quartz spring 5 in evacuated glass column 3. Hydrocarbon vapor was supplied into the column from flask 11. During the sorption experiment, hydrocarbon liquid in the flask was maintained at a constant temperature lower than that of the column (equilibrium temperature) in order to generate constant-pressure vapor. The increase in mass of the film due to sorption of vapor was measured as a function of time by observing the extension of the spring through cathetometer 4. When the film reached equilibrium with the surrounding vapor, i.e., no extension of spring was observed, the solubility of hydrocarbon in polystyrene could be determined by the mass difference between initial and equilibrium conditions. The vapor pressure of hydrocarbon supplied from flask 11 was given from the Antoine equation shown in the literature²²⁾ by measuring the temperature inside the flask.

1.3 Results

Tables 1 to 4 show the solubilities thus obtained for

Table 1. Solubilities of *m*-xylene vapor in polystyrene

130°C		150°C		175°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0441	14.9	0.0352	20.5	0.0186	21.1
0.0473	15.3	0.0376	20.5	0.0226	25.8
0.0875	28.8	0.0390	20.6	0.0508	52.2
0.116	33.9	0.0605	34.7	0.0514	52.4
0.144	41.5	0.0652	34.8	0.0678	68.1
0.167	43.8	0.0683	36.7	0.0786	74.5
		0.0864	45.1		
		0.0904	46.1		
		0.0974	50.9		
		0.126	60.5		

Table 2. Solubilities of nonane vapor in polystyrene

130°C		150°C		175°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0265	16.2	0.0243	23.7	0.0147	27.9
0.0266	16.7	0.0250	23.7	0.0150	27.9
0.0503	26.5	0.0257	23.2	0.0310	53.3
0.0672	31.9	0.0509	44.7	0.0312	53.1
0.119	43.6	0.0550	46.0		
		0.0669	53.3		
		0.0683	54.4		

Table 3. Solubilities of ethylbenzene vapor in polybutadiene

80°C		100°C		130°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0440	3.85	0.0391	5.39	0.0225	6.42
0.0465	3.56	0.0409	5.39	0.0282	7.90
0.0474	3.98	0.0448	5.78	0.0324	9.65
0.0594	4.47	0.0917	10.3	0.0378	10.7
0.102	6.65	0.0971	11.1	0.0543	15.6
0.108	6.42	0.114	12.2	0.0615	16.7
0.108	6.89	0.176	17.1	0.0749	20.3
0.130	7.66	0.222	19.8	0.0898	23.6
0.171	9.33	0.271	22.8	0.120	29.6
0.193	9.65	0.388	27.2	0.137	33.7
0.218	11.0			0.157	37.1
0.240	11.4			0.167	39.6
0.353	13.4				

Table 4. Solubilities of nonane vapor in polybutadiene

80°C		100°C		130°C	
w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]	w_1 [—]	P_1 [kPa]
0.0187	2.49	0.0230	3.95	0.0221	7.29
0.0193	2.01	0.0290	4.22	0.0245	7.01
0.0312	2.48	0.0358	4.77	0.0392	11.1
0.0445	3.17	0.0456	5.29	0.0567	15.3
0.0607	3.99	0.0686	7.75	0.0774	20.1
0.0616	3.97	0.0897	9.26	0.0945	23.9
0.0620	4.12	0.115	10.4	0.109	26.0
0.0851	5.14	0.128	11.7	0.121	28.2
0.126	6.59	0.141	12.3	0.138	32.0
0.139	6.83	0.252	16.8	0.177	37.9
0.169	7.72			0.202	40.8
				0.216	42.0

m-xylene and nonane in polystyrene, and for ethylbenzene and nonane in polybutadiene. In a previous paper,²¹⁾ the reliability of solubilities obtained by the present apparatus was ascertained by comparing the solubilities of ethylbenzene in polystyrene with literature values measured by a similar sorption apparatus, and the mass-fraction Henry constants determined by extrapolation for the solubilities of ethylbenzene in polystyrene with those obtained by gas chromatographic technique.

2. UNIFAC-FV Model

It is very useful if the solubility of hydrocarbon vapor in polymer can be estimated, without any information about the mixture, by a predictive method. In general, the solubility of a solute (subscript 1) in polymer (subscript 2) can be expressed by the single equation

$$P_1 \phi_1 = a_1 f_1^{\text{OL}} \quad (1)$$

where P_1 is the vapor pressure, ϕ_1 is the fugacity coefficient, a_1 is the activity, and f_1^{OL} is the fugacity of pure liquid phase of solute. The fugacity coefficient can be calculated by

$$\phi_1 = \exp(B_1 P_1 / (RT)) \quad (2)$$

where B_1 is the second virial coefficient of solute, R is the gas constant, and T is the absolute temperature. The standard state fugacity f_1^{OL} can be calculated by

$$f_1^{\text{OL}} = P_1^s \phi_1^s = P_1^s \exp(B_1 P_1^s / (RT)) \quad (3)$$

where P_1^s is the saturated vapor pressure. The values of B_1 and P_1^s can be easily obtained from experimental data or a correlation method. Therefore, solubility, w_1 (mass fraction of solute), can be calculated from the activity of solute. To predict the activity of solute without mixture data, a UNIFAC-FV model has been developed.¹⁸⁾ It is given as

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{\text{FV}} \quad (4)$$

where a_1^C , a_1^R , and a_1^{FV} are combinatorial, residual, and free volume terms of the activity of solute, respectively.

The combinatorial term can be written as³⁰⁾

$$\begin{aligned} \ln a_1^C = & \ln \phi'_1 + \phi'_2 + \frac{z}{2} M_1 q'_1 \ln(\theta'_1 / \phi'_1) \\ & - \frac{z}{2} M_1 q'_1 (1 - \phi'_1 / \theta'_1) \end{aligned} \quad (5)$$

where

$$\phi'_i = r'_i w_i / \sum_j r'_j w_j \quad (6)$$

$$\theta'_i = q'_i w_i / \sum_j q'_j w_j \quad (7)$$

$$r'_i = \frac{1}{M_i} \sum_k v_k^{(i)} R_k \quad (8)$$

$$q'_i = \frac{1}{M_i} \sum_k v_k^{(i)} Q_k \quad (9)$$

In Eqs. (5) to (9), ϕ'_i is the segment fraction, θ'_i is the surface fraction, z is the coordination number, M_i is the molar mass, r'_i and q'_i are the pure-component parameters, R_k and Q_k are the group volume and group surface parameters, respectively, and $v_k^{(i)}$ is the number of groups of type k in molecule i .

The residual term of the activity can be written by the following equations.³⁰⁾

$$\ln a_1^R = \sum_k v_k^{(1)} \{ \ln \Gamma_k - \ln \Gamma_k^{(1)} \} \quad (10)$$

$$\begin{aligned} \ln \Gamma_k = & M_k Q'_k \left\{ 1 - \ln \left(\sum_m \Theta'_m \Psi_{mk} \right) \right. \\ & \left. - \sum_m \left(\Theta'_m \Psi_{km} / \sum_n \Theta'_n \Psi_{nm} \right) \right\} \end{aligned} \quad (11)$$

$$\Theta'_m = Q'_m W_m / \sum_n Q'_n W_n \quad (12)$$

$$Q'_k = Q_k / M_k \quad (13)$$

$$\Psi_{mn} = \exp(-a_{mn} / T) \quad (14)$$

where Γ_k is the group activity coefficient, $\Gamma_k^{(1)}$ is the activity coefficient of the group k in pure component 1, θ'_m is the surface fraction of group m , W_m is the mass fraction of group m , M_k is the molar mass of group k , and a_{mn} is the group interaction parameter. The temperature-dependent coordination number and the interaction parameter given by Skjold-Jørgensen *et al.*³⁴⁾ are adopted in this work and the other parameters are taken from the original UNIFAC.¹⁰⁾

For mixtures of liquids whose molecular weight is not too great, $\ln a_1^{\text{FV}}$ is usually negligible. However, for mixtures of solutes (small molecule) and polymers (large molecule), $\ln a_1^{\text{FV}}$ is often significant.³⁰⁾ The derivation of the free volume term from the partition function was shown in a previous paper.¹⁸⁾ The free volume term can be written as

$$\begin{aligned} \ln a_1^{\text{FV}} = & C_1 \left[\ln \frac{\tilde{v}_{f,1}}{\tilde{v}_{f,M}} + \frac{\tilde{v}_1^{5.66}}{(\tilde{v}_1 - 1)^4 \exp(0.3\tilde{v}_1)} \right. \\ & \left. \times \frac{1}{(1.66 - 0.3\tilde{v}_1)} \left\{ \frac{\exp(0.3\tilde{v}_1)}{\tilde{v}_1^{1.66}} - \frac{\exp(0.3\tilde{v}_M)}{\tilde{v}_M^{1.66}} \right\} \right] \end{aligned} \quad (15)$$

where

$$\tilde{v}_i = (\tilde{v} - 1) \exp \left\{ -\frac{18(\tilde{v} - 1)^2 + 9(\tilde{v} - 1) + 2}{6(\tilde{v} - 1)^3} \right\} \quad (16)$$

$$\tilde{v}_1 = v_1/v_1^* \quad (17)$$

$$\tilde{v}_M = \frac{v_1 w_1 + v_2 w_2}{v_1^* w_1 + v_2^* w_2} \quad (18)$$

where C_1 is the one-third external degrees of freedom for solute, v is the specific volume, v^* is the specific hard-core volume, and subscript M denotes the property of mixture.

In a previous paper,¹⁸⁾ v^* was calculated by the method of Bondi.⁴⁾ However, the free volume was defined as the volume available to the center of mass of a single molecule as it moves about the system while holding the positions of all other molecules fixed. Therefore, it seems reasonable to determine v^* as a function of specific volumes at 0 K. For example, a molecule which is large or has many branched chains seems to have relatively large dead space where other molecules cannot enter. Such space is difficult to estimate by the Bondi hard-core volume. On the other hand, the specific volume at 0 K is influenced by the dead space. In the present study, the hard-core volume was estimated from the specific volume at 0 K, v_o , as follows.

$$v^* = v_o/1.39 \quad (19)$$

The values of v_o can be estimated from the group contribution method proposed by Biltz.³⁾ In Eq. (19), the value of 1.39 has been determined to give almost the same values for v^* calculated by the method of Bondi for small molecules such as hexane and toluene. Table 5 shows the values of group parameter V_k^* obtained. The external degrees of freedom can be determined by data of the heat of vaporization of pure solute as follows.¹⁸⁾

$$C_1 = \frac{\Delta h_1^{\text{vap}} - RT(\tilde{v}_1 - 1)^4}{1.23RT} \frac{(\tilde{v}_1 - 1)^4}{\tilde{v}_1^4} (1.66 - 0.3\tilde{v}_1) \quad (20)$$

where Δh_1^{vap} is the heat of vaporization for solute. The external degrees of freedom for group C_k can be obtained by considering the values of C_1 in terms of group contributions. Table 5 also shows the values of C_k . The values of v_i^* and C_1 can be calculated by the following equations.

$$v_i^* = \frac{1}{M_i} \sum_k v_k^{(i)} V_k^* \quad (21)$$

$$C_1 = \sum_k v_k^{(1)} C_k \quad (22)$$

3. Prediction of Vapor-Liquid Equilibria by Using UNIFAC-FV Model

Vapor-liquid equilibria (solubilities) can be calculated from Eqs. (1)–(18), (21), and (22). Since all parameters in the UNIFAC-FV model can be calculated from the group contribution, solubilities of

Table 5. Group hard-core volume parameters and one-third external degrees of freedom

Group	$V_k^* \times 10^6 \text{ [m}^3 \cdot \text{mol}^{-1}\text{]}$	$C_k \text{ [—]}$
CH ₃ –	14.475	0.185
–CH ₂ –	9.835	0.047
–CH(CH ₃)–	19.669	0.072
–C(CH ₃) ₂ –	29.504	0.109
ACH	8.309	0.074
ACCH ₃	18.144	0.123
ACCH ₂ CH ₃	27.979	0.156
ACCH–	8.863	—
–CH=CH–	16.576	—
–CH=C<	11.935	—

hydrocarbons in polymer as well as vapor-liquid equilibria can be predicted on the basis of the knowledge of molecular structure alone. The values of $\ln a_1^C + \ln a_1^R$ can be calculated by UNIFAC.^{10,34)} The pure component values, P_1^s , B_1 , v_1 and v_2 can be obtained from experimental data. If these data are not available, correlation methods can be used. For example, the saturated vapor pressure of solute can be calculated by the Harlacher equation.³²⁾ The second virial coefficient can be evaluated by the method of Tsionopoulos.³⁵⁾ The specific volume of solute, which is necessary to calculate the free volume term, can be calculated by the equation of Francis.⁹⁾ The specific volume of polymer can be evaluated by the method of Bondi.⁴⁾ The parameters in the free volume term, v^* and C_1 , can be calculated by using the group contribution method with group parameters shown in Table 5 based on Eqs. (21) and (22). If a solute is not included in the groups listed in Table 5, one can calculate v^* by Eq. (19) with v_o proposed by Biltz and C_1 by Eq. (20) directly.

Figures 2 and 3 show the solubilities of *m*-xylene in polystyrene and of ethylbenzene in polybutadiene, respectively. The Bondi temperature-reducing parameters θ_L , which are required to calculate the specific volumes of polymers by using the Bondi method, are 860 K for polystyrene and 735 K for polybutadiene. They were determined by measurement of the specific volumes of polystyrene and polybutadiene. The calculated results by the UNIFAC-FV model are in good agreement with the experimental data. However, a discrepancy is found in the low-pressure region of the ethylbenzene-polybutadiene system at 80°C. Almost the same results are obtained for the nonane-polystyrene and the nonane-polybutadiene systems.

The activities of solutes calculated by the UNIFAC-FV model are directly compared with literature values. Those of benzene in natural rubber are shown in Fig. 4 and those of hexane in polyisobutylene in Fig. 5. The correlation is good.

The mass-fraction Henry constant can also be predicted by the UNIFAC-FV model. The mass-

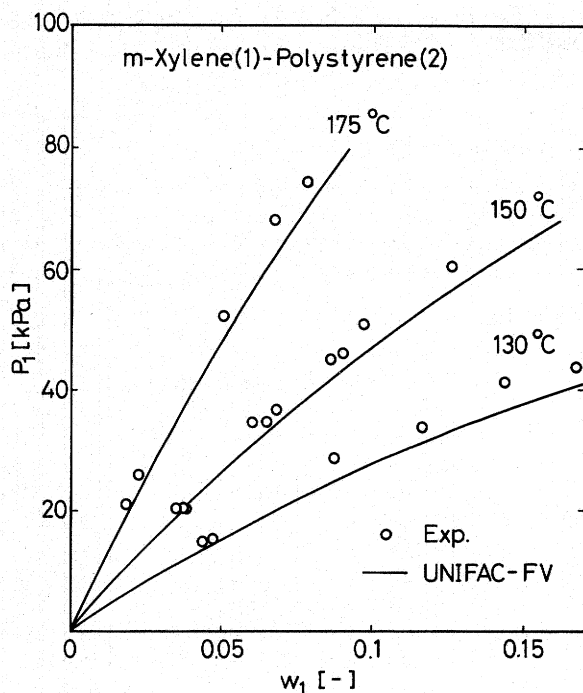


Fig. 2. Solubilities of *m*-xylene in polystyrene

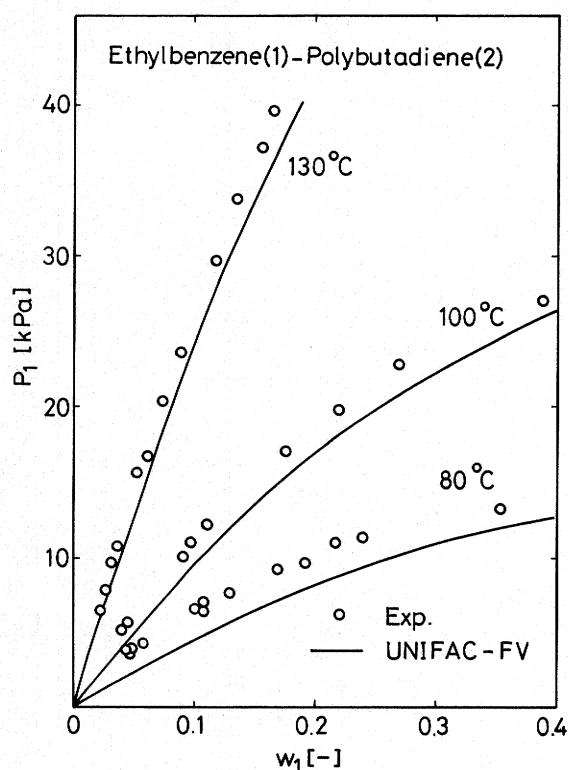


Fig. 3. Solubilities of ethylbenzene in polybutadiene

fraction Henry constant H_1 is defined by the following equation.

$$H_1 = \lim_{w_1 \rightarrow 0} \frac{f_1^V}{w_1} = \lim_{w_1 \rightarrow 0} \frac{a_1}{w_1} f_1^{\circ L} \quad (23)$$

where f_1^V is the fugacity of solute in vapor phase. For example, the mass-fraction Henry constants for sev-

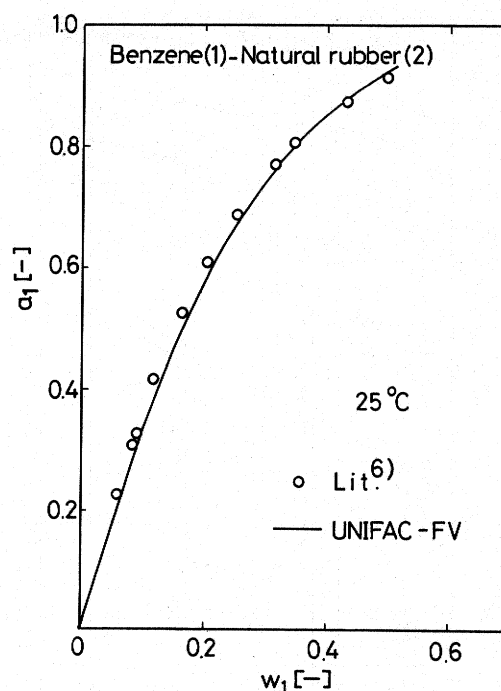


Fig. 4. Activities of benzene in natural rubber

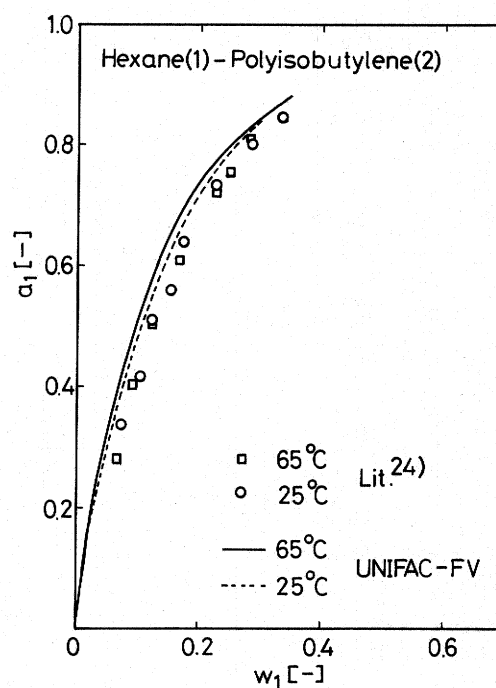


Fig. 5. Activities of hexane in polyisobutylene

eral hydrocarbons in polypropylene are shown in Fig. 6. The Bondi parameter θ_L is 750 K for polypropylene. The calculated results for H_1 show good agreement with the data.²⁸⁾ The UNIFAC-FV model has been applied to the system containing copolymer. As shown in Fig. 7, the calculated results of the mass-fraction Henry constants for octane in styrene-butadiene copolymers (styrene 0, 30, 45, 77, 100 wt%, and Bondi parameters θ_L 735, 764, 781, 823, 860 K, respectively) are also in good agreement with the

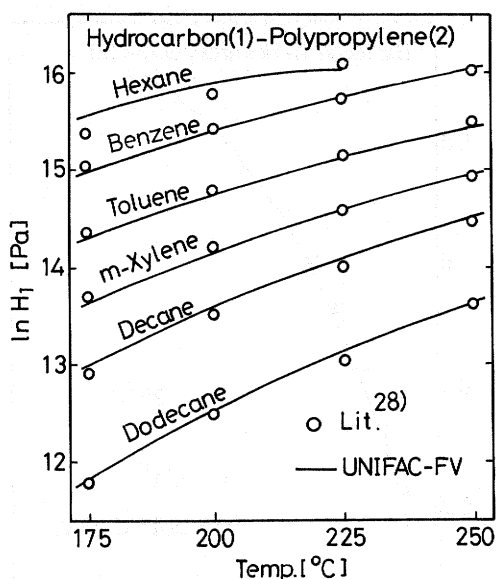


Fig. 6. Henry constants of hydrocarbons in polypropylene

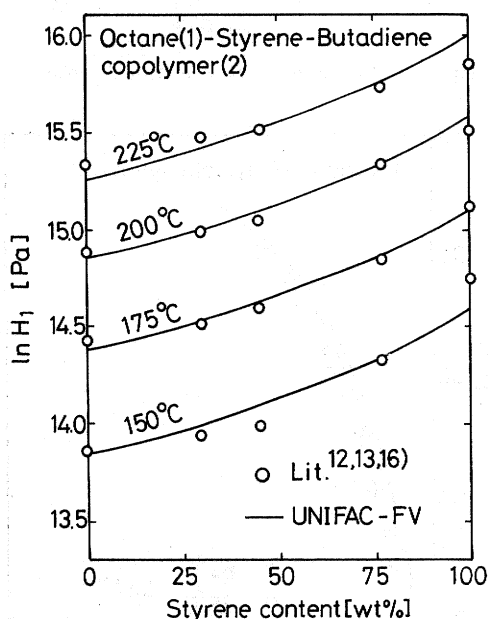


Fig. 7. Henry constants of octane in styrene-butadiene copolymer

experimental data.^{12,13,16)}

Conclusion

The solubilities of *m*-xylene and nonane vapors in polystyrene and of ethylbenzene and nonane vapors in polybutadiene were measured by a sorption apparatus with quartz spring in the temperature range from 130 to 175°C and 80 to 130°C, respectively. The UNIFAC-FV model has been proposed to calculate the activity of solute in polymer solution. The parameters in the UNIFAC-FV model can be calculated from group contribution, and therefore the solubilities of hydrocarbons in polymer (vapor-liquid equilibria) can be predicted from molecular structure

alone. The proposed UNIFAC-FV model was found to be helpful in the prediction of the solubilities of volatile hydrocarbon vapors in polymers.

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Nomenclature

a	= activity	[—]
a_{mn}	= UNIFAC interaction parameter	[K]
B	= second virial coefficient	[m ³ ·mol ⁻¹]
C	= one-third external degrees of freedom	[—]
f	= fugacity	[Pa]
H	= mass-fraction Henry constant	[Pa]
Δh^{vap}	= heat of vaporization	[J·mol ⁻¹]
M	= molar mass	[kg·mol ⁻¹]
P	= pressure	[Pa]
Q_k	= group surface parameter	[—]
Q'_k	= see Eq. (13)	[mol·kg ⁻¹]
q'	= surface parameter	[mol·kg ⁻¹]
R	= gas constant	[J·mol ⁻¹ ·K ⁻¹]
R_k	= group volume parameter	[—]
r'	= volume parameter	[mol·kg ⁻¹]
T	= absolute temperature	[K]
V^*	= hard-core volume per mole	[m ³ ·mol ⁻¹]
v	= volume	[m ³ ·kg ⁻¹]
v_f	= free volume	[m ³ ·kg ⁻¹]
v^*	= hard-core volume per kg	[m ³ ·kg ⁻¹]
v_o	= volume at 0 K	[m ³ ·kg ⁻¹]
W_m	= mass fraction of group m	[—]
w	= mass fraction	[—]
z	= coordination number	[—]
Γ_k	= group activity coefficient	[—]
$\Gamma_k^{(1)}$	= group activity coefficient in pure component 1	[—]
Θ'_m	= surface fraction of group m	[—]
θ'	= surface fraction	[—]
θ_L	= Bondi parameter	[K]
$v_k^{(i)}$	= number of groups of type k in molecule i	[—]
ϕ	= fugacity coefficient	[—]
ϕ'	= segment fraction	[—]
Ψ_{mn}	= see Eq. (14)	[—]

<Subscripts>

i, j	= component i and j
k, m, n	= group k, m , and n
M	= mixture property
1	= solute (volatile hydrocarbon)
2	= polymer

<Superscripts>

C	= combinatorial term
FV	= free volume term
L	= liquid property
R	= residual term
s	= saturated property
V	= vapor property
$^{\circ}$	= pure property
\sim	= reduced property

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