

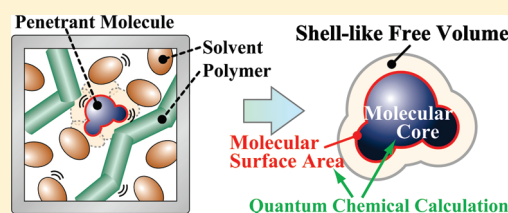
Physical Re-Examination of Parameters on a Molecular Collisions-Based Diffusion Model for Diffusivity Prediction in Polymers

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S Supporting Information

ABSTRACT: Molecular collisions, which are the microscopic origin of molecular diffusive motion, are affected by both the molecular surface area and the distance between molecules. Their product can be regarded as the free space around a penetrant molecule defined as the “shell-like free volume” and can be taken as a characteristic of molecular collisions. On the basis of this notion, a new diffusion theory has been developed. The model can predict molecular diffusivity in polymeric systems using only well-defined single-component parameters of molecular volume, molecular surface area, free volume, and pre-exponential factors. By consideration of the physical description of the model, the actual body moved and which neighbor molecules are collided with are the volume and the surface area of the penetrant molecular core. In the present study, a semiempirical quantum chemical calculation was used to calculate both of these parameters. The model and the newly developed parameters offer fairly good predictive ability.



INTRODUCTION

Molecular diffusivity in polymeric systems is one of the most fundamental dynamic properties, because it is important in many polymeric systems and devices, including cast-drying coating processes,^{1–3} separation membranes,^{4–6} diffusion-controlled polymerization,^{7,8} drug-delivery systems,^{9,10} and so on. Information on the dynamic properties is widely required, and many experimental,^{11–18} simulation,^{19–23} and theoretical studies^{24–26} have been carried out.

In general, microscopic molecular random motion, that is, molecular diffusive motion, is produced by an enormous number of molecular collisions with adjacent molecules in polymeric systems. Although the molecular collisions can be well simulated by molecular dynamics, long simulation times and large computational costs are involved to obtain reliable diffusion coefficients. Adequate incorporation of the microscopic notion of molecular collisions into a theoretical model for polymeric systems would be preferable. However, it has not been attempted until recently, although several theoretical models based on friction,^{27,28} obstruction,^{29,30} molecular,^{31,32} and free volume^{33,34} have been developed.

In response to this situation, we have recently developed a new diffusion model by incorporating the microscopic notion of molecular collisions and by reinterpreting the free-volume concept.^{35,36} Introduction of a physically correct description into the model brings another notable feature for the first time—the model can predict molecular self-diffusivity in polymeric systems using only well-defined single-component parameters and without using any adjustable parameters. The single-component parameters required for the prediction are molecular volume, surface area, free volume, and pre-exponential factor of each

component. This feature makes the model a powerful calculation tool for diffusivity in polymeric systems.

Although the molecular volume at 0 K calculated by the group contribution (GC) method³⁷ was adopted in the previous study, when we revisit the physical meaning of microscopic molecular motion originating from molecular collisions, the actual body moved and which adjacent molecules are collided with are important, and the volume and the surface area of the penetrant molecular core itself should be adopted, respectively. Therefore, in the present study, both were calculated by applying a semiempirical quantum chemical (QC) calculation, which provides accurate information on molecular electron density with high applicability and with relatively low computational cost. Accordingly, free-volume parameters and the pre-exponential factor of each component were also derived. After that, the predictive ability of the combination of the QC-based new parameter set and the model was investigated. At the same time, the single-component parameters for popular solvents and polymers were calculated and tabulated. The tables will help users predict molecular diffusivity in various polymeric systems.

THEORY

From a microscopic point of view, molecular diffusion is driven by an enormous number of molecular collisions with adjacent molecules. This feature has also been clarified by molecular dynamics studies. While the molecular dynamics calculation simulates each single microscopic molecular collision,

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Figure 1. Schematic illustration of fluctuation force acting on a penetrant molecule. When the collision frequency is small, the fluctuation force α is large (left). On the other hand, when the friction frequency is large, the fluctuation force α' becomes small because the friction force imposed on the penetrant molecule from different directions is averaged out (right).

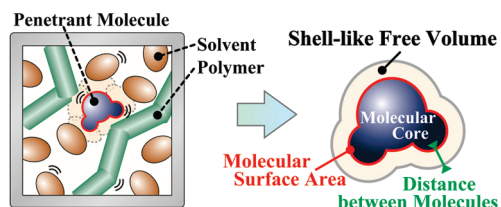


Figure 2. Schematic illustration of molecular diffusive motion originated by molecular collisions and that of shell-like free volume as a product of molecular surface area and distance between molecules.

averaged molecular diffusive motion driven by molecular collisions can be approached by statistical dynamics of an enormous number of molecular collisions over time.

First, the molecular surface of a penetrant is the place that molecular collisions with neighboring molecules occur. When the molecular surface area is large, the collision frequency on the surface is large. As a result, the friction force from different directions on the penetrant molecule is averaged out, and a fluctuation force α that activates molecular diffusive motion becomes small (Figure 1). The molecular diffusivity D_s and the fluctuation force α can be correlated by the following equation

$$D_s = \frac{(kT)^2}{\alpha} \quad (1)$$

where k and T represent Boltzmann's constant and temperature, respectively. When α becomes small, molecular diffusivity becomes large.

On the other hand, the molecular diffusive motion can be described as a random walk and the diffusivity D_s can be expressed as

$$D_s = \frac{d^2}{6\tau} = \frac{ud}{6} \quad (2)$$

where d is the mean distance between molecular collisions, τ is the mean time required to carry out one jump, and u represents the mean molecular kinetic velocity, which is constant at constant temperature because it is determined by the mean kinetic energy of the molecule. When the distance between the penetrant molecule and the adjacent molecule is large, the mean distance between collisions is large and molecular diffusivity is large.

Therefore, when the molecular surface area and/or distance between molecules are large, molecular diffusivity is large. The product of the two components, the free space around a penetrant molecule, was defined as the shell-like free volume (Figure 2) in the previous study³⁵ and can be regarded as a characteristic of

molecular collisions. Unification of the original free-volume theory^{38,39} and the shell-like free volume enables reinterpretation of the traditional free-volume theory as a molecular collisions-based diffusion theory, and the following equation describing self-diffusivity of penetrant $D_{s,1}$ can be obtained

$$D_{s,1} = D_{0,1} \exp \left[-\frac{N_A v_1^*}{s_1} \cdot \frac{\sum_i \omega_i (s_i/M_i)}{\sum_i \omega_i (V_{f,i}/\gamma)} \right] \quad (3)$$

where ω_i , M_i , and N_A are the weight fraction [g/g] and molecular weight [g/mol] of component i and the Avogadro constant [molecules/mol]. v_i^* , s_i , and $D_{0,i}$ express molecular volume [\AA^3 /molecule], molecular surface area [\AA^2 /molecule], and the pre-exponential factor [cm^2/s] of component i . $V_{f,i}/\gamma$ is the specific free volume [cm^3/g] inherent to component i , which is a function of temperature T [K] as

$$V_{f,i}/\gamma = (F_{1i}/\gamma)(F_{2i} + T) \quad (4)$$

where F_{1i}/γ and F_{2i} are the free-volume parameters of component i having units of [$\text{cm}^3/\text{g K}$] and [K], respectively. As mentioned later, the free-volume parameters can be regarded as the characteristic parameters of molecular collisions. The component i represents each of the constituents, solute, solvent, or polymer. The derivation of the model is detailed in our previous papers.^{35,36} Here, molecular volume v_i^* , molecular surface area s_i , free-volume parameters F_{1i}/γ and F_{2i} , and pre-exponential factor $D_{0,i}$ of each component are the only required parameters to predict penetrant molecular diffusivity in polymeric systems.

In the previous study, the molecular volume at 0 K calculated by the GC method and the molecular surface area calculated by the QC method provided fairly good calculation results. However, when reconsidering the microscopic description of molecular motion driven by molecular collisions, the molecular core moves, and the molecule collides with neighboring molecules at the surface of the molecular core. In a physical sense, the volume and the surface area of the penetrant molecular core should be adopted as the molecular volume and the molecular surface area in the collisions-based diffusion model. In the present study, these two parameters were calculated using QC calculations and other parameters required for prediction were derived as in the next section.

CALCULATION OF THE PARAMETERS

Molecular Volume and Molecular Surface Area. In the present study, the molecular volume and molecular surface area are defined as internal volume and surface area of a certain molecular isoelectric surface. The molecular surface is defined as the isoelectric surface with an electron density of 0.0020 au ⁴⁰ (1 au is defined as 6.748 e/\AA^3), and this definition is generally accepted.⁴¹ The molecular structure was optimized and the isoelectric surface was calculated using the PM3 method, which is a semiempirical, QC calculation.⁴² Then, the molecular volume and molecular surface area were calculated. For comparison, the density functional theory (DFT) using Becke–Lee–Yang–Parr (BLYP) density functional^{43,44} with DZVP basis sets and semiempirical AM1⁴⁵ and PM5⁴⁶ methods were also used for calculation of the molecular volume.

To obtain the molecular volume of the polymer segmental unit, n -mer polymer was regarded as the sum of terminal hydrogen

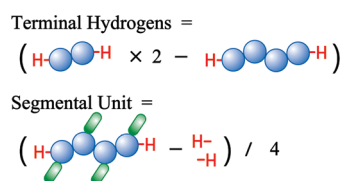


Figure 3. Schematic illustration of calculation of terminal hydrogen size and unit size of polymer.

atoms and n internal units

$$\nu_{n\text{-mer}}^* = n\nu_{\text{unit}}^* + \nu_{\text{termH}_2}^* \quad (5)$$

where $\nu_{n\text{-mer}}^*$, ν_{unit}^* , and $\nu_{\text{termH}_2}^*$ represent the molecular volumes of n -mer polymer, internal unit, and the sum of the two terminal hydrogen molecular volumes, respectively. The size of the terminal hydrogen $\nu_{\text{termH}_2}^*$ should depend on the structure of the main chain; thus, the size of the hydrogen atom was calculated by constructing a corresponding structure for each main chain (for example, polyacrylamide and polymethacrylamide). A schematic illustration of the method is represented in Figure 3. In the previous study,³⁵ n -mer polymer was regarded as the sum of two terminal units and $n - 2$ internal units

$$\nu_{n\text{-mer}}^* = 2\nu_{\text{term unit}}^* + (n - 2)\nu_{\text{unit}}^* \quad (6)$$

where $\nu_{\text{term unit}}^*$ represents the volume of the terminal unit and ν_{unit}^* and $\nu_{\text{term unit}}^*$ were simultaneously adjusted. While the former method gives a more accurate and plausible value, the latter method often gives terminal unit volume larger than monomer volume, which differs from reality (for detail, see Supporting Information, Section S1).

The molecular surface area of the polymer segmental unit is also determined with the same strategy.

Free Volume Parameters and Pre-Exponential Factors. In the present study, the traditional free-volume theory is reinterpreted as the molecular collisions-based diffusion model. In other words, free-volume parameters can be reinterpreted as representing parameters of molecular collisions. Free-volume parameters of each solvent or polymer and pre-exponential factors of each solvent were calculated as follows. The temperature dependence of solvent self-diffusivity can be expressed by Dullien's equation⁴⁷

$$D_{s,\text{solv}} = \frac{0.124 \times 10^{-16} V_{C,\text{solv}}^{2/3} RT}{\eta_{\text{solv}} M_{\text{solv}} V_{\text{solv}}} \quad (7)$$

where $V_{C,\text{solv}}$ is the critical molar volume of the solvent and V_{solv} , and η_{solv} represent the temperature-dependent specific volume [cm^3/g] and viscosity [$\text{g}/(\text{cm} \cdot \text{s})$] of the solvent. On the other hand, the equation of collisions-based diffusion theory can be applied for the diffusivity of the pure solvent by simply assuming $\omega_{\text{solv}} = 1$, and the equation becomes

$$D_{s,\text{solv}} = D_{0,\text{solv}} \exp \left[- \frac{V_{\text{solv}}^*}{(V_{f,\text{solv}}/\gamma)} \right] \quad (8)$$

where V_{solv}^* is the specific molecular volume having unit [cm^3/g] described as $V_{\text{solv}}^* = N_A \nu_{\text{solv}}^* / M_{\text{solv}}$. The following linear relationship between solvent-free volume and temperature is assumed

$$V_{f,\text{solv}}/\gamma = (F_{1,\text{solv}}/\gamma)(F_{2,\text{solv}} + T) \quad (9)$$

By equating eqs 7 and 8, $D_{0,\text{solv}}$, $F_{1,\text{solv}}/(\gamma V_{\text{solv}}^*)$, and $F_{2,\text{solv}}$ can be simultaneously obtained by nonlinear regression. In the previous literature,⁴⁸ the combination of the three parameters for many solvents has already been optimized with molecular volume at 0 K, V_{solv}^* , calculated by the Haward GC method. When V_{solv}^* is replaced by a new value calculated by the QC method, $F_{1,\text{solv}}/\gamma$ should be changed to be proportional to the value of V_{solv}^* used, so as to keep $F_{1,\text{solv}}/(\gamma V_{\text{solv}}^*)$ constant. By this means, $F_{1,\text{solv}}/\gamma$ is recalculated, while holding $D_{0,\text{solv}}$ and $F_{2,\text{solv}}$ constant.

On the other hand, the temperature dependence of polymer viscoelasticity, $\eta_{\text{polym}}(T)$, can be expressed as the following Williams–Landel–Ferry (WLF) equation⁴⁹

$$\log \left(\frac{\eta_{\text{polym}}(T)}{\eta_{\text{polym}}(T_0)} \right) = \frac{-C_1^0(T - T_0)}{C_2^0(T_0 - T)} \quad (10)$$

where T_0 is a particular reference temperature. C_1^0 and C_2^0 are WLF parameters that are extensively tabulated in the literature.^{50,51} On the other hand, the equation of the collisions-based diffusion theory can be applied for viscoelastic properties of pure polymer by applying $\omega_{\text{polym}} = 1$, and the equation becomes

$$\eta_{\text{polym}}(T) = \eta_{0,\text{polym}} \exp \left(\frac{V_{\text{polym}}^*}{V_{f,\text{polym}}/\gamma} \right) \quad (11)$$

where $\eta_{0,\text{polym}}$ and V_{polym}^* are the viscosity pre-exponential factor and specific molecular volume having unit [cm^3/g] described as $V_{\text{polym}}^* = N_A \nu_{\text{unit}}^* / M_{\text{unit}}$. When a linear relationship between polymer-free volume and temperature is assumed

$$V_{f,\text{polym}}/\gamma = (F_{1,\text{polym}}/\gamma)(F_{2,\text{polym}} + T) \quad (12)$$

the following relationship can be derived.

$$\begin{aligned} F_{2,\text{polym}} &= C_2^0 - T_0 \quad \text{and} \quad F_{1,\text{polym}}/\gamma \\ &= V_{\text{polym}}^* / (2.303 C_1^0 C_2^0) \end{aligned} \quad (13)$$

Here free-volume parameters of F_{1i}/γ and F_{2i} are defined to be constant. Further the detailed derivation of eq 13 from eqs 10–12 is described in Supporting Information (Section S2). The WLF equation, which is the temperature dependence of polymeric viscoelastic properties, has been explained using the free-volume concept by Williams et al.⁴⁹ On the other hand, the viscoelastic properties are the scale of the momentum transfer stemming from molecular collisions. Therefore, shell-like free volume, which is the representative of molecular collisions, can explain the free volume theory underlying the WLF equation. In this sense, WLF parameters C_1^0 and C_2^0 can also be reinterpreted as representing parameters of molecular collisions of the shell-like free volume theory.

Limitation of the Parameter Usage. The calculated parameters of popular solvents and polymers are given in Tables 1 and 2, respectively. The parameter sets enable us to calculate self-diffusivity of solvent molecules in both binary and multicomponent polymeric systems.

It should be noted that there are still limitations on the usability of the parameters and the model. First, the present model considers molecular collisions as the origin of molecular diffusive phenomena and does not include other factors affecting diffusion. Therefore, as long as molecules interact with each other

Table 1. Newly Calculated Parameters for Popular Solvents via Semiempirical QC Calculation (PM3 Method) for Predictive Calculation with eqs 3 and 4

substance	ν_{solv}^* [$\text{\AA}^3/\text{molecule}$]	s_{solv}^* [$\text{\AA}^2/\text{monomer}$]	$M_{\text{w,solv}}$ [g/mol]	$F_{1,\text{solv}}/\gamma$ [$\text{cm}^3/\text{g K}$]	$F_{2,\text{solv}}$ [K]	$D_{0,\text{solv}} \times 10^4$ [cm^2/s]
acetic acid	55.13	79.68	60.05	0.49	−22.28	10.20
acetone	70.82	94.45	58.08	1.45	−53.33	3.60
benzene	91.70	113.05	78.11	1.19	−94.32	4.47
<i>n</i> -butylbenzene	172.88	193.28	134.21	1.87	−126.45	1.48
<i>sec</i> -butylbenzene	172.65	189.55	134.21	1.76	−130.64	1.74
carbon tetrachloride	80.49	105.67	153.82	0.57	−101.93	2.52
chloroform	69.21	93.33	119.38	0.49	−29.43	4.07
cumene	152.62	171.35	120.19	2.43	−127.93	1.00
cyclohexane	122.37	136.12	84.16	2.62	−157.81	2.01
cyclohexanol	127.83	142.56	100.16	0.64	−166.09	24.66
<i>cis</i> -decalin	188.10	187.58	138.24	0.96	−100.59	3.40
<i>trans</i> -decalin	188.70	189.73	138.24	0.85	−68.43	4.57
<i>n</i> -decane	219.07	240.63	142.28	1.05	−55.14	5.22
di- <i>n</i> -butylphthalate	298.72	216.58	278.34	0.73	−155.60	2.94
diisobutylphthalate	298.94	342.17	278.34	1.11	−194.06	1.12
dimethylphthalate	177.54	335.14	194.18	1.17	−197.71	1.02
<i>n</i> -dodecane	260.26	281.49	170.33	0.90	−57.96	6.13
ethylbenzene	132.60	152.61	106.16	1.80	−100.81	1.54
ethylene glycol	66.13	91.94	62.07	0.62	−139.38	8.82
formic acid	34.99	56.01	46.03	1.16	−117.94	5.10
<i>n</i> -heptadecane	359.10	382.62	240.46	0.69	−54.49	7.25
<i>n</i> -heptane	157.76	179.30	100.20	1.56	−55.42	3.43
<i>n</i> -hexadecane	340.60	362.02	226.43	0.71	−53.66	7.33
<i>n</i> -hexane	137.39	158.88	86.17	1.66	−41.08	3.50
2-hexanol	142.09	163.24	102.17	1.14	−154.36	11.64
<i>n</i> -hexylbenzene	213.81	234.15	162.26	2.39	−162.46	0.88
methanol	40.55	61.45	32.04	0.93	−48.41	8.75
methyl acetate	77.67	105.73	74.08	0.92	−38.50	5.23
methyl ethyl ketone	91.34	116.11	72.10	0.56	59.63	16.04
naphthalene	138.17	157.70	128.16	0.75	−78.28	4.30
<i>n</i> -nonane	198.33	220.17	128.25	1.15	−54.72	5.01
<i>n</i> -octane	178.45	199.79	114.22	1.30	−51.98	3.67
<i>n</i> -pentadecane	320.53	342.24	212.41	0.76	−56.83	6.87
<i>n</i> -pentane	116.89	138.49	72.15	2.03	−38.89	3.11
<i>n</i> -pentylbenzene	193.58	213.72	148.24	2.46	−160.38	1.02
<i>n</i> -propylbenzene	152.60	172.89	120.19	1.99	−124.11	1.40
1,2-propylene glycol	101.41	122.57	75.09	0.59	−144.24	31.06
styrene	121.45	142.93	104.14	0.94	−68.92	5.52
tetradecane	300.74	321.88	198.38	0.81	−58.99	6.46
tetrahydrofuran	89.04	110.74	72.11	0.62	10.45	14.40
tetralin	158.37	174.37	132.20	1.08	−115.08	2.68
toluene	112.29	133.99	92.14	1.76	−102.72	1.87
<i>n</i> -tridecane	280.61	301.93	184.35	0.84	−57.39	6.42
1,3,5-triisopropylbenzene	274.92	287.43	204.35	1.45	−161.00	1.28
<i>n</i> -undecane	239.69	261.02	156.30	0.99	−68.15	6.11
water	18.27	34.52	18.02	1.24	−152.29	8.55
<i>o</i> -xylene	132.21	151.11	106.16	0.92	−53.45	4.97
<i>p</i> -xylene	132.77	154.96	106.16	0.55	41.65	37.37

only by van der Waals interaction this model and its parameters can be used; however systems containing strong forces, such as hydrogen bonding and electrostatic interaction, are beyond the scope of the model and parameters.

Second, the parameters of polymers should be used above the glass transition temperature (T_g), because viscoelastic properties of the polymers, which are used to derive the WLF parameters, were obtained above T_g . For example, some often-used polymers

Table 2. Newly Calculated Parameters for Popular Polymers via Semiempirical QC Calculation (PM3 Method) for Predictive Calculation with eqs 3 and 4

substance	v_{unit}^* [$\text{\AA}^3/\text{unit}$]	s_{unit}^* [$\text{\AA}^2/\text{unit}$]	$M_{\text{w,unit}}$ [g/mol]	$F_{1,\text{polym}}/\gamma$ [$\text{cm}^3/\text{g K}$]	$F_{2,\text{polym}}$ [K]	$T_{g,\text{polym}}$ [K]
polystyrene	114.40	108.67	104.15	4.53	−327.0	373
poly(α -methylstyrene)	128.45	111.55	118.18	4.37	−395.7	445
poly(p -methylstyrene)	134.29	129.18	118.18	4.12	−330.0	378
poly(ethylstyrene)	150.81	145.95	132.20	3.23	−286.9	355
polyisobutylene	75.12	61.39	56.11	2.02	−100.6	203
cis-polybutadiene	70.13	71.75	54.08	4.99	−111.5	172
polypropylene	58.78	52.66	42.08	4.20	−205.4	253
polyisoprene	90.23	88.32	68.12	3.84	−146.4	200
polychloroprene	81.88	84.99	88.54	3.08	−163.3	228
polycarbonate	227.93	230.67	254.28	4.16	−362.7	418
poly(vinyl acetate)	81.62	86.96	86.09	3.40	−258.2	305
polydimethylsiloxane	81.49	75.14	74.15	6.82	−81.0	150
poly(methyl methacrylate)	96.24	94.99	100.12	2.24	−301.0	381
poly(ethyl methacrylate)	117.88	113.51	114.14	2.33	−269.5	335
poly(butyl methacrylate)	156.75	157.44	157.44	1.75	−203.4	300
poly(hexyl methacrylate)	193.74	194.78	194.78	1.31	−138.6	268
poly(octyl methacrylate)	229.39	232.53	232.53	1.77	−145.7	253
poly(lauryl methacrylate)	305.53	311.61	311.61	1.28	−69.7	208
poly(ethyl hexyl methacrylate)	230.36	219.90	219.90	1.25	−164.1	284
poly(methyl acrylate)	81.30	86.34	86.34	3.00	−231.0	276
poly(ethyl acrylate)	101.71	108.94	108.94	4.49	−209.9	250
poly(butyl acrylate)	140.51	149.33	149.33	3.98	−170.2	218
poly(hexyl acrylate)	179.27	188.63	188.63	3.91	−155.6	213
poly(lauryl acrylate)	294.26	308.35	308.35	8.00	−184.0	243
poly(isopropyl acrylate)	121.51	126.79	126.79	4.26	−208.4	264
poly(isobutyl acrylate)	139.84	142.99	142.99	4.09	−196.7	230
poly(cyclohexyl acrylate)	161.34	159.81	159.81	2.91	−218.0	292
poly(ethyl hexyl acrylate)	214.45	212.67	212.67	4.08	−155.3	218

such as polystyrene and poly(methyl methacrylate) have T_g around 100 °C, much higher than room temperature, and their parameters should be used for systems above 100 °C.

RESULTS AND DISCUSSION

In the Supporting Information, molecular volumes calculated by DFT and semiempirical QC calculations are compared, and it is shown that the PM3 method shows good agreement with the DFT calculations (Figure S1). Therefore, the PM3 method was used hereafter to calculate the molecular volume and the molecular surface area. Note that the PM3 method can be easily replaced by another semiempirical method if needed. It is also confirmed in Figure S2 that the molecular volume by QC calculation is the volume of the molecular core, which is different from the molecular volume at 0 K including molecular interstices calculated by the GC method.

To show the capability of the combination of the PM3-based new parameters in Tables 1 and 2 and the molecular collisions-based shell-like free-volume theory, predictive calculations were carried out for molecular self-diffusivity in several polymeric systems that have been experimentally studied in previous work via the pulsed field gradient spin-echo nuclear magnetic resonance (PFG-NMR) technique.^{52–54} At the same time, the prediction using the previous parameters based on the molecular volume calculated by GC method³⁷ was carried out in order to

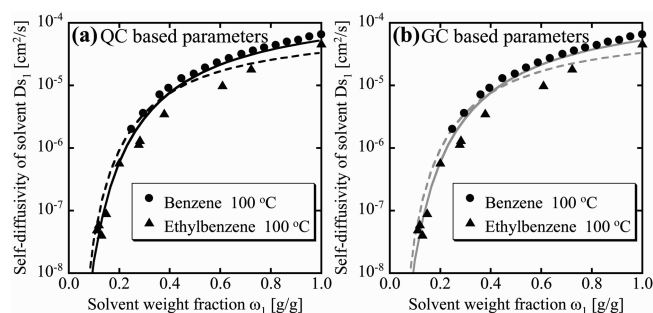


Figure 4. Comparison of experimental and predicted self-diffusivity of benzene/ethylbenzene in benzene/ethylbenzene (1) and polystyrene (2) binary systems. Symbols represent experimental values, and solid and broken lines represent theoretical values for benzene and ethylbenzene, respectively. The predictions were carried out using the molecular collisions-based diffusion model (a) with QC calculation-based parameters and (b) with GC method-based parameters.

compare the predictive ability of the parameters. The GC based parameters can be found elsewhere.^{35,36}

Figures 4–6 show the prediction for benzene/ethylbenzene in polystyrene systems, for hexadecane in polyisobutylene systems, and for triisopropylbenzene in polystyrene and toluene ternary systems, respectively. The examples cover molecules having various

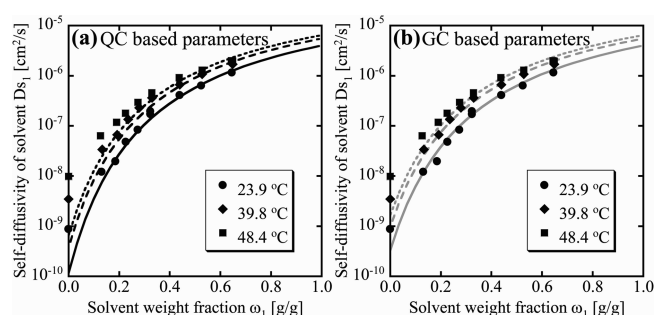


Figure 5. Comparison of experimental and predicted self-diffusivity of *n*-hexadecane in *n*-hexadecane (1) and polyisobutylene (2) binary systems. Symbols represent experimental values, and solid, broken, and dotted lines represent theoretical values for 23.9, 39.8, and 48.4 °C, respectively. The predictions were carried out using the molecular collisions-based diffusion model (a) with QC calculation-based parameters and (b) with GC method-based parameters.

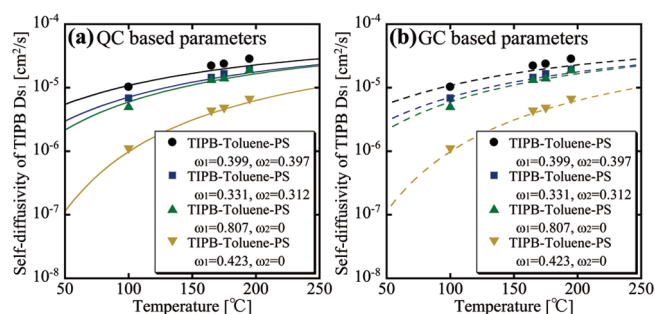


Figure 6. Comparison of experimental and predicted self-diffusivity of triisopropylbenzene (TIPB) in TIPB (1), toluene (2), and polystyrene (3) ternary systems. Symbols represent experimental values, and solid lines represent theoretical values of the molecular collisions-based diffusion model (a) with QC calculation-based parameters and (b) with GC method-based parameters.

shapes from oblate (benzene, ethylbenzene, and triisopropylbenzene) to chainlike (*n*-hexadecane), in a wide temperature and composition range, in binary and multicomponent polymeric systems. In all systems, the QC calculation-based new parameters offer good prediction results.

In Figures 4–6, the prediction results using QC calculation-based parameters shown in each left figure were also compared with those using GC method-based parameters shown in each right figure. Although the predictive ability using QC based parameters for *n*-hexadecane in polyisobutylene near $\omega_{\text{solv}} = 0$ seems slightly worse than that using GC-based parameters, generally the predictive ability with QC-based parameters is very comparable to that with GC-based parameters.

This fact can be explained as below. The molecular volume calculated by the QC method, v_{QC}^* , is proportional to that calculated by the GC method, v_{GC}^* as shown in Figure S2 in Supporting Information

$$v_{\text{QC}}^* = av_{\text{GC}}^* \quad (14)$$

where a is a proportionality factor of around 0.8 originating from above-mentioned molecular interstices. On the other hand, the free-volume parameters $F_{1,i}/\gamma$ of both the polymers and the solvents are proportional to the molecular volume, while $F_{2,i}$ is constant, as derived above. This means that the free volume

is also proportional to the molecular volume and can be described as

$$V_{f,\text{QC}} = aV_{f,\text{GC}} \quad (15)$$

where $V_{f,\text{QC}}$ and $V_{f,\text{GC}}$ represent QC-based and GC-based free volumes. Considering eq 3 of the shell-like free-volume theory, the proportionality factor a in eqs 14 and 15 can be almost canceled so that the predicted results are almost the same. In other words, the predictive ability of the model proved in the previous studies has not lost by using QC based parameters as a is almost unchanged for most of polymers and solvents (Figure S2 of Supporting Information), which is also confirmed in Figures 4–6.

The practical advantage of the QC-based parameters is that the collisions-based model acquires the applicability of the QC calculation, without losing its predictive ability, and could be utilized for more versatile molecules, including steric molecules such as adamantane, cyclodextrin, fullerene, and their derivatives and complexes, which would be of importance in the future material science. In contrast, molecular volume of such steric molecule cannot be calculated by GC method.

Nevertheless, it should be noted that the main point of the present study is that the incorporation of a QC calculation into the molecular collisions-based diffusion model is physically important, because the collisions occur on the surface of the molecule, and the molecular volume, which indeed moves, is not the GC-based molecular volume at 0 K including molecular interstices but the molecular core itself. In both physical and application views, the adoption of the same QC calculation for both the molecular volume and the molecular surface area seems to be quite natural.

CONCLUSIONS

For the molecular collisions-based diffusion model, shell-like free-volume theory requires four pure component parameters, namely, molecular volume, molecular surface area, free volume, and pre-exponential factor, for predictive calculation of molecular diffusivity in polymeric systems. In the present study, a semiempirical QC calculation, the PM3 method, was adopted to calculate the volume and the surface area of the penetrant molecular core, to fulfill the physical description of the model, that the molecular core moves as a result of molecular collisions with neighboring molecules on its surface. Accordingly, the free-volume parameters and the pre-exponential factor were determined using the molecular-core volume. Parameters required for predictive calculations were calculated and tabulated. The combination of the newly proposed parameters and the model successfully predicts diffusivity for various shapes of molecules in a wide temperature and composition range, in binary and multicomponent systems.

ASSOCIATED CONTENT

S Supporting Information. Comparison of two methods for calculating molecular volume and molecular surface area for polymer segmental unit. Derivation of relationship between collision parameters and WLF parameters. Comparison of molecular surface areas calculated using density functional theory and semiempirical quantum chemical calculation. Comparison of molecular volume calculated using QC calculations and GC methods.

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