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Linking the Viscous and Vacancy Behavior of Mixtures of High-Molecular-Weight Hydrocarbons

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A zero-shear viscosity model has now been extended to mixtures of three-branch alkanes with and without cyclopentyl or cyclohexyl attachments. The model links the equilibrium theory of Simha–Somcynsky (SS) statistical thermodynamics of liquids and the Eyring significant structure (ESS) transport theory. The predicted quantity of the hole fraction as a measure of the free volume, computed from the SS equation of state, plays a primary role in the approach to combine both theories. Experimental $PVT\eta$ data from 310 to 408 K and 0.1 to 344.5 MPa have been used. The proportionality constant of the activation energy and the transmission coefficient have been calculated for each species separately, and they are in the expected trend with the fraction of mixtures. Satisfactory agreement in the prediction of viscosity from the hole fraction has been obtained. The volumetric and viscous data of physical mixtures are predicted from and compared with their chemical correspondence.

KEY WORDS: equation of state of mixtures; Eyring significant structure theory; free volume; hole fraction; hyrdrocarbons; Simha–Somcynsky's hole theory; zero-shear viscosity.

1. INTRODUCTION

Free volume approaches to describe rheological properties of polymers and their mixtures are very promising [1–4]. A study of the liquid viscosity, η, as a function of temperature and the pressure-dependent hole fraction, h, has been conducted and applied extensively [5–12]. The hole fraction as

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a measure of the free volume is applied from the Simha–Somcynsky (SS) theory and is a measure of highly mobile vacancies. For this purpose, a correlation between viscosity and hole fraction was developed [5–8, 12] for linear chain molecules, some polymers, and their mixtures. Moreover, it was extended to three-equal-branch chain molecules, and analysis showed that in contrast with linear molecular fluids, the shear viscosity is not a single function of h [9]. Furthermore, a temperature-dependent linearization parameter was introduced in the correlation, but it did not improve the single functionality behavior of h.

To explain the viscous behavior of a chain molecular system in terms of quantities in the SS theory, we make use of the extension of the Eyring significant structure theory (ESS) [13–16] to nonequilibrium phenomena, in particular, to transport properties such as viscosity and diffusion. In an explanation of flow, they assumed that one of the vibrational degrees of freedom is turned into a translational degree of freedom, and furthermore, under the influence of stress, molecular segments successively jump into lattice vacancies as measured by free volume elements of equilibrium thermodynamics.

Our proposed zero-shear viscosity model in terms of hole fraction combines the ESS transport theory [13–16] with the SS statistical thermodynamic theory of liquids [17, 18]. Employing the concept of the hole fraction as an equilibrium property of the SS theory, the transport properties of long chain molecular fluids can be interpreted. Using the proposed model, a successful correlation between the experimental viscosity and hole fraction was obtained. In this paper, the application of the model for three-branch hydrocarbons is now extended to their mixtures.

2. THEORY

2.1. SS-EOS Theory of Mixtures

The equation of state (EOS) based on the SS lattice-hole model [17] has been extended to mixtures by Jain and Simha [19] and recently to both physical and chemical mixtures by Yahsi et al. [20]. At this juncture, we summarize the EOS of mixtures as follows: the temperature and pressure-dependent occupied site fraction, $y(P, T) = 1 - h$, for M multi-component chain molecular mixtures is assumed to be

$$y = \frac{\sum\limits_{i=1}^{M} s_i N_i}{\sum\limits_{i=1}^{M} s_i N_i + N_h} \tag{1}$$

where s_i is the number of segments in the ith molecule, N_i is the number of the ith constituent molecules, and N_h is the number of holes. The hole fraction $h = h(T, P) = 1 - y(T, P)$ is a measure of the free volume [21], as anticipated by the model lattice. The hole fraction has been determined by expressing a variety of equilibrium and nonequilibrium processes such as viscosity and viscoelasticity.

The EOS for mixtures [19, 20] is expressed in terms of the average scaled volume, temperature, and pressure, viz.,

$$\widetilde{V} = V/\langle V^* \rangle\,;\ \widetilde{T} = T/\langle T^* \rangle\,;\ \ \widetilde{P} = P/\langle P^* \rangle \tag{2}$$

where the scaling parameters are as follows: $\langle V^* \rangle$ is defined by $N_A \langle \upsilon^* \rangle / \langle m_0 \rangle$ of molecules where the characteristic mean molar volume of segments, $\langle \upsilon^* \rangle$, is given by the mean segmental location, $\langle r^* \rangle$, of the potential minimum and $\langle m_0 \rangle$ is the mean molar mass of the segments of the mixture. $\langle T^* \rangle$ is taken as $\langle qz \rangle \langle \varepsilon^* \rangle \big/ \langle c \rangle k$ as a balance between mean attraction and thermal energy contributed by the mean external degrees of freedom, and $\langle P^* \rangle$ is defined by the ratio between mean chain attraction energy $\langle qz \rangle \langle \varepsilon^* \rangle$ and mean volume $\langle s \rangle \langle \upsilon^* \rangle$. The following mean quantities of chain molecular mixtures can be immediately defined: the mean degrees of freedom and mean segments, respectively,

$$\langle c \rangle = \sum_i x_i c_i \quad \text{and} \quad \langle s \rangle = \sum_i x_i s_i, \tag{3}$$

the mean number of interchain nearest neighbor pairs,

$$\langle q_z \rangle = \langle s \rangle\,(z-2) + 2$$

with a coordination number z (12 for a close-packed lattice) and the mean molar segmental mass:

$$\langle m_0 \rangle = \sum_i s_i x_i m_{0i} / \langle s \rangle \tag{4}$$

in terms of constituent chain molecular quantities. From these definitions, we can derive the following relation among the parameters:

$$\langle P^* \rangle \langle V^* \rangle / \langle T^* \rangle = \big(\langle c \rangle / \langle s \rangle\big) R / \langle m_0 \rangle. \tag{5}$$

In the theory, the free volume,

$$\upsilon_\mathrm{f} = \langle \upsilon^* \rangle \Big[y\big((y\widetilde{V})^{1/3} - 2^{-1/6}\big) + (1-y)(y\widetilde{V})^{1/3} \Big]^3 \tag{6}$$

was presumed to be a weighted combination of segment and hole contributions averaged linearly over single mode of motion.

Under these definitions, the SS-EOS provides the following equation, derived from the configurational Helmholtz energy:

$$\widetilde{P}\widetilde{V}/\widetilde{T} = [1-Q]^{-1} + (2y/\widetilde{T})(y\widetilde{V})^{-2}[1.011(y\widetilde{V})^{-2} - 1.2045] \tag{7}$$

where $Q = 2^{-1/6}y(y\widetilde{V})^{-1/3}$. The occupied site fraction, y, can be obtained by minimization of the Helmholtz energy of ensemble mixtures:

$$(\langle s\rangle/3\langle c\rangle)\left[(n-1)/n + y^{-1}ln(1-y)\right] = (Q-1/3)/(1-Q) + (y/6\widetilde{T})(y\widetilde{V})^{-2}\left[2.409 - 3.033(y\widetilde{V})^{-2}\right]. \tag{8}$$

The scaling parameters, $\langle P^*\rangle$, $\langle V^*\rangle$, $\langle T^*\rangle$, and the structural parameter, $3\langle c\rangle/\langle s\rangle$, can be obtained by superimposing experimental P-V-T data on the theoretical $\widetilde{P}$-$\widetilde{V}$-$\widetilde{T}$ surface. Details are in Section 3.1.

2.2. Transport Theory of ESS in Terms of SS

Using the Eyring designation, the viscosity of liquid mixtures can be split up as a sum of occupied (segment) and unoccupied (hole) contributions weighted by the fraction of occupied segments, 1-h, and unoccupied sites, h, defined in the SS theory:

$$\eta = \frac{f}{\dot{s}} = (1-h)\frac{f_s}{\dot{s}} + h\frac{f_g}{\dot{s}} = (1-h)\eta_s + h\eta_g \tag{9}$$

where f is the shear stress, $\dot{s}$ is the rate of strain, and the subscripts, s and g, refer to solid and gas, respectively. The viscosity of unoccupied sites can be neglected and the details are given in previous papers [10, 11].

For Newtonian flow, the segmental viscosity is given as follows [10, 11]:

$$\eta_s = \frac{N_A kT}{\sqrt{2}\upsilon k'}\frac{6\langle s\rangle}{\langle q_z\rangle h} \tag{10}$$

where the jumping rate of a segment, k', to a hole with a given activation energy for jumping, E_a, by Eyring, can be expressed as

$$k' = \kappa\frac{kT}{h_p}\frac{Z^*}{Z}\exp\frac{-E_a}{kT} \tag{11}$$

where h_p is Planck's constant and κ is the transmission coefficient. Z and Z^* are the total partition functions of the mean segment of mixture in the initial and activated states, respectively. Equation (11) has been constructed by noting that the partition function for one mode with a vibrational frequency, ν, of harmonic vibrations in the normal state turned into translational degrees of freedom in the activated coordinate. We have an assumption that the normal state has one more translational degree of freedom than the activated state.

Segmental molecules preferentially occupy the most favored states organized about neighboring segments and vacancies. The energy difference between occupied and unoccupied states would be proportional to the sublimation energy and inversely proportional to the number of neighboring holes or the hole fraction with an additive parameter a_2, interpreted as an additional hole fraction necessary for flow. The activation energy, E_a, in Eq. (11) is then given by

$$E_\mathrm{a} = -\frac{1}{2}\frac{1-h}{h+a_2}a' \langle q_z\rangle \langle \Phi\rangle \tag{12}$$

where a' is the proportionality constant and $\langle \Phi\rangle$ is the mean interaction potential energy between a pair of segments. We subsequently obtain the viscosity equation of mixtures as

$$\ln\left(\frac{h}{1-h}\frac{1-e^{-h_\mathrm{p}\nu/kT}}{e^{-h_\mathrm{p}\nu/2kT}}\frac{\upsilon}{\upsilon_f^{1/3}}\frac{\eta}{T^{1/2}}\right) = a_0 + a_1\frac{1-h}{h+a_2}\frac{1}{T} \tag{13}$$

where

$$a_0 = \ln\left(\frac{6\langle s\rangle\sqrt{\pi\langle m_0\rangle k}N_\mathrm{A}^{2/3}}{\langle q_z\rangle \kappa}\right) \tag{14}$$

and

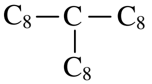
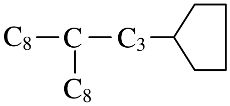
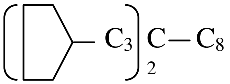
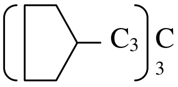
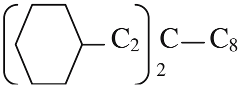
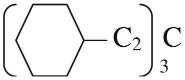
$$a_1 = -a'\frac{\langle q_z\rangle\langle\Phi\rangle}{2k}. \tag{15}$$

3. CALCULATIONS

3.1. Calculations of the Scaling Parameters of the SS-EOS

Experimental PVT data of species listed in Table I are taken from Cutler et al. [22], Sciessler et al. [23], and Spencer [24]. We will refer to the species with the abbreviated names defined in Table I. The experimental data range from 311 to 408 K and from ambient to 344.5 MPa with the number of data points 42, 44, and 31 for $\mathrm{OHD_2 + DCPH_1}$, $\mathrm{OHD_1 +DCPH_2}$, and $\mathrm{OHD_1 + DEHP_2}$, respectively. The indices in the mixture

Table I. Characteristics of Hydrocarbons

Abbreviation (PSU[a] #)	Chemical Names	Structures	M (g)
OHD (25)	9-*n*-Octylheptadecane	 $C_8-\underset{C_8}{\underset{\mid}{C}}-C_8$	352.7
CPHD (110)	9(3-Cyclopentylpropyl) heptadecane		350.7
CCPD (111)	1-Cyclopentyl-4 (3-cyclopentylpropyl) dodecane		348.6
DCPH (113)	1,7-Dicyclopentyl-4 (3-cyclopentylpropyl) heptane		346.6
CHEH (19)	1-Cyclohexyl-3 (2-cyclohexylethyl) hendecane		348.6
DEHP (90)	1,5-Dicyclohexyl-3 (2-ethylhexyl) pentane		346.6

[a] PSU # is the component number given by the API project at Pennsylvania State University.

fluids represent their molar fraction. Although the data are reported up to 1033.6 MPa, we employed them only up to 344.5 MPa to be consistent with the range of the viscosity data.

Three independent parameters, P^*, V^*, T^* with the structural parameter $3c/s$ of the SS theory have to be determined from superimposing the experimental data on the theory. There are a number of ways one may obtain these parameters, but we pursue our novel method [11] that is statistically consistent with simultaneous evaluation of the complete body of the data. In the method, the chain length, s, is set as the number of backbone carbon atoms for the linear part of the molecule plus the corresponding chain length of the ring(s) using the principle of corresponding states with a linear counterpart as explained elsewhere [18, 20]. We later assume the degrees of freedom c, as an adjustable parameter and then substitute each experimental point into the SS-EOS in Eqs. (7) and (8). Eliminating P^* by Eq. (5), we end up with an equation in terms of V^* and T^*. Expanding each equation up to the first power in these parameters, we obtain N equations from N PVT data points and solve for the two unknowns, V^* and T^*, using a pseudoinverse matrix technique. The best V^* and T^* and c parameters are obtained by adjusting c, and they are listed in Table II. Using this technique, we observed that the average error is slightly reduced from the previous approximation technique described in Refs. 9, 10, and 18, and the deviations from the experimental data spread out smoothly on the data. That is an improvement over the evaluation technique, which simultaneously fits all data. The average percentage error in volume calculated from the SS is less than 0.11% and the maximum observed error is 0.27% for the mixtures.

We deal with physical mixtures here, but these physical mixtures in terms of average molar mass and average molecular structure have their chemical equivalents (so called chemical mixtures) [20, 25]. For instance, $OHD_2 + DCPH_1$ with two moles of OHD and one mole of DCPH corresponds to three moles of CPHD. Therefore, we would like to predict the data of $OHD_2 + DCPH_1$ using the parameters of CPHD. In Tables II and III, all the parameters in parentheses are given for the chemical mixtures corresponding to the physical mixtures. Using the CPHD, CCPD, and CHEH parameters [11], the volumes of the respective $OHD_2 + DCPH_1$, $OHD_1 + DCPH_2$, and $OHD_1 + DEHP_2$ physical mixtures are predicted and given in Table II. Percentage errors in volume are 0.15, 0.19, and 0.20% and the maximum errors are 0.51, 0.51, and 0.63%, respectively. Percentage errors almost double, but they are still in the acceptable range. We are also using these parameters to predict the viscosity data of the physical mixtures below.

3.2. Calculation of Viscosity

Equation (13) can be put into a linear functional form:

$$F_{\mathrm{h}} = a_0 + a_1 Y_{\mathrm{h}}. \tag{16}$$

In reality, the parameter a_2 in Y_{h}, interpreted as an additional hole fraction necessary for flow, is needed for the linearization of Eq. (16). In the calculation of Eq. (16), the hole fraction (h), molar volume (υ), and molar free volume (υ_f) are computed from the P-V-T data using the SS-EOS. The C–C stretching frequency, ν, is taken as approximately $3 \times 10^{13}\ \mathrm{s}^{-1}$ [13].

Table II. Computed Characteristic Parameters of SS-EOS for Pures and Mixtures

Fluids	s	c	$10^3 m_0$ (kg)	$10^3 V^*$ ($m^3 \cdot kg^{-1}$)	$10^6 \upsilon^*$ ($m^3 \cdot mol^{-1}$)	T^*(K)	P^*(MPa)	ε^* (K)	$\%\Delta V^a$	$\%\mathrm{Max}^b$
OHD	25	2.97	14.107	1.2068	17.023	13013	755.01	153.37	0.10	0.35
DCPH	23.2	2.70	14.940	1.1075	16.546	14196	830.19	163.81	0.09	0.29
$OHD_2 + DCPH_1$	24.4	2.85	14.371	1.1738	16.869	13449	774.26	155.82	0.084	0.27
(CPHD)		(3.37)		(1.1609)	(16.684)	(12030)	(827.97)	(164.80)	(0.15)	(0.51)
$OHD_1 + DCPH_2$	23.8	3.08	14.649	1.1313	16.572	12811	831.76	164.41	0.11	0.27
(CCPD)		(3.14)		(1.1333)	(16.601)	(12791)	(845.15)	(167.35)	(0.19)	(0.50)
$OHD_1 + DEHP_2$	23.6	2.08	14.773	1.1557	17.073	17266	741.08	150.90	0.061	0.27
(CHEH)		(3.01)		(1.1287)	(16.674)	(13255)	(842.98)	(167.64)	(0.20)	(0.63)

[a] Volumetric percentage error: $\%\Delta V = (100/N) \sum_i \left| V_i^e - V_i^c \right| / V_i^e$ where V_i^e is the experimental volume and V_i^c is the volume calculated from SS theory.

[b] %Max is the maximum volumetric percentage error. Indices in the mixture fluids represent the molar fraction.

The viscosity data [22–25] range from 311 to 408 K and from ambient to 344.5 MPa with the number of data points 42, 44, and 31 for $\mathrm{OHD_2 + DCPH_1}$, $\mathrm{OHD_1 + DCPH_2}$, and $\mathrm{OHD_1 + DEHP_2}$, respectively.

From Eq. (16), the best fitting parameters, $a_i\{i = 0, 1, 2\}$, are calculated for each species listed in Table I and tabulated in Table III together with the correlation coefficient (CC), average deviation from linearity in Eq. (16) ($\%\ \Delta F_\mathrm{h}$), and average percentage error in viscosity ($\%\ \Delta\eta$). The measure of average percentage error in viscosity and the average percentage deviation from linearity in Eq. (16) are defined as $\Delta f = (100/N)\sum_i \left|f_i^\mathrm{exp} - f_i^\mathrm{calc}\right|/f_i^\mathrm{exp}$, where f can be set as η and F, and $F_{\mathrm{h}_i}^\mathrm{exp}$ and $F_{\mathrm{h}_i}^\mathrm{calc}$ are calculated from Eqs. (13) and (16), respectively, using the fitting parameters. The reported errors for the experimental viscosity data are up to 5% [23–25].

F_h is plotted versus Y_h for OHD and DCPH, and $\mathrm{OHD_2 + DCPH_1}$, $\mathrm{OHD_1 + DCPH_2}$, and $\mathrm{OHD_1 + DEHP_2}$ mixtures in Fig. 1, and the lines represent the best fit (linear regression) to the data of each species using Eq. (16). A good linearization for each species is obtained within the full range of the independent variables: $T = 310$–408 K and $P = 0.1$–344.5 MPa. In Fig. 1, each temperature is designated by a different symbol and the temperature decreases from lower to higher on each line at fixed pressure. On the other hand, at fixed temperature, the pressure increases from lower to higher along the line. At the lower part, the lines from all the species are about to come together, while separating from each other on raising the pressure and reducing the temperature. We can interpret this as, heading to the lowest part of the plot, we will have the increasing free volume and free volume fraction causing the migration of the molecule very readily into the holes. At about the lowest point, the transportation of molecules does not distinguish much with respective molar mixtures of OHD with DCPH and somewhat with DEHP in Fig. 1. But if the temperature is reduced and the pressure is increased, the free volume quantity and the hole volume fraction will be reduced and give rise to a decrease in transporting the molecules, especially the ones with an increasing cyclopentyl component fraction of the mixtures or cyclohexyl substitution instead of cyclopentyl on each arm of the three-branch alkanes. As a result, the higher the fraction of the cyclopentyl attached component, the less the transport, since increasing the cyclopentyl component requires a larger free volume fraction.

The slope of each line in Fig. 1 gives a_1 in Eq. (13) as a measure of the activation energy. In the calculation of the activation coefficients, a', the mean potential has to be calculated for each point. We observed that the value of Φ is a very slightly changing function and the maximum

Table III. Values of Fitting a_0, a_1, a_2 and Related Parameters for Pures and Mixtures

Fluids	$-a_0$	a_1	a_2	$-\Phi$ (K)	$a\prime$	κ	$\%\Delta\eta$	$\%\Delta F_h$	CC^a
OHD	17.489	254.56	0.075	219.7±0.6	0.230	0.168	1.41	0.11	0.99989
DCPH	16.872	185.76	0.032	234.8±0.5	0.157	0.0935	4.99	0.41	0.99918
$OHD_2 + DCPH_1$	17.270	223.47	0.059	223.3±0.7	0.200	0.137	1.12	0.086	0.99995
(CPHD)	(17.070)	(213.08)	(0.050)		(0.179)	(0.112)	(3.18)		
$OHD_1 + DCPH_2$	17.028	210.49	0.044	235.6±0.6	0.177	0.108	3.89	0.31	0.99941
(CCPD)	(17.012)	(201.70)	(0.041)		(0.167)	(0.107)	(4.75)		
$OHD_1 + DEHP_2$	17.143	184.50	0.031	216.2±1.0	0.169	0.122	3.32	0.27	0.99958
(CHEH)	(16.858)	(188.79)	(0.021)		(0.156)	(0.092)	(8.93)		

[a] CC denotes correlation coefficient for linear regression.

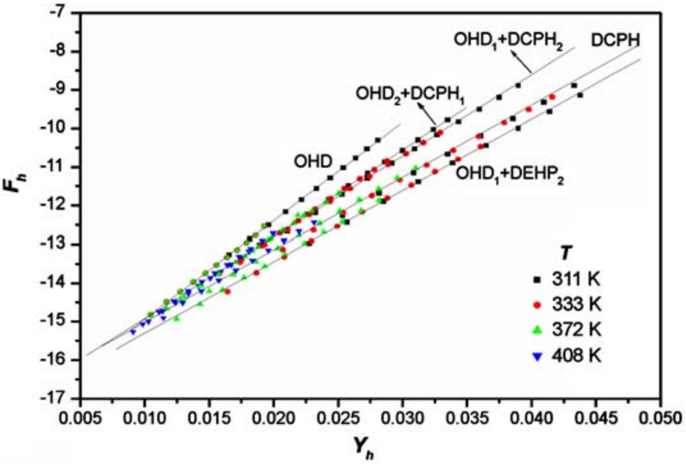


Fig. 1. F_h versus Y_h (see Eq. (16)) for OHD, DCPH, OHD_2+ $DCPH_1$, OHD_1+ $DCPH_2$, and OHD_1+ $DEHP_2$. Solid line is the best fit curve for the data of each species.

from average is about 0.46% for a given temperature and pressure. Thus, to calculate the activation coefficients, a', from Eq. (15), we take the average values of Φ without losing any significance given in Table II. Both a measure and the coefficient of the activation energy are decreasing with an increase in the fraction of the cyclopentyl component of the mixture or cyclohexyl substitution instead of cyclopentyl on each arm of the three-branch alkanes. This can be understood by comparison between linear and cyclopentyl substituted arms of the three-branch chain. Instead of a linear chain in the arms, substitutions of the cyclopentyl rings to each arm cause the structure of the three-branch alkane to be more compact and mobile, so it will have a smaller activation energy coefficient. The more cyclopentyl in the mixture, the less the factorial contribution to the activation energy and the less viscous behavior it will show at a *constant hole fraction* with a given temperature (at fixed Y_h value).

The intercept constant, a_0, is best fitted by Eq. (13), and the transmission coefficient, κ, in Eq. (14) is also calculated and given in Table III. Both quantities increase with increasing chain length, as expected.

A prediction of the viscosity of physical mixtures using the parameters of chemical correspondence is carried out and given in parentheses in Table III. Using the CPHD, CCPD, and CHEH parameters, the viscosity of the respective $OHD_2 + DCPH_1$, $OHD_1 + DCPH_2$, and $OHD_1 + DEHP_2$ physical mixtures are predicted. Percentage errors in viscosity are 3.18, 4.75, and 8.93%, respectively. The predicted data seem to have higher errors, but these parameters have been already fitted to these species with the percentage errors 2.00, 4.09, and 8.00%, respectively [11] (see Yahsi and Sahin [11]). Eventually, the chemical correspondence of a physical mixture has an advantage to predict mixture data, if the raw data are not available.

4. CONCLUSION

The transportation of chain molecules has been extended to mixtures of three-branch hydrocarbons with and without ring attachments to each arm. The model is constructed with the framework of the ESS theory, with the quantities derived from equilibrium theories such as the SS-EOS. The free volume, or more importantly hole fraction concept as a measure of free volume, plays a primary role in the calculation and interpretation of the viscosity. The linearization of the experimental viscosity data with a reasonable error has been attained with the hole fraction computed from SS-EOS and an additional hole fraction parameter in the activation energy. The model has also been tested with the chemical correspondence of physical mixtures. The results are promising and must be extended to other macromolecular structures.

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NOMENCLATURE

a':	proportionality constant of activation energy
a_0:	intercept of Eq. (13)
a_1:	slope of Eq. (13)
a_2:	additive parameter for hole fraction in Eq. (12)
$3c_i$:	total degrees of freedom of ith molecule
$3\langle c \rangle$:	total mean degrees of freedom
E_a:	activation energy
$\langle \varepsilon^* \rangle$:	mean attraction energy of segments
Z, Z^*:	total partition function of a segment in the equilibrium and activated states, respectively
F_h:	left-hand site of Eq. (13)
Y_h:	$(1-h)/((h+a_2)T)$ quantity in Eq. (13)
ΔF_h:	average deviation from linearity
$\Delta\eta$:	average percentage error in viscosity

h_{p}:	Planck's constant
h:	hole fraction
k':	jumping rate of a segment
k:	Boltzmann's constant
m_{0i}:	segmental molar mass of ith molecule
$\langle m_0 \rangle$:	mean molar segmental mass of a mixture
N_{h}:	number of holes
N_{A}:	Avogadro's number
N_i:	number of ith molecule
P, V, T:	pressure, volume, temperature
$\widetilde{P}, \widetilde{V}, \widetilde{T}$:	reduced pressure, volume, temperature
$\langle P^* \rangle, \langle V^* \rangle, \langle T^* \rangle$:	mean scaling parameters of pressure, volume, and temperature
$\langle q_z \rangle$:	mean number of interchain nearest neighbor pairs in a lattice
$\langle r^* \rangle$:	mean segmental location of the potential minimum
R:	gas constant
s_i:	number of segments of ith molecule (chain length)
$\langle s \rangle$:	mean number of segments of a mixture
$\dot{s}$:	rate of strain
υ:	molar segmental volume
υ_f:	free molar volume
$\langle \upsilon^* \rangle$:	characteristic mean molar volume of segments
x_i:	molar fraction of ith molecule
y:	occupied site fraction
z:	coordination number
η:	viscosity
η_{g}:	viscosity of holes
η_{s}:	viscosity of segments
κ:	transmission coefficient
ν:	vibrational frequency
$\langle \Phi \rangle$:	mean interaction potential energy between a pair of segments

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