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Open-Cell Model Equation of State for Liquids. 1. *P–V–T* Behavior for Liquids and Liquid Polymers

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ABSTRACT: An open-cell model equation of state has been proposed, which relaxes the restrictions of the cell theory and allows more flexibilities in describing the structure of liquids. To test its capability, this equation has been applied to a variety of liquids, including 17 heavy molecular weight hydrocarbons, 10 organic solvents, and 15 polymers, in particular. The calculated density grand average AADρ for the equation proposed here are 0.062, 0.057, and 0.054 per cent against the results for the equation of state by Simha and Somcynsky, 0.081, 0.093, and 0.072 percent for the above three groups of liquids, respectively. Good agreement between our calculated results and experimental data indicates that our model is an improvement over the Simha and Somcynsky equation of state, which has been evaluated as one of the best equations. Moreover, this equation can be easily extended to describe the properties of polymer solutions and polymer blends, which will be addressed in our subsequent paper.

1. Introduction

Equations of state (EOSs) are widely used to describe the thermodynamic properties for liquids. To establish an EOS, a feasible approach is to figure out a model to represent the physical structure of liquids. As a result, on the basis of the cell theory, many EOSs have been proposed. Among them, some specifically apply to liquid polymers and long chain molecules that are of great interest in processing polymer materials.

As is well-known, in the cell theory all the molecules are confined in their cells with restricted moves. Actually, this structural picture shows a preference for solids. As a result, when this theory is applied to the properties for liquids, not enough entropy is generated and the fluidity of liquids cannot be described correctly. To modify it, some hole theory EOSs[1–4] have been developed. However, the confinement of the cells and holes still hinders the application of this theory. To overcome this drawback, we here propose an open-cell concept, in which a molecule possessing enough energy can move out of the cell. Then, a new free volume expression and an open-cell model equation of state (OCM EOS) are derived. Finally, this EOS is applied to a variety of liquids, including organic solvents, heavy molecular weight hydrocarbons, and polymers to test its capability for estimation of their *P–V–T* relations. The test will provide sound grounds for the extension of the OCM EOS to liquid mixtures, which will be addressed in another paper.

2. Open-Cell Model and Its Free Volume Expression

A cell theory was proposed by Lennard-Jones and Devershire[5] and substantially developed by Prigogine et al.[6] In this theory, the properties of liquids are related to molecular interactions in terms of some assumptions. For a liquid at high densities, each molecule moves within its cell in the potential field of its nearest neighbors. By assuming the interaction between molecules is described by the square well potential, the free volume is expressed as

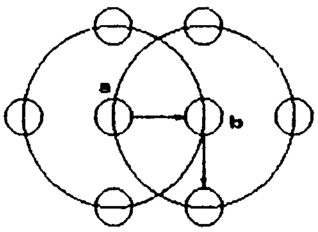

Figure 1. Open-cell model: (a) central molecule; (b) pushed away molecule.

$$V_{\rm f} = (V^{1/3} - \lambda^{-1/3}V^{*1/3})^3 \qquad (1)$$

where v is the cell volume, λ is the geometric factor, and v^* is the hard core volume.

For the fact that each cell has exactly one molecule in it at all densities, the cell theory is unsatisfactory for a rather wide density range. However, this cell theory provides a basic prototype for other refinements.

One of the developments is the introduction of the "hole" concept to relax the restriction of exactly one molecule per cell. Simha and Somcynsky[1] proposed a hole theory EOS, which has been successfully used to describe the *P–V–T* behavior for liquid polymers, in particular. Similar to Henderson's model,[7] the free volume $V_{\rm f}$ in the SS EOS is represented by a linear superposition of gas- and solidlike free lengths, weighted by the hole and occupied-site fractions:

$$V_{\rm f} = [y(w^{1/3} - \lambda^{-1/3}v^{*1/3}) + (1-y)w^{1/3}]^3 \qquad (2)$$

where w is the cell volume

$$w = \frac{V}{N_0 + Ns} \qquad (3)$$

where V is the volume and N, N_0, and s are the number of molecules and holes in the system and the number of segments per molecule in the system, respectively. y represents the occupied-site fraction, λ is the geometric factor that is set to $2^{1/2}$ for the face-centered cubic lattice, and v^* is the molar characteristic volume of a segment.

In this work, an open-cell concept is introduced, where the molecules having enough energy can move to another cell. As an illustration, Figure 1 shows that having high energy, molecule a can push molecule b away from its original position to replace it and move into another cell.

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As a result, the cells here are "open" for high energy molecules to migrate. On the basis of this physical picture and the significant structure theory of Eyring,[8] a new free volume expression is derived as follows.

As shown in Figure 1, the probability of occupying a neighbor position for the central molecule a is represented by $e^{-\epsilon/kT}$. Accordingly, if there are n_h possible positions about molecule a, the positions molecule a can occupy are expressed as $(1 + n_h e^{-\epsilon/kT})$.[8] We here propose the free volume for an open-cell, V_f, in terms of the free volume expression, V_f', of Simha and Somcynsky[1] by the introduction of a new parameter β:

$$V_f = V_f'(1 + \beta n_h e^{-\epsilon/kT}) \tag{4}$$

Equation 4 indicates that though $(1 + n_h e^{-\epsilon/kT})$ positions are available for the central molecule a (see Figure 1), the free volume for an open cell does not simply increase by this factor with respect to the free volume for the SS EOS. Therefore, parameter β accounts for the influence of the spatial structures of cells and the shapes of molecules on the free volume. Obviously, this parameter is substance dependent and varies with temperature and pressure, and thus can be regressed by fitting experimental data. However, it is noticeable that from our experience β can be taken as a constant in the calculation of the properties for most polymers, organic solvents, and n-paraffins, which is discussed in a later section.

From Eyring's work,[8] n_h and ϵ in eq 4 are given by

$$n_h = \eta \frac{V - V_s}{V_s} \tag{5}$$

$$\epsilon = \frac{\alpha E_s V_s}{V - V_s} \tag{6}$$

where V and V_s are the liquid molar volume and solid molar volume, respectively, E_s is the sublimation energy, and η and α are two factors that can be estimated in terms of the properties near the melting point of the substance of interest. For the liquid near the melting point still possessing lattice structure,

$$z\frac{V - V_s}{V} = z\frac{V_s}{V}\frac{V - V_s}{V_s} = \eta\frac{V - V_s}{V_s} \tag{7}$$

where z is the coordination number, set to 12. If argon is investigated, near its melting point[8]

$$V = 1.12V_s \tag{8}$$

and we obtain

$$\eta = 10.7 \tag{9}$$

From the virial theorem, the kinetic energy at melting is half the total melting energy,[8]

$$\frac{\alpha E_s V_s}{V - V_s} = \frac{\eta - 1}{z}\frac{1}{2}E_m \doteq \frac{\eta - 1}{z}\frac{1}{2}\frac{V - V_s}{V}E_s \tag{10}$$

Therefore, for argon

$$\alpha = \frac{\eta - 1}{z}\frac{1}{2}\frac{V - V_s}{V}\frac{V - V_s}{V_s} = 0.0052 \tag{11}$$

where $(\eta - 1)/z$ represents that interacting with $(\eta - 1)$ molecules and each molecule moves to a hole with a zth of the kinetic energy at melting.

Since η and α change slightly with different substances, we take the value for argon as reference ones, while the variations of η and α for different substances are taken into account by the introduction of the substance dependent parameter β.

Assuming the occupied-site fraction, y,

$$y = \frac{Ns}{Ns + N_0} \doteq \frac{V_s}{V} \tag{12}$$

and substituting the values of η and α into eqs 5 and 6, we obtain

$$n_h = 10.7\frac{1 - y}{y} \tag{13}$$

$$\epsilon = \frac{0.0052E_s y}{1 - y} \tag{14}$$

Furthermore, let the sublimation energy equal the energy to generate a hole,

$$E_s = \frac{(z - 2)\epsilon^*}{2N_a} \tag{15}$$

where ϵ^* is the energy parameter in the Lennard-Jones potential and N_a is the Avogadro constant.

Finally, substituting eqs 13–15 into eq 4, we get the free volume expression for the open-cell model

$$V_f = V_f'\left(1 + 10.7\beta\frac{1 - y}{y}e^{-[0.0052(z-2)\epsilon^* y]/2(1-y)RT}\right) \tag{16}$$

3. Derivation of the Open-Cell Model Equation of State

In the hole theory, the configurational partition function, Z, is composed of three contributions and is given by[1]

$$Z = gV_f^{cN}e^{-E_0/kT} \tag{17}$$

where g denotes the combinatorial factor, E_0 is the lattice energy, and $3c$ is the number of external degrees of freedom per chain.

Following the approach of Simha and Somcynsky,[1] Flory's combinatorial factor is adopted, and the L-J potential is used to describe the lattice energy:

$$g \propto y^{-N}(1 - y)^{-Ns(1-y)/y} \tag{18}$$

$$E_0 = \frac{1}{2}yNqz\epsilon^*[1.011(v^*/w)^4 - 2.409(v^*/w)^2] \tag{19}$$

In eqs 18 and 19, y is the occupied-site fraction. ϵ^* and v^* represent the characteristic energy and volume parameters, respectively. qz is the number of nearest neighbor sites per chain, and $qz = (z - 2)s + 2$, where z is the coordination number per segment. Note that in eq 18 only the terms related to derivation of an EOS remain.

For a long chain molecule,[3]

$$qz \doteq s(z - 2) \tag{20}$$

By substituting eq 20 and $T^* = qz\epsilon^*/cR$ into eq 16, an explicit free volume expression from the open-cell model is derived as

$$V_f = V_f'\left(1 + 10.7\beta\frac{1 - y}{y}e^{-[0.0052cy]/[2s\tilde{T}(1-y)]}\right) \tag{21}$$

where $\tilde{T}$ is the reduced temperature and $\tilde{T} = T/T^*$.

The occupied-site fraction, y, can be solved by the minimization of the Helmholtz free energy, A:

$$(\partial A/\partial y)_{T,V} = 0 \tag{22}$$

Therefore, combining eqs 17–19, 21, and 22 with the fundamental thermodynamic equation, $A = -kT \ln Z$, we

Table 1. Comparison of P–V–T Calculations between β = 0.2 and β as an Adjustable Parameter for OCM EOS

polymer	temp range (K)	pressure range (MPa)	no. of data points	β = 0.2 AADρ[a]	β as an adjustable parameter AADρ	T^* (K)	P^* (MPa)	V^* (mL/g)	β
LPE	426.1–462.8	0.1–200	63	0.046	0.045	11 609	731.2	1.168	0.176
PP	473.2–563.2	0–200	41	0.055	0.054	14 012	492.2	1.234	0.238
PcHM	395.9–472.1.	0.1–200	89	0.054	0.054	13 749	756.0	0.916	0.193
PB	277.1–328.3	0.1–210	86	0.045	0.044	10 967y	754.5	1.097	0.221
				0.050[b]	0.049[b]				

[a] AADρ = $1/N\sum|\rho_i^{\mathrm{calc}} - \rho_i^{\mathrm{exp}}|/\rho_i^{\mathrm{exp}} \times 100$. [b] Grand average.

get

$$\frac{S}{3c}\left[\frac{(S-1)}{S} + y^{-1}\ln(1-y)\right] = \frac{y}{6\bar{T}(y\bar{V})^2}[2.045 - 3.033(y\bar{V})^{-2}] + \left[2^{-1/6}y(y\bar{V})^{-1/3} - \frac{1}{3}\right][1 - 2^{-1/6}y(y\bar{V})^{-1/3}]^{-1} + RR \quad (23)$$

where

$$RR = \frac{1+U}{3y(10.7\beta)^{-1}\mathrm{e}^{U} + 3(1-y)} \quad (24)$$

and

$$U = \frac{0.0052cy}{2\bar{T}s(1-y)} \quad (25)$$

Consequently, from the thermodynamic relation $P = -(\partial A/\partial V)_T$, we obtain

$$\frac{\bar{P}\bar{V}}{\bar{T}} = [1 - 2^{-1/6}y(y\bar{V})^{-1/3}]^{-1} + \frac{2y}{\bar{T}(y\bar{V})^2}[1.011(y\bar{V})^{-2} - 1.2045] \quad (26)$$

where $\bar{P}$ and $\bar{V}$ ar the reduced pressure and volume, respectively,

$$\bar{P} = P/P^* \qquad P^* = qz\epsilon^*/sv^* \quad (27)$$

$$\bar{V}/V^* \qquad V^* = v^*/M_0$$

where M_0 is the segmental molar weight.

A relation between the three parameters T^*, P^*, and V^* exists:

$$\frac{P^*V^*}{T^*} = \frac{cR}{sM_0} \quad (28)$$

As a result, eqs 23 and 26 form the so-called open-cell model EOS (OCM EOS) proposed in this work.

4. Results

To test its capability, the OCM EOS has been applied to the calculation of the P–V–T behavior for a variety of liquids including polymers, heavy molecular weight hydrocarbons, and organic solvents, covering wide ranges of pressure and temperature. The calculation results have been compared with experimental data and those estimated by us from the SS EOS which has been evaluated as one of the best EOSs for polymer and large molecule liquids, in particular.[9]

In the OCM EOS, there are four parameters regressed from the experimental P–V–T data: T^*, P^*, V^*, and the so-called spatial structure parameter, β. The first three correspond to three molecular parameters, ϵ^*, v^*, and s (or c given by eq 28). In the regression of the parameters, three steps were taken for steady convergence. First, we set the β value to a constant, for example 0.5, and the atmospheric pressure data were used for the regression of T^* and V^*. These T^* and V^* were then used to solve P^* for all the PVT data. Finally, P^*, V^*, and T^* obtained above were taken as initial values and all the PVT data were fit again to get the four parameters needed in the EOS. On the basis of our experience, parameter β can be treated as a universal constant, 0.2, for many substances of interest here. As a result, only three adjustable parameters are needed in most calculations, which are discussed in later sections.

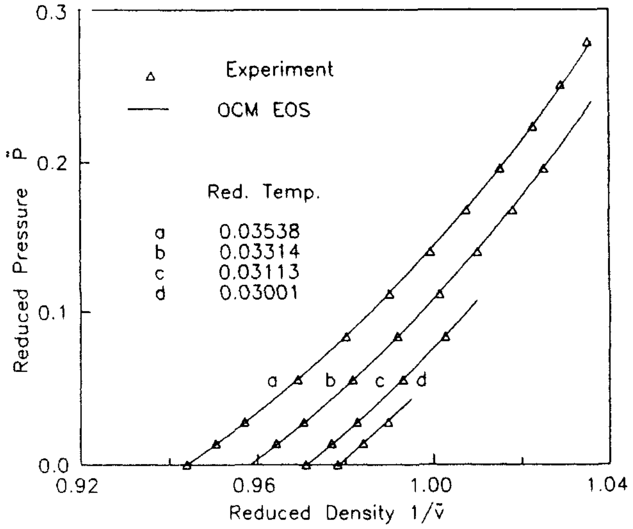

Figure 2. Reduced pressure versus reduced density at four reduced temperatures for polystyrene.

(1) **P–V–T for Polymers.** Firstly, the P–V–T relations for four commonly used polymers, linear polyethylene (LPE), polypropylene (PP), poly(cyclohexyl methacrylate) (PcHM), and *cis*-1,4-polybutadiene (PB), have been calculated. As is suggested by Simha and Somcynsky,[1] the value of $s/3c$ is here set to unity.

It is found in the calculations (see Table 1) that the optimum β values vary in the vicinity of 0.2. Therefore, it is worth attempting to set β to 0.2 for all the calculations for polymers. As shown in Table 1, fortunately, the same quality description has been obtained in this case. Furthermore, 15 polymers have been investigated and the density deviations AADρ (see the definition in the tables) are shown in Table 2, along with those from the SS EOS. It is found that the OCM EOS presents better results, with the grand average AADρ percent 0.054 against 0.072 for the SS EOS. It is noticeable that, except for poly(4-methylpentene) (PMP) and poly(methyl methacrylate) (PMMA), the β values for the other 13 polymers are constant, equal to 0.2. The larger deviation for poly(tetrafluoroethylene) (PTFE) in the calculation is probably attributable to the experimental uncertainty. The volume accuracy in the experimental measurements is 0.003 cm^3/g,[10] rather than 0.0003 cm^3/g in the others. As an illustration, Figure 2 represents good agreement between the calculated and experimental results for polystyrene (PST) at four reduced temperatures.

Table 2. Deviations of Densities for Polymer Liquids and Parameters for OCM EOS

					OCM EOS					
polymer[a]	temp range (K)	pressure range (MPa)	no. of data points	SS EOS AADρ[b]	AADρ	T^* (K)	P^* (MPa)	V^* (mL/g)	β	data source
LPE	426.1–462.8	0.1–200	63	0.066	0.046	11 698	740.2	1.167	0.200	12
BPE	408.3–471.2	0.1–100	53	0.053	0.052	12 378	631.4	1.194	0.200	12
PP	473.2–563.2	0–200	41	0.079	0.055	13 755	502.1	1.233	0.200	13
PIB	323.9–383.2	10–100	70	0.010	0.008	13 161	656.9	1.111	0.200	14
PDMS	298.1–343.1	10–100	60	0.015	0.026	9 249	481.4	0.977	0.200	14
PcHM	395.9–472.1	0.1–200	89	0.065	0.054	13 788	757.1	0.916	0.200	12
PBMA	307.1–472.7	0.1–200	118	0.078	0.061	12 028	784.6	0.952	0.200	12
PET	553.1–613.1	10–200	46	0.047	0.038	14 443	1111.	0.766	0.200	13
PVA	308.1–373.0	0–80	110	0.016	0.022	11 027	904.2	0.828	0.200	15
PTFE	603.5–645.4	0–40	21	0.196	0.152	11 016	553.4	0.473	0.200	16
PSI	388.5–468.7	1.0–200	64	0.032	0.027	14 851	681.7	0.978	0.200	17
PoMS	412.5–470.7	0.1–160	43	0.038	0.032	14 858	725.2	0.992	0.200	17
PB	277.1–328.3	0.1–210	86	0.042	0.045	10 884	750.9	1.097	0.200	18
PMP	513.5–592.1	0–200	97	0.128	0.096	12 834	479.7	1.237	0.134	19
PMMA	397.7–432.2	0.1–200	48	0.220	0.098	19 444	710.1	0.896	0.586	12
				0.072[c]	0.054[c]					

[a] LPE = linear polyethylene, BPE = branched polyethylene, PcHM = poly(cyclohexyl methacrylate), PMMA = poly(methyl methacrylate), PBMA = poly(*n*-butyl methacrylate), PVA = poly(vinyl acetate), PTFE = poly(tetrafluoroethylene), PST = polystyrene, PoMS = poly(*o*-methylstyrene), PB = *cis*-1,4-polybutadiene, PP = polypropylene, PMP = poly(4-methylpentene-1), PET = poly(ethylene terephthalate), PIB = polyisobutylene, PDMS = poly(dimethylsiloxane). [b] AADρ = $1/N\sum|\rho_i^{\text{calc}} - \rho_i^{\text{exp}}|/\rho_i^{\text{exp}} \times 100$. [c] Grand average.

Table 3. Deviations of Densities for High Molecular Weight Hydrocarbons and Parameters for OCM EOS

					OCH EOS					
hydrocarbon[a]	temp range (K)	pressure range (MPa)	no. of data points	SS EOS AADρ[b]	AADρ	T^* (K)	P^* (MPa)	V^* (mL/g)	β	data source
n-C8	303.15–393.15	0–120	32	0.090	0.055	7 443	558.3	1.322	0.200	20
n-C9	303.15–413.15	0–200	54	0.148	0.112	7 723	558.7	1.304	0.200	21
n-C12	281.35–313.25	0.1–200	21	0.060	0.041	8 249	580.2	1.254	0.200	22
HMDS	298.15–343.15	0.1–500	30	0.063	0.032	6 759	446.3	1.168	0.200	23
n-C15	310.95–408.15	0.1–207	37	0.086	0.070	8 881	875.2	1.247	0.200	24
n-C16	298.15–373.15	0.1–400	25	0.076	0.056	8 919	644.6	1.239	0.200	25
n-C18	333.15–408.15	0.1–207	32	0.089	0.076	9 253	676.3	1.234	0.200	24
PPH	310.95–408.15	0.1–207	43	0.090	0.079	10 738	694.3	1.085	0.200	24
DPD	310.95–408.15	0.1–207	32	0.059	0.049	10 361	779.7	1.137	0.200	24
OHT	310.95–408.15	0.1–207	41	0.085	0.063	10 868	654.3	1.228	0.447	24
CCH	310.95–408.15	0.1–207	43	0.082	0.065	11 609	707.0	1.157	0.414	24
CPPH	310.95–408.15	0.1–207	43	0.100	0.069	11 315	687.0	1.195	0.507	24
CCPD	310.95–408.15	0.1–207	43	0.103	0.092	10 898	722.9	1.154	0.338	24
DCCH	310.95–408.15	0.1–207	43	0.078	0.065	11 189	721.4	1.124	0.316	24
PEH	310.95–408.15	0.1–207	43	0.058	0.048	10 872	729.0	1.154	0.382	24
CHEH	310.95–408.15	0.1–207	42	0.075	0.062	10 950	704.1	1.187	0.400	24
NPD	310.95–408.15	0.1–207	21	0.029	0.028	8 952	844.3	1.060	0.014	24
				0.081[c]	0.062[c]					

[a] *n*-C8 = *n*-octane, *n*-C9 = *n*-nonane, *n*-C12 = *n*-dodecane, HMDS = hexa(dimethylsilosane), *n*-C15 = *n*-pentadecane, *n*-C16 = *n*-hexadecane, *n*-C18 = *n*-octadecane, OHT = 9-*n*-octylheptadecane, PPH = 1-phenyl-3-(2-phenylethyl)hendecane, CCH = 1-cyclohexyl-3-(2-cyclohexylethyl)hendecane, CPPH = 9-(3-cyclopentylpropyl)heptadecane, CCPD = 1-cyclopentyl-4-(3-cyclopentylpropyl)dodecane, DCCH = 1.7-dicyclopentyl-4-(3-cyclopentylpropyl)heptane, PEH = 9-(2-pentylethyl)heptadecane, CHEH = 9-(2-cyclohexylethyl)heptadecane, NPD = 1-naphthylpentadecane, DPD = 1-decylpentadecane. [b] AADρ = $1/N\sum|\rho_i^{\text{calc}} - \rho_i^{\text{exp}}|/\rho_i^{\text{exp}} \times 100$. [c] Grand average.

(2) *P–V–T* for Heavy Molecular Weight Liquid Hydrocarbons. For these large molecules, we simply adopt the relation, $s + 3 = 3c$, proposed by Simha,[11] which apparently reduces to the boundary, i.e. $s/3c = 1$, when s approaches infinity.

The *P–V–T* relations for 17 heavy molecular weight liquid hydrocarbons have been calculated by the use of the OCM EOS. For *n*-paraffins, β values are set to 0.2. In contrast, those for aromatic and cyclic hydrocarbons are regressed by fitting experimental data and shown in Table 3. Apparently, the OCM EOS provides better results and satisfactory accuracy, with the density grand average AADρ 0.062 percent against 0.081 percent for the SS EOS. Meanwhile, Figure 3 is a good description of the variation of the reduced density versus the reduced pressure at four reduced temperatures for *n*-hexadecane.

(3) *P–V–T* for Organic Solvents. Ten organic substances that are usually used as solvents and are of moderate molecular weight have been investigated here. For their normal molecular size, it is reasonable to set s to unity. As is seen in Table 4, except for toluene and *o*-xylene, all the β values are equal to 0.2. The density grand average AAD percent is 0.057, which is a substantial improvement over the deviation 0.093 percent for the SS EOS. Moreover, a fair description of the *P–V–T* behavior for isopentane is presented in Figure 4.

It should be pointed out that Figures 2–4 are schematic drawings to show the accuracy for the OCM EOS, which cannot be simply distinguished from that for the SS EOS in these diagrams.

5. Discussion and Conclusion

An open-cell model has been proposed in this work to relax the restrictions of the cell theory. From this model, a new free volume expression, eq 21, is derived. Following the approach of Simha and Somcynsky,[1] the open-cell model equation of state has been developed. To test the capability of the OCM EOS, we have applied it to liquids, including 15 polymers, 17 heavy molecular weight hydrocarbons, and 10 organic solvents. As is seen in Tables 2–4, the OCM EOS provides better fits to the experimental data over wide ranges of temperature and pressure with

Table 4. Deviations of Densities for Organic Solvents and Parameters for OCM EOS

					OCM EOS					
solvent	temp range (K)	pressure range (MPa)	no. of data points	AADρ[a]	AADρ	T^* (K)	P^* (MPa)	V^* (mL/g)	β	data source
carbon tetrachloride	273.15–323.15	0.1–198	25	0.039	0.035	7268	725.9	0.573	0.200	26
n-butane	313.15–363.15	2.0–20	28	0.246	0.134	6921	387.2	1.471	0.200	27
n-pentane	293.15–373.15	1.0–20	42	0.087	0.037	6625	499.8	1.391	0.200	27
isopentane	223.15–298.15	0.1–203	41	0.077	0.046	6247	540.5	1.383	0.200	26
cyclohexane	313.15–383.15	0.1–214	32	0.103	0.069	7751	644.7	1.199	0.200	28
n-hexane	343.15–433.15	1.0–30	29	0.086	0.058	6960	506.1	1.361	0.200	27
benzene	280.15–400.15	0.1–50	42	0.072	0.055	7555	812.8	1.044	0.200	27
m-xylene	293.15–473.15	0.1–40	29	0.126	0.043	8461	627.3	1.109	0.200	27
toluene	223.15–298.15	0.1–203	42	0.032	0.032	5600	896.9	1.025	0.001	26
o-xylene	298.15–423.15	0.1–40	26	0.066	0.059	9316	645.1	1.106	0.393	27
				0.093[b]	0.057[b]					

[a] $AAD\rho = 1/N\sum|\rho_i^{calc} - \rho_i^{exp}|/\rho_i^{exp} \times 100$. [b] Grand average.

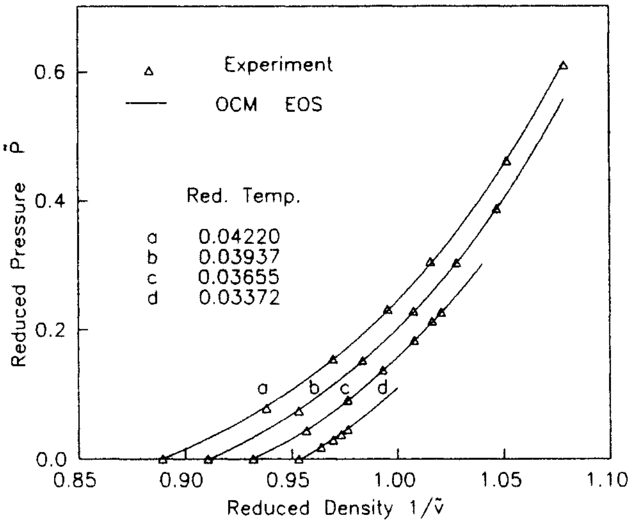

Figure 3. Reduced pressure versus reduced density at four reduced temperatures for *n*-hexadecane.

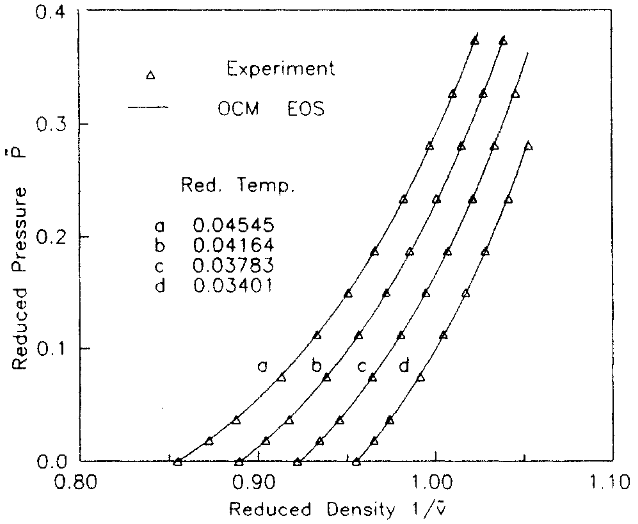

Figure 4. Reduced pressure versus reduced density at four reduced temperatures for isopentane.

the density grand average AADρ percent 0.054, 0.062, and 0.057 against 0.072, 0.081, and 0.093 from the SS EOS for these three groups of liquids, respectively. Consequently, the OCM EOS is a good improvement over the SS EOS which has been highly evaluated as one of the best EOSs for polymers and large molecules.[9]

It should be pointed out that in the derivation of the OCM EOS, a so-called spatial structure parameter, β, is introduced into the expression of the free volume. However, as mentioned above, for most polymers, organic solvents, and *n*-paraffins discussed here, β values can be treated as constant and set to 0.2 with almost undetectable loss of accuracy. This regularity of parameter β, which is probably attributed to the main group CH_2 in all these molecules, delivers convenience in the application of the OCM EOS to polymer solutions and polymer blends. Nevertheless, since many postulates have been introduced in the derivation of the OCM EOS, β can behave abnormally sometimes. As a result, it is considered as an empiric parameter and determined by fitting experimental $P-V-T$ data for some systems. To continue this work, we have extended the OCM EOS to liquid mixtures for the estimation of $P-V-T$ behavior, the excess volumes and enthalpies, activity of solvents in polymers, and phase behavior for polymer solutions and blends, in particular. All the results will be addressed in our subsequent paper.

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