無極性 分子의 液體比重 推定

배　　재　　호*

Estimation of Liquid Density for Non-Polar Molecules

*Jae Ho Bae

*Gulf Research & Development Co.
Pittsburgh, Pa.* 15230 *U. S. A.*

Abstract

A simple method of estimating liquid densities at moderately high temperature and pressure was obtained from the existing theories for liquids. For pure liquids the smoothed potential cell model was used in conjunction with the empirical equation for saturated liquid densities and the method was extended to the binary mixtures by the use of the average potential model.

The results of sample calculation show that the deviation of estimated values from experiments is about 1% up to 700 psia and about 5% at 4500 psia for pure liquids. It is about 4% for binary mixture of $C_3H_8+C_6H_6$. These are comparable with the deviations of other methods.

The main advantage of the present method is that it requires only two constants which can be obtained from two saturated liquid densities which are easy to obtain experimentally. No knowledge on the densities of high pressure is required beforehand as is the case with other methods based on the principle of corresponding states. It is not a correlation method of data, but a prediction method of unknown data.

Introduction

In the petroleum reservoir engineering calculations, accurate values of the volume of liquid hydrocarbons are essential. A successful prediction of the performance of oil reservoirs will depend on the knowledge of the volumetric behavior of liquid hydrocarbons contained in it. It is always desirable to have a good method of estimation for this property.

While the available correlations for predicting the behavior of gases are quite successful, those for liquid behaviors are not satisfactory. In fact, the liquids have neither the fluidity of gases nor the rigidity of

solids. Consequently, the liquid state is not so welldefined. At present, the methods of estimating liquid densities are based mainly on the principle of corresponding states. Extensive data for the whole temperature and pressure range for some liquids are required to construct these correlations. Moreover, the critical temperature, pressure and volume which are not easy to obtain experimentally are usually required. In addition to these, occasionally one or more of experimental density at certain temperature and pressure are needed. Reid and Sherwood[1] review the available methods and estimate the error to be 2 to 5%. In this report a straightforward method of estimating the liquid densities at moderately high

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pressures and temperatures is presented. This is obtained by extending the existing theory for liquids. A detailed derivation is given to clarify the limitations of the present method.

Smoothed Potential Cell Model

There is a wide variety of theories relating to the liquid state. Early stage of the progress in the liquid model was made by Lennard-Jones and Devonshire[2] using the cell model. A simplified model, proposed by Prigogine and Mathot[3,4] is employed here. It is called the smoothed potential cell model.

In the liquid state far below critical temperature a certain regular spacing of molecules is postulated with a mean intermolecular distance of the order of the molecular diameter. The cell model of the liquid state assumes that each molecule is confined to its own cell formed by neighboring molecules. It is assumed that the central atom can move inside a polyhedron formed by the neighboring molecules at their equilibrium positions. At high densities this polyhedron may be approximated by a sphere. The mean energy of interaction takes the value of 0 or ∞ in the smoothed potential cell model which makes the following assumption regarding $W(r)$:

$$W(r)-W(o)=0 \qquad 0<r<(a-\sigma)$$

$$W(r)-W(o)=\infty \qquad (a-\sigma)<r \qquad (1)$$

where

$W(r)=$ mean energy of interaction of the central molecule with neighboring molecules;

$W(o)=$ value of $W(r)$ when all molecules are at centers of their cells;

$r \quad =$ distance between molecular centers;

$a \quad =$ distance from cell center to the center of neighboring molecules;

$\sigma \quad =$ diameter of the hard sphere molecules.

Then the cell partition function, ψ, corresponding to a molecule in the cell referred to the energy of the molecule at the center of the cell can be expressed as:

$$\psi=4\pi \int_{\text{cell}} exp\left[-\frac{1}{kT}\left[W(r)-W(o)\right]\right]r^2\,dr \qquad (2)$$

where

$k=$ the Boltzman constant;

$T=$ absolute temperature.

The pressure, due to the potential energy of all molecules placed at the centers of the cell and the motions of the molecules in the cell, can be readily obtained from the cell partition function as:

$$P=\frac{-1}{2}\left[\frac{\partial\,W(0)}{\partial V}\right]_T+kT\left(\frac{\partial\,ln\psi}{\partial V}\right)_T \qquad (3)$$

For the general case we consider that a pair of molecules interact according to the Lennard-Jones (n, m) potential energy function.

$$U(r)=\frac{\varepsilon^*}{(n-m)}\left[m\left(\frac{r^*}{r}\right)^n-n\left(\frac{r^*}{r}\right)^m\right] \qquad (4)$$

where

$U(r)=$ mutual potential energy of interaction of an isolated pair of molecules;

$r \quad =$ distance between centers of molecules;

$r^* \quad =$ value of r at minimum $U(r)$;

$\varepsilon^* \quad =$ value of $-U(r)$ at minimum $U(r)$, maximum energy of attraction;

$m \quad =$ attraction exponent;

$n \quad =$ repulsion exponent, $n>m$.

Then the average energy of interaction of one neighboring molecule with the central one can be obtained by averaging the interaction energy for all orientations of the central molecule in the cell. Each position is equally weighted.

$$\bar{U}(r)=\frac{\int_0^{2\pi}\int_0^{\pi}U(r^2+a^2-2ar\,\cos\theta)^{\frac{1}{2}}\sin\,\theta\,d\theta\,d\phi}{\int_0^2\int_0^{\pi}\sin\,\theta\,d\theta\,d\phi} \qquad (5)$$

where

$\bar{U}(r)$ = average energy of interaction;

θ = inclination of the central atom from the axis of a neighboring molecule and the cell center;

ϕ = azimuthal angle of the central molecule;

a = average distance between first neighbors.

The mean energy of interaction is that of average interaction energy multiplied by the number of neighboring molecules. This is done with the relationships:

$$a^3 = \gamma V$$

$$r^{*3} = \gamma V^*$$

where γ is a numerical factor which depends on the geometrical arrangement of the molecule. We now have the following expression, taking into account the lattice energy of more distant molecules.

$$W(o) = \frac{Z\varepsilon^*}{(n-m)}\Big[mC\Big(\frac{V^*}{V}\Big)^{\frac{n}{3}} - nD\Big(\frac{V^*}{V}\Big)^{\frac{m}{3}}\Big] \quad (6)$$

where

C and D = lattice summation constants;

V = volume per mole;

V^* = value of V at $r = r^*$;

Z = number of nearest neighboring molecules.

The partition function in Equation (2) can now be written as:

$$\psi = \frac{4}{3}\pi r^{*3}\Big(\frac{V}{V^*}\Big)\Big[1 - \frac{1}{s}\Big(\frac{V^*}{V}\Big)^{\frac{1}{3}}\Big]^3 \quad (7)$$

where s is r^*/σ and is a function of n and m. It can be found by the relationship of

$$s = \Big(\frac{n}{m}\Big)^{1/(n-m)}$$

Combining Equations (6), (7), and (3), the expression for P is obtained.

$$P = \frac{m\,n\,Z\,\varepsilon^*}{6(n-m)V}\Big[C\Big(\frac{V^*}{V}\Big)^{\frac{n}{3}} - D\Big(\frac{V^*}{V}\Big)^{\frac{m}{3}}\Big] + \frac{kT}{V}\Big/\Big[1 - \frac{1}{s}\,\frac{V^*}{V}^{\frac{1}{3}}\Big] \quad (8)$$

Thus, we obtained the equation of state for the liquids from the smoothed potential cell model.

Empirical Relationship for Liquid Density

For nonpolar molecules Reed[5] has shown that the following empirical equation holds well over the whole saturated liquid range up to approximately $T/Tc = 0.8$.

$$\frac{1}{V^2} = A - BT \quad (9)$$

where

A and B = positive constants characteristic of each substance,

V = molar volume.

This equation correlates the liquid density at low pressures. The validity of this equation was checked by calculating the molar volume at absolute zero of temperature, which demonstrated quite satisfactory agreement with values estimated by other methods[5].

The theoretical significance of A and B was found by Reed and McKinley[6]. At zero pressure Equation (8) can be rearranged as

$$\Big(\frac{D}{C}\Big)x^{(m-n-6)/3} + \frac{kT}{Z\varepsilon^*}\,k\Big[\frac{x}{\alpha C}^{(6-n)/3}\Big] = x^2 \quad (10)$$

where

$$x = \frac{V^*}{V}$$

$$\alpha = 1 - x^{\frac{1}{3}}/s$$

$$k = \frac{6(n-m)}{nm}$$

Comparison of Equation (10) with Equation (9) gives:

$$A = \left(\frac{D}{C}\right)\left[x^{(m-n+6)/3}/V^{*2}\right] \qquad (11)$$

$$B = \frac{k}{Z\varepsilon^*}\, k\left[x^{(6-n)/3}/\alpha C V^{*2}\right] \qquad (12)$$

Thus, A is related to r^* and A/B to ε^*.

Working Equation

For our present purpose of predicting the liquid densities at high pressures, we take advantage of Equations (11) and (12). When these equations are combined with Equation (8), we have:

$$\frac{1}{V^2} = A - BT + \frac{B\,P\,V}{k}\left(1 - x^{\frac{1}{3}}/s\right) \qquad (13)$$

In order to obtain a numerical value of s, we choose the usual value of 12 and 6 for n and m, respectively. The exponent 6 for attractive force was first proved quantum-mechanically by London[7]. However, the value of 12 is chosen for a cubic close-packed structure. In this case $s = 2^{1/6}$. Then the value of V^* can be approximated in the following way. It can be shown[4] that for a face-centered cubic lattice:

$$\frac{V}{V^*} = 0.916 \text{ for } T \to 0 \qquad (14)$$

Since $V = A^{-1/2}$ at $T = 0$, we have

$$V^* = (0.916 A^{1/2})^{-1} \qquad (15)$$

Finally, we have the working equation from Equations (13) and (15).

$$\frac{1}{V^2} = A - BT + f(p) \qquad (16)$$

where

$$f(p) = 0.083\frac{PBV}{R} \qquad (17)$$

When V is in cc/mole, A in (mole/cc)^2, B in (mole/cc)^2/$^\circ K$, and P in atm, then $R = 82.06$ cc atm/mole$^\circ K$.

There is a difficulty in using Equation (16) for actual calculation of the liquid volume. To evaluate the last term of Equation (16) one has to know the volume which he wants to calculate. This difficulty can be solved in the following manner. As a first approximation we calculate V from A and B at the temperature of the calculation; that is, we set $f(p) = 0$. Then we use this value in the next calculation with a small increment of pressure. The procedure is iterated until the value at the desired pressure is found. If one wants a better accuracy, one can feed back the value of V in the next calculation until there is no change in V at each pressure. This kind of iteration should not be a problem on a high-speed computer.

Binary Mixtures

In order to extend the present method of estimation to mixtures we adopt the refined version of the average potential model of Prigogine. In this model two hypothetical liquids are introduced which are centered on each component. For the liquid which is centered on species 1, the effective interaction is found by summing up the pair interactions of 1 with its neighbors.

$$\langle U(r)\rangle_1 = x_1 U_{11}(r) + x_2 U_{12}(r) \qquad (18)$$

where $\langle U(r) \rangle$ is the average interaction potential and x is the mole fraction. The subscripts refer to the molecular species in the mixture. For the two-centered liquid we can express $\langle U(r) \rangle_2$ similarly. Now if we assume that the isolated-pair interactions are all of the form of the Lennard-Jones 6-12 potential, we obtain the expressions for the parameters of the effective potential for one-centered liquids as:

$$\langle \varepsilon^* \rangle_1 = \frac{(x_1 \varepsilon_{11}{}^* r_{11}{}^{*6} + x_2 \varepsilon_{12}{}^* r_{12}{}^{*6})^2}{x_1 \varepsilon_{11}{}^* r_{11}{}^{*12} + x_2 \varepsilon_{12}{}^* r_{12}{}^{*12}} \qquad (19)$$

$$\langle r^* \rangle_1 = \left(\frac{x_1 \varepsilon_{11} r_{11}{}^{*12} + x_2 \varepsilon_{12}{}^* r_{12}{}^{*12}}{x_1 \varepsilon_{11} r_{11}{}^{*6} + x_2 \varepsilon_{12}{}^* r_{12}{}^{*6}} \right)^{\frac{1}{6}} \qquad (20)$$

while similar expressions can be written for the two-centered liquid. Then the mixture behaves as the weighted average of these two hypothetical liquids.

To simplify these equations we define new parameters as follows:

$$\xi_1 = \frac{\varepsilon_{11}{}^* r_{11}{}^{*6}}{\varepsilon_{12}{}^* r_{12}{}^{*6}} - 1 \qquad (21)$$

$$\phi_1 = \frac{\varepsilon_{11}{}^* r_{11}{}^{*12}}{\varepsilon_{12}{}^* r_{12}{}^{*12}} \qquad (22)$$

Then Equations (19) and (20) become,

$$\langle \varepsilon^* \rangle_1 = \varepsilon_{12}{}^* \left[\frac{(x_1 \xi_1 + 1)^2}{x_1 \phi_1 + 1} \right] \qquad (23)$$

$$\langle r^* \rangle_1 = r_{12}{}^* \left(\frac{x_1 \phi_1 + 1}{x_1 \xi_1 + 1} \right)^{\frac{1}{6}} \qquad (24)$$

Similarly, $\langle \varepsilon \rangle_2$ and $\langle r^* \rangle_2$ can be obtained. At this point we want to express these equations in terms of the constants A and B. From Equations (11) and (12) we have:

$$\frac{A}{B} = \varepsilon^* C_1 \qquad (25)$$

$$A = C_2 r^{*-6} \qquad (26)$$

Where C's are constants characteristic to the exponents n and m and others. We assume that C's are the same for pure components and throughout the composition range of the mixture, though this assumption may not necessarily be correct. We define another parameter here.

$$n = \left[\left(A_1^{\frac{1}{6}} + A_2^{\frac{1}{6}} \right) \Big/ 2 \right]^6 \qquad (27)$$

Then, after some algebraic manipulations, we have:

$$\xi_1 = \left[\left(A_1 A_2 B_1 B_2 \right)^{\frac{1}{2}} \frac{1}{n B_1} \right] - 1 \qquad (28)$$

$$\phi_1 = \left[\left(\frac{B_1 B_2}{A_1 A_2} \right)^{\frac{1}{2}} \frac{A_1^2 A_2^2}{A_1 B_1 \eta^2} \right] - 1 \qquad (29)$$

$$\langle A \rangle_1 = \frac{A_1 A_2}{\eta} \left(\frac{x_1 \xi_1 + 1}{x_1 \phi_1 + 1} \right) \qquad (30)$$

$$\langle B \rangle_1 = B_1 \left(\frac{\xi_1 + 1}{x_1 \xi_1 + 1} \right) \qquad (31)$$

$$\frac{1}{\langle V \rangle_1^2} = \langle A \rangle_1 - B_1 T + f_1(p) \qquad (32)$$

$$f_1(p) = 0.083 \frac{P B_1 \langle V \rangle_1}{R} \qquad (33)$$

Similar expressions can also be written for two-centered liquids. The molar volume of the liquid of the mixture is given by:

$$V_m = x_1 \langle V \rangle_1 + x_2 \langle V \rangle_2 \qquad (34)$$

We are thus able to calculate the liquid volume of binary mixtures through Equation (34) only from the knowledge of the values of A and B for pure components. The calculational procedures for $\langle V \rangle_1$

and $\langle V \rangle_2$ will be the same as that for pure components.

Discussions

The values of A and B in Equation (9) for light hydrocarbons are listed in Table I. The saturated liquid density data are taken from the API Project 44[8]. With these values Equation (9) should give saturated liquid density for the temperature range up to 0.8 T_c with accuracy of about 0.5%. An advantage of this empirical equation is that it can be used for all nonpolar molecules with above accuracy, regardless of the molecular size.

TABLE 1. Values of Constants A and B

Molecule	$A \times 10^4$ Mole²/cc²	$B \times 10^7$ Mole²/cc² °K
O_2	22. 903	112. 84
N_2	15. 540	93. 777
CH_4	12. 2598	47. 2516
C_2H_6	6. 1554	15. 4521
C_3H_8	3. 3907	7. 1711
$n-C_4H_{10}$	2. 0983	3. 7770
$n-C_5H_{12}$	1. 4451	2. 3670
$n-C_6H_{14}$	1. 0588	1. 6173
$n-C_7H_{16}$	0. 8081	1. 1648
$n-C_8H_{18}$	0. 6345	0. 9726
$n-C_9H_{20}$	0. 5121	0. 6774
$n-C_{10}H_{22}$	0. 4221	0. 5400
$Cy-C_6H_{12}$	1. 4571	2. 0506
C_6H_6	2. 1561	3. 0345

TABLE II. Liquid Volume of Pure Component*

$n-C_7H_{16}$

P, Atm.	300. 2°K Expt.	300. 2°K Calc.-Expt. % Dev.	373. 2°K Expt.	373. 2°K Calc.-Expt. % Dev.
7. 12	148. 11	−0. 55	162. 88	+0. 04
19. 08	147. 94	−0. 87	162. 10	−0. 17
31. 04	147. 41	−0. 94	—	—
43. 0	147. 18	−1. 20	—	—
52. 31	146. 91	−1. 32	—	—
82. 20	146. 31	−1. 86	159. 50	−1. 73
112. 10	145. 69	−2. 32	158. 44	−2. 35
171. 89	144. 58	−3. 16	156. 47	−3. 37
231. 68	143. 47	−3. 83	154. 8	−4. 24
291. 46	142. 49	−4. 42	153. 27	−4. 97
351. 25	141. 57	−4. 96	151. 93	−5. 63

* Volume in cc/gm-mole.

TABLE II. (cont'd):Liquid Volume of Pure Component*

$n-C_8H_{18}$

P, Atm.	373. 2°K Expt.	373. 2°K Calc.-Expt. % Dev.	398. 2°K Expt.	398. 2°K Calc.-Expt. % Dev.
5	179. 22	+0. 11	186. 07	−0. 03
10	178. 65	+0. 15	185. 50	−0. 05
15	178. 30	+0. 07	185. 04	−0. 12
20	178. 07	−0. 07	184. 70	−0. 25
25	177. 85	−0. 22	184. 47	−0. 44
30	177. 65	−0. 36	184. 13	−0. 56
50	176. 70	−0. 84	182. 99	−1. 11
100	174. 76	−1. 97	180. 47	−2. 25
150	172. 93	−2. 83	178. 19	−3. 14
200	171. 45	−3. 66	176. 36	−3. 99
250	170. 08	−4. 36	174. 65	−4. 67
300	168. 71	−4. 91	173. 16	−5. 29

* Volume in cc/gm-mole.

TABLE II. (cont'd):Liquid Volume of Pure Component*

P, Atm.	423. 2°K Expt.	423. 2°K Calc.-Expt. % Dev.	448. 2°K Expt.	448. 2°K Calc.-Expt. % Dev.
5	193. 84	−0. 23	203. 32	−0. 79
10	193. 04	−0. 20	202. 29	−0. 73
15	192. 49	−0. 28	201. 49	−0. 80
20	192. 01	−0. 42	200. 92	−0. 95
25	191. 67	−0. 60	200. 35	−1. 10
30	191. 32	−0. 77	199. 78	−1. 23
50	189. 84	−1. 35	197. 83	−1. 83
100	186. 64	−2. 55	193. 84	−3. 11
150	183. 90	−3. 50	190. 07	−3. 88
200	181. 50	−4. 29	187. 10	−4. 63
250	179. 44	−4. 95	184. 58	−5. 29
300	177. 50	−5. 50	182. 30	−5. 82

* Volume in cc/gm-mole.

To demonstrate the present method, the liquid volumes of $n-C_7H_{19}$[9] and $n-C_8H_{18}$[10] were calculated. These data were arbitrarily chosen simply because they were in hand. The results of the calculation are shown in Table II. These values were obtained by successive calculation from zero pressure to the desired pressure with an interval of 10 psi.

As is shown in this table, the deviation of the calculated values from experiments increases as the pressure goes up. It is about 1% up to about 50 atmospheres (735 psia), but is about 5% at 300

atmospheres (4410 psia). The average deviation was not calculated since it would have no meaning in this kind of result. A small improvement can be made by iterating the computation of each pressure in the calculation. However, it was felt that the main source of deviation is the shortcomings of the theory itself.

In Table III the calculation of $C_3H_8+C_6H_6$ system is shown. The data [11] are for the mixture of 0.5 mole fraction of C_3H_8. This should be a severe test for the method since the largest deviation usually occurs in the middle of the composition range. The deviation of the calculated values from experiments is about 4%.

TABLE III. Liquid Volume of Binary Mixture*

$C_3H_8+C_6H_6$

P, psia	560°R		620°R	
	Expt.	Calc. −Expt. % Dev.	Expt.	Calc. −Expt. % Dev.
200	1.419	+3.38	—	—
400	1.414	+3.46	1.51	+3.84
600	1.409	+3.55	1.504	+3.86
800	1.405	+3.56	1.498	+3.94
1000	1.401	+3.59	1.492	+4.09
1250	1.395	+3.73	1.485	+4.11
1500	1.391	+3.67	1.478	+4.19
1750	1.386	+3.75	1.471	+4.28
2000	1.382	+3.69	1.465	+4.37
2250	1.377	+3.77	1.459	+4.38
2500	1.373	+3.79	1.454	+4.40
2750	1.369	+3.80	1.449	+4.34
3000	1.366	+3.74	1.443	+4.43
3500	1.359	+3.68	1.434	+4.39
4000	1.352	+3.62	1.424	+4.42
4500	1.346	+3.49	1.414	+4.45
5000	1.340	+3.51	1.406	+4.41

* Volume in cu ft/lb-mole.

In the cell model of liquid state the one-particle description is used. This is clearly an oversimplification of the many body problems in the condensed phase. Apart from this general defect of the cell model, the smoothed potential cell model has arbitrary assumptions in Equation (1). Moreover, the use of the Lennard-Jones 6-12 potential for large, nonspherical molecules is not adequate for the well-known reasons. Also, in the derivation of the working equations for numerical calculation, the

constants of the face-centered cubic lattice was used. In the case of mixture the constants in Equations (25) and (26) were assumed to be the same for different compositions. In view of these, the deviation is not at all surprising and is comparable with other methods. The present method should give better results when used for the mixture system of similar molecular species.

The advantage of the method is that it requires only two easily measurable saturated liquid densities at low temperatures to predict the densities of pure component and mixtures at moderate high temperature and pressure. It requires no knowledge on the density at high pressures before hand as is the case with other methods based on the principle of corresponding states.

Conclusion

The present method of estimating the liquid volume of nonpolar molecules, for both pure components and binary mixtures, at moderately high pressure and temperatures up to 0.8 Tc is a reliable one with the accuracy comparable with other methods. [1]

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