Liquid Molar Volume Relations for Homologous Series of Hydrocarbons

STUART T. HADDEN[1] and ROBERT SIMHA[2]
Department of Chemical Engineering, New York University, New York, N. Y.

AN EQUATION of state for liquid *n*-alkanes, an earlier study by the authors (*7, 8*), established the relation between its parameters and the terms in the empirical molar volume relation of Kurtz (*4*) for *n*-alkanes. The recent derivation of equations of state for liquid alkylated ring hydrocarbons and the evaluation of their parameters (*2*) now permit determining the relation of additional Kurtz constants to parameters in the equation of state.

For liquid hydrocarbons with nonfused rings the Kurtz molar volume, V, relation (*4*) is expressed as

$$V = K_1N_1 + K_2N_2 - K_4N_4 + K_5 \tag{1}$$

The procedure for identifying the K_i in terms of the parameters in the equation of state is essentially the same as that followed for *n*-alkanes (*7*). The equation of state derived (*2*) for alkylated ring hydrocarbons is

$$\frac{PV}{N_AkT} = \frac{(s+s'+3-d)}{3} \times \frac{1}{1-(\bar{v}^*/v)^{1/3}2^{-1/6}}$$

$$+\,2(s+s'+3-d) \times \frac{[1.011\,(\bar{v}^*/v)^2 - 1.2045]}{1.011\,(\bar{v}^*/v)^2 - 2.409} + \frac{2}{kT}$$

$$(q_aze^*_{aa} + q_bze^*_{bb} + 2X_{ab}w) \times (\bar{v}^*/v)^2[1.011\,(\bar{v}^*/v)^2 - 1.2045] \tag{2}$$

where

$q_az = s(z-2)+1$
$q_bz = s'(z-2)+1$
$X_{ab} = q_azq_bz/(q_az+q_bz)$
$w = e^*_{ab} - (e^*_{aa} + e^*_{bb})/2$
$z = 12$

In Equation 2, s and s' are the number of subunits into which the alkyl chain (each unit approximately $—C_2H_4—$) and ring (in aryl rings approximately $—C_3H_3—$ and in cyclohexyl rings approximately $—C_2H_4—$) are subdivided, respectively. The reasons for this choice have been discussed elsewhere (*2, 4, 6, 7*). When the equation of state is used for *n*-alkyl benzenes, $d = 0$, and for *n*-alkyl cyclohexanes, $d = 1$. The first step in developing the terms in Equation 1 is to exapnd Equation 2 in the quantity

$$h = 1 - \bar{v}^*/v = 1 - N_A\bar{v}^*(s+s')/V \tag{3}$$

At the temperatures of concern $1 > \bar{v}^*/v > 0.94$ for the alkylated ring hydrocarbons being considered. Expanding and dropping h^2 and higher power terms lead to Equation 4 as an equation of state for low pressure. The C_i quantities are linear functions of $Y_{ii} = e_{ii}/kT$, and the D_i, the products of a constant and w/kT as shown in Table I.

$$h = \frac{\bar{C}_1 - \dfrac{D_1}{(s+s')\,5+1} - \dfrac{10D_1}{(1+s'/s)\,5+1/s} + sC_2 + s'\left[C'_2 - \dfrac{10D_1}{(s+s')\,5+1} - \dfrac{100D_1}{(1+s'/s)\,5+1/s}\right]}{\bar{C}_3 + \dfrac{D_2}{(s+s')\,5+1} + \dfrac{10D_2}{(1+s'/s)\,5+1/s} + sC_4 + s'\left[C'_4 + \dfrac{10D_2}{(s+s')\,5+1} + \dfrac{100D_2}{(1+s'/s)\,5+1/s}\right]} \tag{4}$$

Table I. Linear Relations for C_i and D_i in Equation 4

$C_2 = 3.332 - 3.87\ Y_{aa}$
$C'_2 = 3.332 - 3.87\ Y_{bb}$
$C_4 = 5.815 + 32.70\ Y_{aa}$
$C'_4 = 5.815 + 32.70\ Y_{bb}$
$D_1 = 0.387\ w/kT$
$D_2 = 3.27\ w/kT$

For $d = 0$ of Equation 2	For $d = 1$ of Equation 2
$\bar{C}_1 = 9.996 - 0.774\ \bar{Y}$	$\bar{C}_1 = 6.664 - 0.774\ \bar{Y}$
$\bar{C}_3 = 17.444 + 6.54\ \bar{Y}$	$\bar{C}_3 = 11.629 + 6.54\ \bar{Y}$

where $\bar{Y} = \frac{1}{2}\ (Y_{aa} + Y_{bb})$ with subscripts a and b referring to alkane and ring elements, respectively.

A relation from which the Kurtz K_i of Equation 1 can be identified is obtained by solving Equation 4 for v by means of Equation 3 and expanding in $1/s$. The result for large values of s (i.e., dropping terms with the first and higher powers of $1/s$) is, after replacing s by its equivalent of $n/2 + \frac{1}{2}$, as follows:

$$V = (N_Av^*_a/2)[C_4/(C_4 - C_2)]n$$

$$+\,(N_Av^*_a)\,[C_4/(C_4 - C_2)]\,s' \times \left[1 + \frac{\Delta v^*}{v^*} + \frac{C'_4 + 20D_2}{C_4}\right.$$

$$\left. -\,\frac{(C'_4 - C'_2 + 20(D_1 + D_2)}{C_4 - C_2}\right] + (N_Av^*_a)\,[C_4/(C_4 - C_2)]$$

$$\left[\frac{(\bar{C}_1 + \frac{1}{2}(C_4 - C_2) + D_1 + 4D_2}{C_4 - C_2} - \frac{C_2(\bar{C}_3 + 2D_2)}{C_4(C_4 - C_2)}\right] \tag{5}$$

where n = number of carbon atoms in the alkyl chain (Kurtz's N_1),

and

$$\frac{\Delta v^*}{v^*} = \frac{N_Av^*_b - N_Av^*_a}{N_Av^*_a}$$

In Equation 5 the term $\Delta v^*/v^*$ arises from defining

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[1] Present address, Engineering Department, The Dow Chemical Co., Midland, Mich.

[2] Present address, Department of Chemistry, University of Southern California, Los Angles 7, Calif.

$$N_A\overline{v^*} = (N_A v_a^* s + N_A v_b^* s')/(s + s') \tag{6}$$

rather than the conventional $(N_A v_a^* + N_A v_b^*)/2$ (*3, 5*).

When Equation 5 is applied to alkyl cyclohexanes, then $N_2 = 2s'$. (Compare Equation 1 and the definition of s' for the cyclohexane ring.) For this type of hydrocarbon, coefficient of 2 s' is K_2. For all types of hydrocarbons, the last term in Equation 5 is Kurtz's K_5. Whatever end effects or molecular effects there are will be included in K_5. Using the definition of K_1, Equation 5 can be symbolized as

$$V = K_1 N_1 + 2s' K_1 X' + K_5 \tag{7}$$

where X' stands for the quantities enclosed in brackets in the middle term of Equation 5.

When Equation 7 is applied to alkyl benzenes, X' has a different value, i.e. X''. For such hydrocarbons, s' is related to both the number of ring carbon atoms and the number of double bonds. Consequently, the value of the middle term in Equation 7 is the resultant of the terms with K_2 and K_4 in the Kurtz relation of Equation 1. The definition of s' for cyclohexane and for benzene rings (for clarity, use s'') leads to

$$\begin{aligned} N_2 &= 2s' && \text{(cyclohexane)} \\ N_2 &= 3s'' = {}^3\!/_2(2s'') && \text{(benzene)} \\ N_4 &= N_2/2 && \end{aligned} \tag{8}$$

The empirical Equation 1 implies the existence of a unique set of K_i's independent of the type of hydrocarbon under consideration. The theory, in turn, exhibits (see Equation 5) the invariance of the analytical expression for K_1. The logic of the procedure for the separation of the double bond contribution K_4 from the ring carbon term K_2 make these by definition also invariant. On the other hand, the theoretical K_5 derived earlier (*7*) for *n*-alkanes and that now obtained for ring hydrocarbons are not identical. They even differ for the two types of rings because the e_{bb}^* differ. This, of course, arises from the fact that K_5 is determined by the nature of the terminal units in the molecule. Part of the relatively large difference in K_5 for *n*-alkane and alkylated rings (Table II) may be the result of our disregard for the end effects in the analytical treatment.

Using the foregoing, an algebraic expression can be derived for K_4. As the numerical value of K_4 can be obtained directly, the algebraic expression is omitted. This completes the derivation of Equation 1.

EVALUATION OF PARAMETERS

The evaluation of the K_i is straightforward from the defining relations. However, as the values for the equation of state parameters are available at two different temperatures for benzene-alkane and for cyclohexane-alkane elements (*2*), some adjustment to a common temperature of 20° C. is required. The changes in $N_A v_b^*$, e_{bb}^*/k and e_{ab}^*/k were made equal to the changes for $N_A v_a^*$, e_{aa}^*/k and e_{aa}^*/k for alkanes, respectively, between 75° and 20° C. This method of adjustment leaves w/k unchanged. The values for the parameters are summarized in Table II along with the computed values for C_i and D_i.

In the lower portion of Table II computed values of the K_i are presented along with Kurtz's empirical values for comparison. On using the Kurtz values in example computations of molar volumes (Table III), it was observed that the computed V were systematically low. As the bias seemed to result largely from K_1, new values for K_1 and K_5 were obtained (which are essentially those of Kurtz's (*4*) Equation 9-a.) from experimental molar volumes for three heavy paraffins at 20° C.

As indicated earlier, a new definition is used for $N_A\overline{v^*}$ (Equation 6). This must lead to different values of the K_i for two reasons. First, the conventional averaging replaces the factor v_a^* in K_1 (EQuation 5) by $\overline{v^*}$. Second, the conventional averaging omits $\Delta v^*/v_a^*$ in the K_2 term of Equation 5 and produces a similar change in K_4. Values for the K_i using the conventional procedure are also presented in Table II.

Table II. Molecular Theory Parameters and Kurtz Constants at 20° C.

Equation of State Parameters (*2*)

Hydrocarbon Type	$N_A v^*$	e_{ii}^*/k	w/k	w/kT	$y = e_{ii}^*/kT$	$\bar{y}$
Alkanes	32.10	205.0	...	...	0.6994	...
Cyclohexane ring	31.20	226.0	+112.88	0.3850	0.7709	0.7351
Benzene ring (adj.)	34.36	255.6	+71.52	0.2440	0.8720	0.7857

Computed Values of the C_i and D_i (Table I)

Quantity	Alkanes	Cyclohexane	Benzene
$\overline{C}_1$	9.455	6.095	9.388
$\overline{C}_3$	22.018	16.436	22.584
C_2	0.625	...	...
C_2'	...	0.348	−0.043
C_4	28.682	...	...
C_4'	...	31.027	34.329
D_1	...	0.1490	0.0944
D_2	...	1.259	0.7979

Kurtz Constants

		n-Alkyl				Conventional $N_A\overline{v^*}$	
Constants	Alkanes (*7*)	Cyclohexane	Benzene	Kurtz (*4*) Empirical	Least Squares, Alkane	Cyclohexane	Benzene
K_1	16.41	16.41	16.41	16.28	16.38	16.18	17.04
K_2	...	13.68	13.68	13.15	...	13.75	13.75
K_4	...	...	6.34	6.2	...	...	7.07
K_5	26.91	29.12	30.62	31.2	30.91	28.71	31.79

Table III. Comparisons of Experimental and Computed Molar Volumes

	Exptl.	Weighted $N_A v^*$		Kurtz, K_i		Least Squares, K_1 and K_5 Kurtz, K_2, K_4		Conventional $N_A\bar{v}^*$	
Hydrocarbon	V^a	V^b	Error^c	V	Error^c	V	Error^c	V^b	Error^c
$(C_6H_{11})C_{20}H_{41}$	438.2	440.9	+2.7	435.7	−2.5	437.4	−0.8	434.8	−3.4
$(C_6H_5)C_{20}H_{41}$	419.7	421.9	+2.2	417.1	−2.6	418.8	−0.9	433.9	+14.2
$(C_6H_{11})C_8H_{17}$	241.3	244.0	+2.7	240.3	−1.0	240.5	−0.5	240.6	−0.7
$(C_6H_5)C_8H_{17}$	222.2	225.0	+2.8	221.7	−0.5	222.2	0.0	229.4	+7.2

[a] Experimental densities (*1*).
[b] Using K_i in the appropriate column, Table II.
[c] Sign of error is + when computed V exceeds the experimental V.

Examples of computed and experimental molar volumes are presented in Table III where theoretically consistent values of K_i for the particular type of hydrocarbons were used.

Tables II and III lead to the following conclusions: The K_i from molecular theory using a weighted $N_A\bar{v}^*$ are as satisfactory as the empirical Kurtz values. The K_i from molecular theory using the conventional $N_A\bar{v}^*$ are inferior to those using the weighted $N_A\bar{v}^*$, and K_1 is not unique.

SUMMARY

Starting with equations of state derived by molecular theory for alkylated ring hydrocarbons, it is shown that suitable expansion leads to the form of the empirical molar volume relations for such liquid hydrocarbons. Further, good agreement is obtained for the numerical values of the constants K_i (i = 1, 2, 4, and 5) as shown in Table II. The checking of these numerical values hinges upon departing from the classical empirical rules for evaluating the molecular interaction parameters. One important feature is to make the characteristic volume per mole of centers ($N_A v^*$) a molecularly weighted average rather than the usual arithmetic average of the values for the different centers.

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NOMENCLATURE

C_i = quantities (Table I)
D_i = quantities (Table I)
d = 0 or 1, constant in Equation 2 for cyclohexyl and aryl rings, respectively.
e_{ii}^* = characteristic energy parameter: $i = a$, chain elements; $i = b$, ring elements.
h = $1 - N_A\bar{v}^*(s + s')/V$
K_i = Kurtz constants associated with N_i; temperature and pressure dependent
k = Boltzman's constant
N_A = Avogadro's number
N_i = number of carbon atoms: i = 1, in alkyl chain; i = 2, in rings; i = 4 for number of double bonds
n = number of carbon atoms in alkyl radical, $C_nH_{2n-1}^{-2}$
P = total pressure
q_i = effective number of centers, $i = a$ for chain portion; $i = b$ for ring portion of a molecule
s = number of centers in the alkyl side chain
s', s'' = number of centers in the ring portion of a molecule (for cyclohexyl or aryl and aryl rings, respectively)
T = absolute temperature (degrees Kelvin)
V = gram molar volume, ml.
v = volume per center, ml.
v^* = characteristic volume per center, ml.
$\bar{v}^*$ = average characteristic volume per center, Equation 6
w = interchange energy between chain (a) and ring (b) centers, of Equation 2
X_{ab} = quantity defined for Equation 2
Y_{ii} = e_{ii}^*/kT
$\bar{Y}$ = $(Y_{aa} + Y_{bb})/2$
z = 12, number of nearest neighbors in the space lattice

Subscripts

a = alkane elements
b = ring elements

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