Correlation for Saturated Liquid Densities of Hankinson and Thomson (COSTALD)

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Hankinson and Thomson (1979) developed a correlation for saturated densities of liquids and their mixtures, which overcame mathematical discontinuity (Yen and Woods, 1966; Gunn and Yamada, 1971) and pure compound limiting problems (Spencer and Danner, 1972) in the equations used. In addition, the COSTALD correlation leads to an average absolute percent error in pure compounds and mixtures liquid densities lower than in the Yen-Woods and Spencer-Danner correlations. Moreover, COSTALD was later successfully extended to compressed liquids and liquid mixtures (Thomson et al., 1982). These features make it possible to label this correlation as highly predictive, accurate and reliable.

The aim of this work is to enhance the capability of prediction of this correlation by introducing the group-contribution approach in the single adjustable parameter V^*, called the characteristic volume, required for each pure compound.

COSTALD Correlation

From Hankinson and Thomson (1979), we have the following pure compounds:

$$V_s/V^* = V_r^{(o)}[1 - \omega_{SRK} V_r^{(\delta)}] \tag{1}$$

$$V_r^{(o)} = 1 + \sum_{1}^{4} {}_k A_k (1 - T_r)^{k/3} \quad 0.25 < T_r < 0.95 \tag{2}$$

$$V_r^{(\delta)} = \left[\sum_{0}^{3} {}_k B_k T_r^k \right] \Big/ (T_r - 1.00001) \quad 0.25 < T_r < 1.0 \tag{3}$$

and for mixtures:

$$T_{cm} = \left(\sum_i \sum_j x_i x_j v_{ij}^* T_{cij} \right) \Big/ V_m^* \tag{4}$$

$$V_m^* = 1/4 \left[\sum_i x_i V_i^* + 3 \left(\sum_i x_i V_i^{*2/3} \right) \left(\sum_i x_i V_i^{*1/3} \right) \right] \tag{5}$$

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V_j^* T_{cj})^{1/2} \tag{6}$$

$$\omega_{SRKm} = \sum_i x_i \omega_{SRKi} \tag{7}$$

where A_k and B_k are constants in Table 1.

Characteristic Volume, V^*

In this work, we calculate the van der Waals volumes (V_W) with the group contributions proposed by Bondi (1968) for all pure compounds with V^* determined with experimental liquid density data only (Hankinson and Thomson, 1979, Table 6). A plot of V^* vs. V_W is shown in Figure 1. The clear correlation between the van der Waals and characteristic volumes observed in Figure 1 makes it worthwhile to propose an interpolation equation as a function of V_w to predict V^*:

$$V^* = \sum_{1}^{6} {}_k C_k V_w^k \qquad V_w < 300 \tag{8}$$

The C_k parameters presented in Table 1 were determined using 167 pure compounds giving an average absolute percent error F to predict V^* of 1.67%.

The characteristic volume can also be evaluated using the following equation when no liquid density was available as suggested by Hankinson and Thomson:

$$V^* = (R^* T_c/P_c)(a + b\omega_{SRK} + c\omega_{SRK}^2) \tag{9}$$

Table 1. Parameters A_k, B_k and C_k of Eqs. 2, 3, and 8, respectively

k	A	B	C
0	—	−0.29612	—
1	−1.52816	0.38691	5.3850
2	1.43907	−0.04273	−5.1022E−3
3	−0.81446	−0.04806	7.9524E−5
4	0.19045	—	−9.9316E−8
5	—	—	1.0088E−10
6	—	—	−1.1527E−12

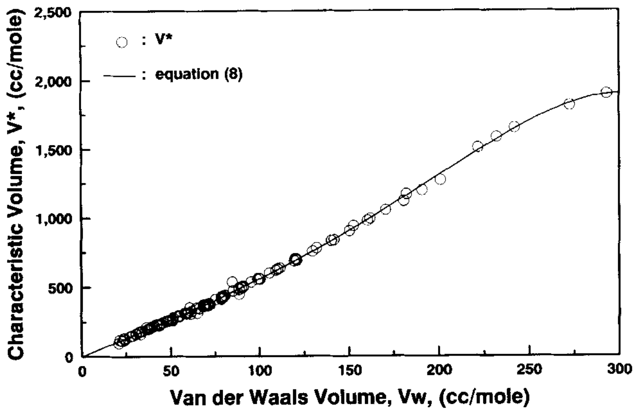

Figure 1. Characteristic volume V^* determined with experimental liquid density and the van der Waals volume V_w.

where a, b, and c differ for each class of fluids (for example, paraffins and aromatics).

A third alternative to predict V^* is to use the critical volume instead. The authors of COSTALD claimed that the discrepancy between the characteristic volume and the critical volume is very low. Thus, we also consider:

$$V^* = V_c \tag{10}$$

Results

Table 2 presents for each class of fluid the average absolute error percent given in Eq. 8 to predict V^*, while Table 3 compares the performance of Eqs. 8, 9 and 10. Unfortunately, Table 3 does not take into account as many systems as in Table 2 due to the lack of critical properties (Reid et al., 1977, 1987) or the set a, b, and c required by Eq. 9. From Tables 2 and 3, Eq. 8 holds the lowest error and the highest predictive capability. Equation 8 is not class-dependent and it uses only structural parameters.

Figure 2 shows, for example, the saturated liquid density predicted with COSTALD in Eq. 8 and the experimental data of methyl-pentyl ether, di-butyl-ether and di-hexyl-ether (Obama et al., 1985) and propanoic acid (Bernardo-Gil et al., 1990). For none of them, a, b, c and V^* were available.

Table 2. Average Absolute % Error F of Eq. 8 to Predict Characteristic Volume, V^*
$F = 100\,|\Sigma[V^* - V^*(\text{calc.})]/V^*|\,1/N$

Groups	N	F
Paraffins	40	1.28
Olefins and Diolefins	22	1.22
Cycloparaffins	10	2.69
Acetylenes	4	5.67
Aromatics	13	1.30
Fluorocarbons	7	1.37
Sulfur Compounds	57	0.74
Alcohols	4	3.36
Glycols	4	10.21
Others	6	4.71
All	167	1.67

Table 3. Comparison of Eqs. 8-10 to Predict Characteristic Volume, V^*
$F = 100\,|\Sigma[V^* - V^*(\text{calc.})]/V^*|\,1/N$

Groups	F				
	N	Eq. 8	Eq. 9	N	Eq. 10
Paraffins	34	1.12	1.30	32	2.74
Olefins and Diolefins	21	1.25	1.55	16	2.36
Cycloparaffins	8	3.04	4.01	8	1.51
Aromatics	8	1.75	0.90	7	0.76
Fluorocarbons	7	1.37	0.75	7	0.66
Sulfur compounds	5	0.49	4.50	4	1.92
All	83	1.38	1.73	74	2.10

Notation

$A_kB_kC_k$ = constants of Eqs. 2, 3 and 8, respectively
a,b,c = parameters of Eq. 9, Hankinson and Thomson (1979, Table 8)
N = number of pure compounds
R = gas constant
T = temperature, K
V = volume, cm^3/mol
x = mole fraction

Greek letter

ω_{SRK} = acentric factor from Soave equation of state

Superscript

$*$ = characteristic

Subscripts

c = critical property

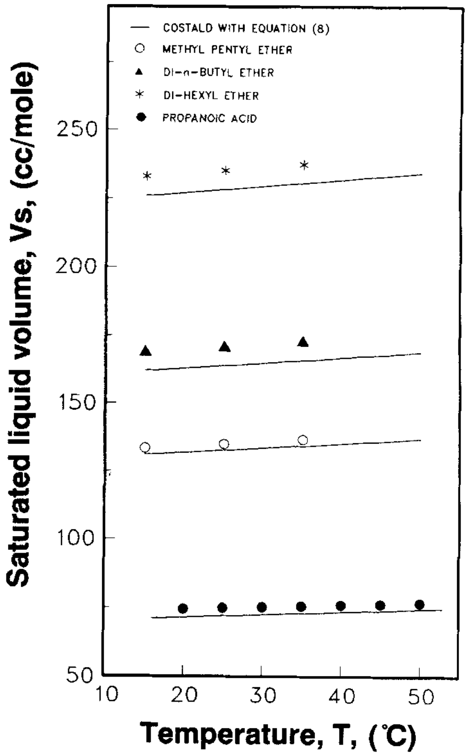

Figure 2. Saturated liquid volumes.

i = component i
m = mixture property
r = reduced property
s = saturated
w = van der Waals

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Manuscript received Sept. 16, 1991.

Errata

- In the article titled "Reaction-Driven Convection in a Porous Medium" by Farr et al. (July 1991, p. 963), the plus sign in Eq. 55 should be a minus sign. All the results reported were calculated with the correct equations.
- In the article titled "Modeling of Reaction-Induced Flow Maldistributions in Packed Beds" by Stroh and Balakotaiah (July 1991, p. 1035), v in Eq. A13 should be $\bar{v}$ (complex conjugate). All the results reported were calculated with the correct equations.
- Equation 3 of the R&D note titled "Sorption with Oscillations in Solid Polymers" by Adib and Neogi (January 1987, p. 164) should read:

$$\frac{M_t}{M_\infty} = 1 - \theta e^{-T/De} - \sum_{m=1}^{2} \sum_{k=o}^{\infty} \frac{\left(1 - \frac{y_k}{y_k + De^{-1}}\,\theta\right) e^{y_k T}}{\frac{\xi_k^2}{2} - \frac{De\xi_k^4}{2}\,\frac{(1-\omega)}{(De y_k + 1)^2}} \tag{3}$$

The figures in the note have been drawn using the correct equation.