

# Comments on 'an improved characteristic molecular volume parameter for linear solvation energy relationships of acyclic alkanes'

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**ABSTRACT:** The characteristic molecular volume parameter suggested by Palatinus *et al.* [*J. Phys. Org. Chem.*, DOI: 10.1002/poc.1065] is used in predicting the enthalpies of vaporization of 41 branched acyclic alkanes. Calculations provide one additional example illustrating where the use of the Palatinus *et al.* characteristic molecular volume parameter over the Abraham-McGowan molecular volume parameter led to a better mathematical description/description of thermodynamic and/or physical property data for branched acyclic alkanes. Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** enthalpies of vaporization; acyclic alkanes; characteristic molecular volume

In a recent paper appearing in this journal, Palatinus *et al.*<sup>1</sup> suggested calculating the characteristic volume parameter of branched acyclic alkanes from

$$V_Y(\text{for branched acyclic alkanes}) = 0.0498 \left( \frac{T_{\text{bp}} + 270}{230.14} \right)^3 + 0.0015 \quad (1)$$

the molecule's normal boiling point temperature,  $T_{\text{bp}}$ . The mathematical correlation between  $V_Y$  and  $T_{\text{bp}}$  was established based on the Abraham-McGowan volumes,  $V_X$ , and boiling point temperatures of n-alkanes from propane to hexadecane (for n-alkanes  $V_Y = V_X$ ), and then used to calculate  $V_Y$  values for 168 branched alkanes having from 4 to 12 carbon atoms. The authors presented an impressive set of correlations involving gas chromatographic and reversed-phase HPLC retention indices, and Ostwald coefficients in both hexadecane and methanol, documenting the superiority of  $V_Y$  over the Abraham-McGowan molecular volumes. The Abraham-McGowan<sup>2</sup> molecular volumes are calculated from atomic sizes and chemical bond numbers; hence, all isomers of a given

$\text{C}_n\text{H}_{2n+2}$  alkane must have an identical Abraham-McGowan molecular volume.

We wish to point out that the authors' method of computing the characteristic molecular volume parameter of branched acyclic alkanes also leads to much better predictions of standard molar enthalpies of vaporization of 298.15 K,  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$ . In Table 1, we have compiled values of 16 n-alkanes (pentane through eicosane), along with the molecule's Abraham-McGowan molecular volume,  $V_X$ . Linear least-squares analysis of the 16 ordered data pairs gave

$$\Delta_{\text{vap}}H_{298\text{K}}^\circ = 35.371V_Y - 2.175 \quad (2)$$

$$N = 16, \quad R^2 = 1.00, \quad \text{and} \quad SD = 0.218$$

The experimental values in the regression analysis were the 'recommended values' in an IUPAC critical review and data compilation<sup>3</sup> of enthalpies of vaporization of organic compounds.

The obtained correlation is then used to estimate  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$  values of 41 branched acyclic alkanes. The characteristic molecular volumes used in the computations were based on Eqn (1) and experimental boiling point temperatures,  $T_{\text{bp}}$ . The results of our calculations are given in Table 2, along with the numerical values that

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Table 1. Standard molar enthalpies of vaporization data and Abraham-McGowan characteristic molecular volume parameters for n-alkanes

n-Alkane	$V_X$	$\Delta_{\text{vap}}H_{298\text{K}}^\circ$ (kJ/mole)
Pentane	0.8131	26.75
Hexane	0.9540	31.73
Heptane	1.0949	36.66
Octane	1.2358	41.53
Nonane	1.3767	46.43
Decane	1.5176	51.39
Undecane	1.6590	56.43
Dodecane	1.7994	61.51
Tridecane	1.9400	66.43
Tetradecane	2.0812	71.30
Pentadecane	2.2221	76.11
Hexadecane	2.3630	81.38
Heptadecane	2.5039	86.02
Octadecane	2.6448	91.4 <sup>a</sup>
Nonadecane	2.7857	96.4 <sup>a</sup>
Eicosane	2.9226	101.8 <sup>a</sup>

<sup>a</sup>Enthalpy of vaporization data is from Chickos and Hanshaw<sup>4</sup>.

would be calculated using the Abraham-McGowan characteristic volume,  $V_X$ . The average absolute deviation between the 41 observed and calculated values based on  $V_Y$  is 0.598 kJ/mole, which is significantly less than the average absolute deviation between observed and calculated values of 3.541 kJ/mole based on  $V_X$ . These calculations provide one additional example illustrating where the use of the  $V_Y$  characteristic molecular volume parameter led to a better mathematical description/description of thermodynamic and/or physical property data for branched acyclic alkanes. The computations are important in that experimental enthalpy of vaporization data is fairly sparse for branched acyclic alkanes. Equation (2) should be able to provide reasonably accurate predictions of  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$  in the absence of a measured value.

We note that combination of Eqns (1) and (2) yields a direct mathematical relationship

$$\Delta_{\text{vap}}H_{298\text{K}}^\circ = 1.7614 \left( \frac{T_{\text{bp}} + 270}{230.14} \right)^3 - 2.1219 \quad (3)$$

between  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$  and  $T_{\text{bp}}$  for branched acyclic alkanes. Relationships between  $T_{\text{bp}}$  and physical (and thermodynamic) properties can be found in the literature. For example, Mackay *et al.*<sup>6</sup> developed a mathematical expression involving vapor pressure and  $T_{\text{bp}}$  based on Trouton's rule. White<sup>7</sup> observed a linear relationship, the experimental gas chromatographic retention index and  $T_{\text{bp}}$  for 48 planar polycyclic aromatic hydrocarbons. Screttas and Micha-Screttas reported that the  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$  of hydrocarbons in general cluster around the straight line given by

$$\Delta_{\text{vap}}H_{298\text{K}}^\circ = 0.151 T_{\text{bp}} - 19.735 \quad (4)$$

Table 2. Standard molar enthalpies of vaporization data and Abraham-McGowan characteristic molecular volume parameters for branched acyclic alkanes

n-Alkane	$V_Y^a$	$\Delta_{\text{vap}}H_{298\text{K}}^\circ$ (kJ/mole)		
		Exp.	Calc- $V_Y$	Calc- $V_X$
Isopentane	0.7621	25.22	24.781	26.585
Neopentane	0.6913	22.39	22.277	26.585
3-Methylpentane	0.9142	30.47	30.161	31.569
2,2-Dimethylbutane	0.8530	27.93	27.997	31.569
2,3-Dimethylbutane	0.8888	29.33	29.263	31.569
2-Methylhexane	1.0387	34.98	34.565	36.553
3-Methylhexane	1.0476	35.16	34.880	36.553
3-Ethylpentane	1.0555	35.32	35.161	36.553
2,2-Dimethylpentane	0.9866	32.56	32.722	36.553
2,3-Dimethylpentane	1.0373	34.36	34.515	36.553
2,4-Dimethylpentane	0.9927	33.02	32.938	36.553
3,3-Dimethylpentane	1.0192	33.15	33.875	36.553
2,2,3-Trimethylbutane	0.9942	32.19	32.991	36.553
2-Methylheptane	1.1804	39.72	39.577	41.537
3-Methylheptane	1.1873	39.88	39.821	41.537
4-Methylheptane	1.1809	39.75	39.595	41.537
3-Ethylhexane	1.1852	39.69	39.747	41.537
2,2-Dimethylhexane	1.1339	37.36	37.932	41.537
2,3-Dimethylhexane	1.1697	38.83	39.199	41.537
2,4-Dimethylhexane	1.1370	37.83	38.042	41.537
2,5-Dimethylhexane	1.1355	37.92	37.989	41.537
3,3-Dimethylhexane	1.1501	37.60	38.505	41.537
3,4-Dimethylhexane	1.1809	39.03	39.595	41.537
3-Ethyl-2-methylpentane	1.1697	38.56	39.199	41.537
3-Ethyl-3-methylpentane	1.1836	38.05	39.690	41.537
2,2,3-Trimethylpentane	1.1391	36.98	38.116	41.537
2,2,4-Trimethylpentane	1.0846	35.24	36.188	41.537
2,3,3-Trimethylpentane	1.1649	37.33	39.029	41.537
2,3,4-Trimethylpentane	1.1580	37.82	38.785	41.537
2,2,5-Trimethylhexane	1.2149	40.21	40.801	46.520
2,3,5-Trimethylhexane	1.2552	41.45	42.223	46.520
2,2,4,4-	1.2057	38.55	40.472	46.520
Tetramethylpentane				
3,3-Diethylpentane	1.3401	42.05	45.226	46.520
2-Methylnonane	1.4650	49.64	49.644	51.504
3-Methylnonane	1.4700	49.72	49.820	51.504
5-Methylnonane	1.4533	49.35	49.230	51.504
2,4-Dimethyloctane	1.3975	47.14	47.256	51.504
2-Methyldecane	1.6066	54.29	54.652	56.506
4-Methyldecane	1.5915	53.77	54.118	56.506
2,4,7-Trimethyloctane	1.4712	49.93	49.863	56.506
2,2,4,6,6-	1.5328	49.00 <sup>b</sup>	52.042	61.472
Pentamethylheptane				

<sup>a</sup>Numerical values are calculated using the boiling point temperatures given in IUPAC compilation<sup>3</sup>.

<sup>b</sup>Numerical value was taken from Chickos and Acree<sup>5</sup>.

$$N = 58, \quad R = 0.989$$

Equation (4) forms the basis of one additional predictive method based on normal boiling point temperature. Equation (4) predicts the  $\Delta_{\text{vap}}H_{298\text{K}}^\circ$  values of the 41 branched acyclic alkanes listed in Table 2 to within an average absolute deviation of 1.107 kJ/mole, which is larger than the correlation that we have developed based

on the characteristic molecular volume suggested by Palantinus *et al.*<sup>1</sup>

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