ABRAHAM SOLVATION PARAMETER MODEL: PREDICTION OF ENTHALPIES OF VAPORIZATION AND SUBLIMATION OF MONO-METHYL BRANCHED ALKANES USING MEASURED GAS CHROMATOGRAPHIC DATA

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Abraham model L solute descriptors have been determined for 174 additional mono-methyl branched alkanes based on published linear-programmed gas chromatographic retention indices. Standard molar enthalpies of vaporization and sublimation at 298 K are calculated for the 174 mono-methylated alkanes using the reported solute descriptors and our recently published Abraham model correlations. Calculated vaporization and sublimation enthalpies derived from the Abraham model compare very favourably with values based on a popular atom-group additivity model. Unlike the additivity model the Abraham model gives different predicted values for each mono-methyl alkane having a given C_nH_{2n+2} molecular formula.

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INTRODUCTION

Gas-liquid chromatographic measurements[1-10] have been used in the indirect determination of both standard molar enthalpies of vaporization, $\Delta H_{vap,298K}$, and standard molar enthalpies of sublimation, $\Delta H_{sub,298K}$, of organic compounds at 298 K. For example, Hamilton[1] determined the $\Delta H_{vap,298K}$ of eleven herbicide esters based on experimental gas chromatographic retention volumes, V_g, measured on a nonpolar SE-30 stationary phase. The method assumed that the ratio of the enthalpy of vaporization of each herbicide ester to that of the reference compound (which in this case was dibutyl phthalate) was independent of temperature. The $\Delta H_{vap,298K}$ of each individual ester herbicide was calculated from the slope of the graph of $ln(V_{g,ester}/V_{g,reference})$ versus the natural logarithm of the vapor pressure of the reference compound at the column temperature T, $ln\ P_{reference,T}$, in accordance to Eqn. (1).

$$ln\left(\frac{V_{g,ester}}{V_{g,reference}}\right) = \left[1 - \frac{\Delta H_{vap,ester,298K}}{\Delta H_{vap,reference,298K}}\right] ln\ P_{reference,T} + C \quad (1)$$

Peacock and Fuchs[2-4] developed a method for determining $\Delta H_{vap,298K}$ based on solution calorimetric measurements of liquid organic compounds being dissolved in the stationary phase solvent. The enthalpy of vaporization was calculated as the difference in the measured enthalpy of solution of the organic liquid, $\Delta H_{soln,298K}$, minus the chromatographically-measured enthalpy of solution of the gaseous compound in the stationary phase liquid. The later value was determined from the variation in the compound's retention volumes with temperature, and then corrected back to 298 K using liquid-phase and gas-phase heat capacities.

Chickos and coworkers[5] proposed a method for determination of $\Delta H_{vap,298K}$ based on linear plots of the chromatographically-measured ΔH_{soln} values of gaseous reference compounds in the liquid stationary phase versus the compounds' known $\Delta H_{vap,298K}$ values. Enthalpies of vaporization of additional compounds can then be calculated from the linear mathematical relationship established by the reference compounds. The authors demonstrated the applicability of their method using 102 hydrocarbon and mono-functional hydrocarbon derivatives. Enthalpies of vaporization based on the authors' method differed from published literature values by a standard deviation of 1.27 kJ mol^{-1}. The method was later extended to the determination of $\Delta H_{sub,298K}$ by combining $\Delta H_{vap,298K}$ values measured by correlation gas chromatography with calorimetric enthalpy of fusion, $\Delta H_{fus,298K}$, adjusted to 298 K.[6] Numerical values of $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ determined in this fashion depend on the reference compounds used in establishing the ΔH_{soln} versus $\Delta H_{vap,298K}$ mathematical correlation.

Our method of obtaining $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values is more of a computational method that uses gas chromatographic retention data to calculate Abraham model solute descriptors. Once calculated, the numerical values of the solute descriptors are then used in conjugation with our published Abraham model correlations[11,12] to calculate the desired $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values of organic, organometallic and inorganic compounds. The Abraham solvation parameter model is among the most widely used linear free energy relationship in the prediction of solute properties having chemical and biological significance. To

date predictive mathematical correlations have been reported for describing solute transfer into more than 130 different organic nonelectrolyte mono-solvents[13-19] and into more than 100 different ionic liquid solvents.[20-29] Mathematical correlations have also been developed for predicting enthalpies of solvation of organic vapors and inorganic gases into water and 35 common organic solvents[30-40] blood-to-body tissues/fluids partition coefficients,[41-45] lethal median concentrations of organic compounds towards fish and other aquatic organisms,[46-49] nasal pungency,[50-53] eye irritation thresholds and Draize eye scores,[53-55] and many other solute properties.[56-61] More recently the Abraham model has been extended to predicting enthalpies of vaporization[11] and sublimation[12] and the vapor pressure of organic and organometallic compounds.[62]

In the present communication we illustrate the application of the Abraham solvation parameter model in predicting $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values. First, we calculate the Abraham model solute descriptors of mono-methyl branched alkanes from published gas chromatographic retention indices of Krkosova and co-workers.[63] Once calculated, the solute descriptors will be substituted into our previously published Abraham model correlations.[11,12]

$$\Delta H_{vap,298K}\ (\text{kJ mol}^{-1}) = 6.100 - 7.363\ \boldsymbol{E} + 9.733\ \boldsymbol{S} + 4.025\ \boldsymbol{A} + 2.123\ \boldsymbol{B} + 9.537\ \boldsymbol{L} - 1.180\ \boldsymbol{S \cdot S} + 77.871\ \boldsymbol{A \cdot B} - 5.781\ \boldsymbol{I}_{\text{amine}} - 14.783\ \boldsymbol{I}_{\text{non-}\alpha,\omega\text{-diol}} - 17.873\ \boldsymbol{I}_{\alpha,\omega\text{-diol}} \quad (2)$$

(N = 703, SD = 2.09, R^2 = 0.986, F = 4925.6) and

$$\Delta H_{sub,298K}\ (\text{kJ mol}^{-1}) = 13.93 - 16.90\ \boldsymbol{E} + 9.66\ \boldsymbol{S} + 10.02\ \boldsymbol{A} + 1.82\ \boldsymbol{B} + 13.57\ \boldsymbol{L} - 0.30\ \boldsymbol{S \cdot S} + 35.43\ \boldsymbol{A \cdot B} - 0.05\ \boldsymbol{L \cdot L} - 9.09\ \boldsymbol{I}_{\text{OH,adj}} + 17.26\ \boldsymbol{I}_{\text{OH,non}} + 7.37\ \boldsymbol{I}_{\text{NH}} \quad (3)$$

(N = 864, SD = 9.94, R^2 = 0.867, F = 503.2)

Thus enabling the estimation of $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values for those compounds for which solute descriptors are known. Solute descriptors are identified in Eqns. 2 and 3 by the capitalized alphabetical characters, and are defined as follows: the solute excess molar refractivity expressed in units of (cm^3 mol^{-1}) / 10(***E***); the solute dipolarity/polarizability (***S***); the overall or summation hydrogen-bond acidity and basicity (***A*** and ***B***, respectively); and the logarithm of the gas-to-hexadecane partition coefficient at 298 K (***L***). Both Abraham model correlations use indicator variables ($\boldsymbol{I}_{\text{amine}}$, $\boldsymbol{I}_{\text{NH}}$, $\boldsymbol{I}_{\text{non-}\alpha\omega\text{-diol}}$, $\boldsymbol{I}_{\alpha\omega\text{-diol}}$, $\boldsymbol{I}_{\text{OH,adj}}$, $\boldsymbol{I}_{\text{OH,non}}$) to improve the predictions or organic compounds having amino- and more than one hydroxy-functional group. Mono-methylalkanes do not contain either of these functional groups, so no further discussion of indicator variables is needed. The two mathematical correlations were developed based on $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values for N = 703 and N = 864 compounds, respectively. As indicated by the standard deviation (SD), squared correlations coefficient (R^2), and Fisher F-statistic (F), both Abraham model correlations provide reasonably accurate mathematical correlations of the $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ data for wide range of organic compounds.

Several earlier publications have illustrated the calculation of Abraham model solute descriptors from either liquid-liquid partition coefficients,[64] or high-performance liquid chromatographic retention data,[65] or in the case of crystalline nonelectrolyte compounds from saturation solubilities.[66-70] The latter papers primarily focused on using the calculated solute descriptors to select organic solvents for recrystallization and/or biphasic partitioning systems for liquid extraction. The intended audience of the solubility studies were chemical engineers and industrial working in the chemical manufacturing sector. Recrystallizations and liquid extractions are commonly used purification methods in chemical syntheses. A more recent publication[71] reported Abraham solute descriptors of terpene esters determined from gas-liquid chromatographic retention data of solutes eluted on several stationary phase liquids. Here the application was to predict the human odor thresholds of the terpene esters. Solute descriptors of terpene hydrocarbons[72] had been reported previously. There was very little information in the afore-mentioned studies that would attract the attention of chemical thermodynamic experts or computation chemists, which is the intended audience of the current communication. The calculated solute descriptors of mono-methyl branched alkanes will be used to predict thermodynamic properties, namely $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values. These thermodynamic quantities are required in the calculation of gas-phase standard molar enthalpies of formation from measured enthalpies of combustion, and in describing how the vapour pressure of a compound varies with temperature. Such information is also needed by individuals working in the chemical manufacturing sector.

CALCULATION OF ABRHAM MODEL SOLUTE DESCRIPTORS

Determination of solute descriptors generally involves constructing a series of Abraham model correlations that involve solute transfer between two condensed phases (Eqn. 4) or solute transfer from the gas phase into a condensed phase (Eqn. 5).

$$\text{Solute property} = c_p + e_p \cdot \boldsymbol{E} + s_p \cdot \boldsymbol{S} + a_p \cdot \boldsymbol{A} + b_p \cdot \boldsymbol{B} + v_p \cdot \boldsymbol{V} \quad (4)$$

$$\text{Solute property} = c_k + e_k \cdot \boldsymbol{E} + s_k \cdot \boldsymbol{S} + a_k \cdot \boldsymbol{A} + b_k \cdot \boldsymbol{B} + l_k \cdot \boldsymbol{L} \quad (5)$$

Solute properties used in these computations have included the logarithms of partition coefficients, logarithms of molar solubility ratios, logarithms of chromatographic retention factors, and chromatographic retention indices. Two of the solute descriptors, ***E*** and ***V*** (McGowan volume), can be reasonably estimated from the solute's molecular structure. For solutes that lack an acidic hydrogen capable of hydrogen-bond formation, the ***A*** solute descriptor can be set equal to zero. This leaves either four solute descriptors (***S, A, B*** and ***L***) or three solute descriptors (***S, B*** and ***L***) to be determined from the Abraham model correlations from the measured solute properties.

The numerical values of c_p, e_p, s_p, a_p, b_p, v_p, c_k, e_k, s_k, a_k, b_k, and l_k in Eqns. 4 and 5 are known as the solute properties are measured in systems having known values of solvent/process coefficients. The set of Abraham model equations are then solved simultaneously to yield numerical descriptor values for the given solute molecule.

In the case of mono-methyl branched alkane solutes the computation is greatly simplified as $\boldsymbol{E} = 0$, $\boldsymbol{S} = 0$, $\boldsymbol{A} = 0$ and $\boldsymbol{B} = 0$. Mono-methyl branched alkane solutes possess no excess molar refraction ($\boldsymbol{E} = 0$) or polarity/polarizability ($\boldsymbol{S} = 0$), and are not capable of hydrogen-bond formation ($\boldsymbol{A} = 0$ and $\boldsymbol{B} = 0$) with surrounding solvent molecules. Only the $\boldsymbol{L}$ solute descriptor remains to be calculated. We calculate the $\boldsymbol{L}$ solute descriptor of the mono-methyl branched alkanes by first establishing a linear relationship between the measured temperature-programmed linear retention indices, *RI*, and the $\boldsymbol{L}$ solute descriptor based on the values for the n-alkanes and 22 of the 196 compounds studied by Krkosova and coworkers[63] for which we have a known $\boldsymbol{L}$ solute descriptor.

$$\boldsymbol{L} = 0.505(0.000)\ (RI/100) - 0.381(0.007) \qquad (6)$$

($N = 49$, $SD = 0.022$, $R^2 = 1.000$, $F = 1323009$)

Standard errors in the equation coefficients are given in parenthesis immediately following the respective coefficient. Numerical values for the 49 compounds used in constructing Eqn. (6) are tabulated in Table 1. The derived mathematical relationship then allows us to calculate the L-solute descriptors of the remaining 174 mono-methyl branched alkanes. These calculations are summarized in the last column of Table 1. Examination of the numerical entries reveals that eqn. (6) provides reasonably accurate back-calculation of the known **L** descriptor values as one might expect from the correlation's small standard deviation, SD = 0.022, and near unity value for the squared correlation coefficient, $R^2 = 1.000$.

Table 1. Retention Indices, *RI*, and Abraham Model $\boldsymbol{L}$ Solute Descriptors for n-Alkanes and Mono-methyl Branched Alkanes.

Compound	*RI*	*L* value (database)	*L* value Eqn. 6
Butane	400.00	1.615	1.643
2-Methylpropane	354.77	1.409	1.414
Pentane	500.00	2.162	2.149
2-Methylbutane	466.23	2.013	1.978
Hexane	600.00	2.668	2.655
2-Methylpentane	561.31	2.503	2.459
3-Methylpentane	578.05	2.581	2.544
Heptane	700.00	3.173	3.161
2-Methylhexane	662.48	3.001	2.971
3-Methylhexane	672.19	3.044	3.020
Octane	800.00	3.677	3.667
2-Methylheptane	764.32	3.480	3.486
4-Methylheptane	765.88	3.483	3.494
3-Methylheptane	772.17	3.510	3.526
Nonane	900.00	4.182	4.173
4-Methyloctane	864.06	3.961	3.991
2-Methyloctane	865.00	3.966	3.996
3-Methyloctane	871.89	3.998	4.031
Decane	1000.00	4.686	4.679
5-Methylnonane	961.09	4.432	4.482
4-Methylnonane	962.83	4.441	4.491
2-Methylnonane	965.39	4.453	4.504
3-Methylnonane	972.06	4.486	4.538
Undecane	1100.00	5.191	5.185
5-Methyldecane	1058.94	4.963	4.977
4-Methyldecane	1062.04	4.963	4.993
2-Methyldecane	1065.62	4.981	5.011
3-Methyldecane	1072.06	5.037	5.044
Dodecane	1200.00	5.696	5.691
6-Methylundecane	1156.16		5.469
5-Methylundecane	1157.36		5.475
4-Methylundecane	1161.21		5.495
2-Methylundecane	1165.48		5.516
3-Methylundecane	1172.15		5.550
Tridecane	1300.00	6.200	6.197
6-Methyldodecane	1254.15		5.965
5-Methyldodecane	1256.18		5.975
4-Methyldodecane	1260.75		5.998
2-Methyldodecane	1265.36		6.022
3-Methyldodecane	1272.12		6.056
Tetradecane	1400.00	6.705	6.703
7-Methyltridecane	1351.94		6.460
6-Methyltridecane	1352.60		6.463
5-Methyltridecane	1355.43		6.477
4-Methyltridecane	1360.35		6.502
2-Methyltridecane	1365.35		6.528
3-Methyltridecane	1372.33		6.563
Pentadecane	1500.00	7.209	7.209
7-Methyltetradecane	1450.13		6.957
6-Methyltetradecane	1451.63		6.964
5-Methyltetradecane	1454.71		6.980
4-Methyltetradecane	1460.18		7.008
2-Methyltetradecane	1465.37		7.034
3-Methyltetradecane	1472.51		7.070
Hexadecane	1600.00	7.714	7.715
8-Methylpentadecane	1548.19		7.453
7-Methylpentadecane	1548.85		7.456
6-Methylpentadecane	1550.66		7.465
5-Methylpentadecane	1554.24		7.483
4-Methylpentadecane	1559.97		7.512
2-Methylpentadecane	1565.24		7.539
3-Methylpentadecane	1572.67		7.577
Heptadecane	1700.00	8.218	8.221
8-Methylhexadecane	1646.96		7.953
7-Methylhexadecane	1647.63		7.956
6-Methylhexadecane	1650.07		7.968
5-Methylhexadecane	1653.97		7.988
4-Methylhexadecane	1659.91		8.018
2-Methylhexadecane	1665.35		8.046
3-Methylhexadecane	1672.99	8.073	8.084
Octadecane	1800.00	8.722	8.727
9-Methylheptadecane	1745.40		8.451
8-Methylheptadecane	1745.55		8.451
7-Methylheptadecane	1746.93		8.458
6-Methylheptadecane	1749.71		8.473
5-Methylheptadecane	1753.65		8.492
4-Methylheptadecane	1759.94		8.524

2-Methylheptadecane	1765.29		8.551
3-Methylheptadecane	1773.21	8.573	8.591
Nonadecane	1900.00	9.226	9.233
9-Methyloctadecane	1844.03		8.950
8-Methyloctadecane	1844.56		8.952
7-Methyloctadecane	1846.51		8.962
6-Methyloctadecane	1849.34		8.977
5-Methyloctadecane	1853.61		8.998
4-Methyloctadecane	1859.97		9.030
2-Methyloctadecane	1865.28		9.057
3-Methyloctadecane	1873.44		9.099
Eicosane	2000.00	9.731	9.739
10-Methylnonadecane	1942.61		9.449
9-Methylnonadecane	1943.01		9.451
8-Methylnonadecane	1943.74		9.454
7-Methylnonadecane	1945.79		9.465
6-Methylnonadecane	1948.99		9.481
5-Methylnonadecane	1953.45		9.503
4-Methylnonadecane	1959.94		9.536
2-Methylnonadecane	1965.23		9.563
3-Methylnonadecane	1973.84		9.607
Heneicosane	2100.00	10.236	10.245
10-Methyleicosane	2041.65		9.950
9-Methyleicosane	2042.17		9.952
8-Methyleicosane	2043.28		9.958
7-Methyleicosane	2045.45		9.969
6-Methyleicosane	2048.79		9.986
5-Methyleicosane	2053.39		10.009
4-Methyleicosane	2060.16		10.043
2-Methyleicosane	2065.34		10.070
3-Methyleicosane	2074.15		10.114
Docosane	2200.00	10.740	10.751
11-Methylheneicosane	2140.37		10.449
10-Methylheneicosane	2140.48		10.450
9-Methylheneicosane	2141.20		10.453
8-Methylheneicosane	2142.57		10.460
7-Methylheneicosane	2144.97		10.473
6-Methylheneicosane	2148.36		10.490
5-Methylheneicosane	2153.24		10.514
4-Methylheneicosane	2160.05		10.549
2-Methylheneicosane	2165.23		10.575
3-Methylheneicosane	2174.30		10.621
Tricosane	2300.00	11.252	11.257
11-Methyldocosane	2239.26		10.950
10-Methyldocosane	2239.65		10.952
9-Methyldocosane	2240.71		10.957
8-Methyldocosane	2242.27		10.965
7-Methyldocosane	2244.66		10.977
6-Methyldocosane	2248.15		10.995
5-Methyldocosane	2253.04		11.019
4-Methyldocosane	2260.03		11.055
2-Methyldocosane	2265.06		11.080
3-Methyldocosane	2274.34		11.127
Tetracosane	2400.00	11.758	11.763
12-Methyltricosane	2338.03		11.449
11-Methyltricosane	2338.15		11.450
10-Methyltricosane	2338.69		11.453
9-Methyltricosane	2340.01		11.459
8-Methyltricosane	2341.69		11.468
7-Methyltricosane	2344.25		11.481
6-Methyltricosane	2347.92		11.499
5-Methyltricosane	2352.88		11.525
4-Methyltricosane	2360.07		11.561
2-Methyltricosane	2365.04		11.586
3-Methyltricosane	2374.70		11.635
Pentacosane	2500.00	12.264	12.269
12-Methyltetracosane	2437.35		11.952
11-Methyltetracosane	2437.61		11.953
10-Methyltetracosane	2438.25		11.957
9-Methyltetracosane	2439.74		11.964
8-Methyltetracosane	2441.52		11.973
7-Methyltetracosane	2444.20		11.987
6-Methyltetracosane	2447.95		12.006
5-Methyltetracosane	2452.97		12.031
4-Methyltetracosane	2460.14		12.067
2-Methyltetracosane	2465.07		12.092
3-Methyltetracosane	2474.86		12.142
Hexacosane	2600.00	12.770	12.775
13-Methylpentacosane	2536.47		12.454
12-Methylpentacosane	2536.54		12.454
11-Methylpentacosane	2536.98		12.456
10-Methylpentacosane	2537.74		12.460
9-Methylpentacosane	2539.36		12.468
8-Methylpentacosane	2541.32		12.478
7-Methylpentacosane	2543.98		12.492
6-Methylpentacosane	2547.85		12.511
5-Methylpentacosane	2553.15		12.538
4-Methylpentacosane	2560.60		12.576
2-Methylpentacosane	2565.29		12.599
3-Methylpentacosane	2575.45		12.651
Heptacosane	2700.00	13.276	13.281
13-Methylhexacosane	2635.44		12.954
12-Methylhexacosane	2635.87		12.957
11-Methylhexacosane	2636.31		12.959
10-Methylhexacosane	2637.35		12.964
9-Methylhexacosane	2639.09		12.973
8-Methylhexacosane	2641.09		12.983
7-Methylhexacosane	2643.84		12.997
6-Methylhexacosane	2647.91		13.017
5-Methylhexacosane	2653.06		13.043
4-Methylhexacosane	2660.71		13.082
2-Methylhexacosane	2665.30		13.105
3-Methylhexacosane	2675.72		13.158
Octacosane	2800.00	13.780	13.787
14-Methylheptacosane	2734.93		13.458
13-Methylheptacosane	2735.00		13.458
12-Methylheptacosane	2735.45		13.460
11-Methylheptacosane	2736.16		13.464
10-Methylheptacosane	2737.21		13.469
9-Methylheptacosane	2739.14		13.479
8-Methylheptacosane	2741.07		13.489
7-Methylheptacosane	2743.87		13.503
6-Methylheptacosane	2747.82		13.523
5-Methylheptacosane	2753.22		13.550
4-Methylheptacosane	2760.86		13.589
2-Methylheptacosane	2765.26		13.611
3-Methylheptacosane	2776.09		13.666
Nonacosane	2900.00	14.291	14.293

14-Methyloctacosane	2834.42		13.961
13-Methyloctacosane	2834.57		13.962
12-Methyloctacosane	2835.14		13.965
11-Methyloctacosane	2835.88		13.969
10-Methyloctacosane	2837.14		13.975
9-Methyloctacosane	2839.07		13.985
8-Methyloctacosane	2841.19		13.995
7-Methyloctacosane	2843.96		14.009
6-Methyloctacosane	2848.04		14.030
5-Methyloctacosane	2853.40		14.057
4-Methyloctacosane	2861.18		14.097
2-Methyloctacosane	2865.70		14.119
3-Methyloctacosane	2876.38		14.173
Triacontane	3000.00	14.794	14.799
15-Methylnonacosane	2933.77		14.464
14-Methylnonacosane	2933.82		14.464
13-Methylnonacosane	2934.26		14.466
12-Methylnonacosane	2934.85		14.469
11-Methylnonacosane	2935.54		14.473
10-Methylnonacosane	2937.00		14.480
9-Methylnonacosane	2938.90		14.490
8-Methylnonacosane	2941.11		14.501
7-Methylnonacosane	2943.93		14.515
6-Methylnonacosane	2948.14		14.537
5-Methylnonacosane	2953.43		14.563
4-Methylnonacosane	2961.56		14.604
2-Methylnonacosane	2965.72		14.626
3-Methylnonacosane	2976.43		14.680

PREDICTION OF STANDARD MOLAR ENTHALPIES OF VAPORIZATION AND SUBLIMATION

The chromatographic retention measurements performed by Krkosova and coworkers[63] allowed us to have a complete set of solute descriptors for an additional 180 saturated hydrocarbons. Previously we had only the five solute descriptors (***E, S, A, B***, and ***V***) needed for Eqn. (4). Published studies have shown, however, that Eqn. (5) of the Abraham model provides the better set of predicted values for several thermodynamic properties such as enthalpies of vaporization[11] and enthalpies of solvation of organic vapours and inorganic gases dissolved both in water and in organic solvents.[30-40] Having a complete set of solute descriptors will provide better applicability for these important thermodynamic quantities.

We illustrate the application of the Abraham model by calculating the enthalpies of vaporization (Eqn. 7) and enthalpies of solvation (Eqn. 8) of the 174 mono-methyl branched alkanes for which we have just determined the ***L*** descriptor. For the convenience of the reader we have simplified the predictive expressions to contain only the non-zero terms.

$$\Delta H_{vap,298K}\ (\text{kJ mol}^{-1}) = 6.100 + 9.537\ \boldsymbol{L} \qquad (7)$$

$$\Delta H_{sub,298K}\ (\text{kJ mol}^{-1}) = 13.93 + 13.57\ \boldsymbol{L} - 0.05\ \boldsymbol{L}\cdot\boldsymbol{L} \qquad (8)$$

Enthalpy of sublimation predictions given in Table 2, start with the C_{20}-compounds as most of the smaller compounds is liquid at 298 K. Predicted values of $\Delta H_{vap,298K}$ are given in Table 3 for all compounds as vaporization enthalpies of compounds that are crystalline at 298 K can be easily determined using the method of correlation gas chromatography.[5]

Table 2. Comparison of the Enthalpies of Sublimation, $\Delta H_{sub,298K}$ (kJ mol^{-1}), Predicted by the Abraham Model Eqn. (6) and the Group-Additivity Method of Naef and Acree (Eqn. 11).

Compound	$\Delta H_{sub,298K}$ **Eqn. 8**	$\Delta H_{sub,298K}$ **Eqn. 11**
10-Methylnonadecane	137.68	140.76
9-Methylnonadecane	137.71	140.76
8-Methylnonadecane	137.76	140.76
7-Methylnonadecane	137.89	140.76
6-Methylnonadecane	138.09	140.76
5-Methylnonadecane	138.38	140.76
4-Methylnonadecane	138.79	140.76
2-Methylnonadecane	139.13	140.76
3-Methylnonadecane	139.68	140.76
10-Methyleicosane	144.00	147.11
9-Methyleicosane	144.03	147.11
8-Methyleicosane	144.10	147.11
7-Methyleicosane	144.24	147.11
6-Methyleicosane	144.45	147.11
5-Methyleicosane	144.75	147.11
4-Methyleicosane	145.18	147.11
2-Methyleicosane	145.50	147.11
3-Methyleicosane	146.06	147.11
11-Methylheneicosane	150.27	153.46
10-Methylheneicosane	150.27	153.46
9-Methylheneicosane	150.32	153.46
8-Methylheneicosane	150.41	153.46
7-Methylheneicosane	150.56	153.46
6-Methylheneicosane	150.77	153.46
5-Methylheneicosane	151.08	153.46
4-Methylheneicosane	151.51	153.46
2-Methylheneicosane	151.84	153.46
3-Methylheneicosane	152.42	153.46
11-Methyldocosane	156.52	159.81
10-Methyldocosane	156.55	159.81
9-Methyldocosane	156.61	159.81
8-Methyldocosane	156.71	159.81
7-Methyldocosane	156.86	159.81
6-Methyldocosane	157.08	159.81
5-Methyldocosane	157.39	159.81
4-Methyldocosane	157.83	159.81
2-Methyldocosane	158.15	159.81
3-Methyldocosane	158.73	159.81
12-Methyltricosane	162.74	166.16
11-Methyltricosane	162.75	166.16
10-Methyltricosane	162.79	166.16
9-Methyltricosane	162.87	166.16

8-Methyltricosane	162.97	166.16
7-Methyltricosane	163.14	166.16
6-Methyltricosane	163.37	166.16
5-Methyltricosane	163.68	166.16
4-Methyltricosane	164.13	166.16
2-Methyltricosane	164.44	166.16
3-Methyltricosane	165.05	166.16
12-Methyltetracosane	168.98	172.51
11-Methyltetracosane	168.99	172.51
10-Methyltetracosane	169.03	172.51
9-Methyltetracosane	169.13	172.51
8-Methyltetracosane	169.24	172.51
7-Methyltetracosane	169.40	172.51
6-Methyltetracosane	169.64	172.51
5-Methyltetracosane	169.95	172.51
4-Methyltetracosane	170.40	172.51
2-Methyltetracosane	170.71	172.51
3-Methyltetracosane	171.32	172.51
13-Methylpentacosane	175.17	178.86
12-Methylpentacosane	175.17	178.86
11-Methylpentacosane	175.20	178.86
10-Methylpentacosane	175.25	178.86
9-Methylpentacosane	175.35	178.86
8-Methylpentacosane	175.47	178.86
7-Methylpentacosane	175.64	178.86
6-Methylpentacosane	175.88	178.86
5-Methylpentacosane	176.21	178.86
4-Methylpentacosane	176.67	178.86
2-Methylpentacosane	176.97	178.86
3-Methylpentacosane	177.60	178.86
13-Methylhexacosane	181.33	185.21
12-Methylhexacosane	181.36	185.21
11-Methylhexacosane	181.38	185.21
10-Methylhexacosane	181.45	185.21
9-Methylhexacosane	181.56	185.21
8-Methylhexacosane	181.68	185.21
7-Methylhexacosane	181.85	185.21
6-Methylhexacosane	182.10	185.21
5-Methylhexacosane	182.42	185.21
4-Methylhexacosane	182.90	185.21
2-Methylhexacosane	183.18	185.21
3-Methylhexacosane	183.83	185.21
14-Methylheptacosane	187.50	191.56
13-Methylheptacosane	187.50	191.56
12-Methylheptacosane	187.53	191.56
11-Methylheptacosane	187.57	191.56
10-Methylheptacosane	187.64	191.56
9-Methylheptacosane	187.76	191.56
8-Methylheptacosane	187.88	191.56
7-Methylheptacosane	188.05	191.56
6-Methylheptacosane	188.29	191.56
5-Methylheptacosane	188.63	191.56
4-Methylheptacosane	189.10	191.56
2-Methylheptacosane	189.37	191.56
3-Methylheptacosane	190.04	191.56
14-Methyloctacosane	193.64	197.91
13-Methyloctacosane	193.65	197.91
12-Methyloctacosane	193.68	197.91
11-Methyloctacosane	193.73	197.91
10-Methyloctacosane	193.80	197.91
9-Methyloctacosane	193.92	197.91
8-Methyloctacosane	194.05	197.91
7-Methyloctacosane	194.22	197.91
6-Methyloctacosane	194.48	197.91
5-Methyloctacosane	194.81	197.91
4-Methyloctacosane	195.28	197.91
2-Methyloctacosane	195.56	197.91
3-Methyloctacosane	196.22	197.91
15-Methylnonacosane	199.74	204.26
14-Methylnonacosane	199.75	204.26
13-Methylnonacosane	199.77	204.26
12-Methylnonacosane	199.81	204.26
11-Methylnonacosane	199.85	204.26
10-Methylnonacosane	199.94	204.26
9-Methylnonacosane	200.06	204.26
8-Methylnonacosane	200.19	204.26
7-Methylnonacosane	200.37	204.26
6-Methylnonacosane	200.63	204.26
5-Methylnonacosane	200.95	204.26
4-Methylnonacosane	201.45	204.26
2-Methylnonacosane	201.70	204.26
3-Methylnonacosane	202.36	204.26

Table 3. Comparison of the Enthalpies of Vapoiization, $\Delta H_{vap,298K}$ (kJ mol^{-1}), Predicted by the Abraham Model, Eqn. 7, and the Group-Additivity Method of Naef and Acree, Eqn. 10

Compound	$\Delta H_{vap,298K}$ **Eqn. 7**	$\Delta H_{vap,298K}$ **Eqn. 10**
6-Methylundecane	58.26	59.83
5-Methylundecane	58.32	59.83
4-Methylundecane	58.50	59.83
2-Methylundecane	58.71	59.83
3-Methylundecane	59.03	59.83
6-Methyldodecane	62.99	64.59
5-Methyldodecane	63.09	64.59
4-Methyldodecane	63.31	64.59
2-Methyldodecane	63.53	64.59
3-Methyldodecane	63.86	64.59
7-Methyltridecane	67.71	69.35
6-Methyltridecane	67.74	69.35
5-Methyltridecane	67.88	69.35
4-Methyltridecane	68.11	69.35
2-Methyltridecane	68.35	69.35
3-Methyltridecane	68.69	69.35
7-Methyltetradecane	72.45	74.11

6-Methyltetradecane	72.52	74.11
5-Methyltetradecane	72.67	74.11
4-Methyltetradecane	72.93	74.11
2-Methyltetradecane	73.18	74.11
3-Methyltetradecane	73.53	74.11
8-Methylpentadecane	77.18	78.87
7-Methylpentadecane	77.21	78.87
6-Methylpentadecane	77.30	78.87
5-Methylpentadecane	77.47	78.87
4-Methylpentadecane	77.75	78.87
2-Methylpentadecane	78.00	78.87
3-Methylpentadecane	78.36	78.87
8-Methylhexadecane	81.94	83.63
7-Methylhexadecane	81.98	83.63
6-Methylhexadecane	82.09	83.63
5-Methylhexadecane	82.28	83.63
4-Methylhexadecane	82.57	83.63
2-Methylhexadecane	82.83	83.63
9-Methylheptadecane	86.69	88.39
8-Methylheptadecane	86.70	88.39
7-Methylheptadecane	86.77	88.39
6-Methylheptadecane	86.90	88.39
5-Methylheptadecane	87.09	88.39
4-Methylheptadecane	87.40	88.39
2-Methylheptadecane	87.65	88.39
9-Methyloctadecane	91.45	93.15
8-Methyloctadecane	91.48	93.15
7-Methyloctadecane	91.57	93.15
6-Methyloctadecane	91.71	93.15
5-Methyloctadecane	91.92	93.15
4-Methyloctadecane	92.22	93.15
2-Methyloctadecane	92.48	93.15
3-Methyloctadecane	92.87	93.15
10-Methylnonadecane	96.21	97.91
9-Methylnonadecane	96.23	97.91
8-Methylnonadecane	96.27	97.91
7-Methylnonadecane	96.36	97.91
6-Methylnonadecane	96.52	97.91
5-Methylnonadecane	96.73	97.91
4-Methylnonadecane	97.05	97.91
2-Methylnonadecane	97.30	97.91
3-Methylnonadecane	97.72	97.91
10-Methyleicosane	100.99	102.67
9-Methyleicosane	101.02	102.67
8-Methyleicosane	101.07	102.67
7-Methyleicosane	101.17	102.67
6-Methyleicosane	101.34	102.67
5-Methyleicosane	101.56	102.67
4-Methyleicosane	101.88	102.67
2-Methyleicosane	102.13	102.67
3-Methyleicosane	102.56	102.67
11-Methylheneicosane	105.75	107.43
10-Methylheneicosane	105.76	107.43
9-Methylheneicosane	105.79	107.43
8-Methylheneicosane	105.86	107.43
7-Methylheneicosane	105.98	107.43
6-Methylheneicosane	106.14	107.43
5-Methylheneicosane	106.38	107.43
4-Methylheneicosane	106.70	107.43
2-Methylheneicosane	106.95	107.43
3-Methylheneicosane	107.39	107.43
11-Methyldocosane	110.53	112.19
10-Methyldocosane	110.55	112.19
9-Methyldocosane	110.60	112.19
8-Methyldocosane	110.67	112.19
7-Methyldocosane	110.79	112.19
6-Methyldocosane	110.96	112.19
5-Methyldocosane	111.19	112.19
4-Methyldocosane	111.53	112.19
2-Methyldocosane	111.77	112.19
3-Methyldocosane	112.22	112.19
12-Methyltricosane	115.29	116.95
11-Methyltricosane	115.30	116.95
10-Methyltricosane	115.33	116.95
9-Methyltricosane	115.39	116.95
8-Methyltricosane	115.47	116.95
7-Methyltricosane	115.59	116.95
6-Methyltricosane	115.77	116.95
5-Methyltricosane	116.01	116.95
4-Methyltricosane	116.36	116.95
2-Methyltricosane	116.60	116.95
3-Methyltricosane	117.06	116.95
12-Methyltetracosane	120.09	121.71
11-Methyltetracosane	120.10	121.71
10-Methyltetracosane	120.13	121.71
9-Methyltetracosane	120.20	121.71
8-Methyltetracosane	120.29	121.71
7-Methyltetracosane	120.42	121.71
6-Methyltetracosane	120.60	121.71
5-Methyltetracosane	120.84	121.71
4-Methyltetracosane	121.19	121.71
2-Methyltetracosane	121.42	121.71
3-Methyltetracosane	121.90	121.71
13-Methylpentacosane	124.87	126.47
12-Methylpentacosane	124.87	126.47
11-Methylpentacosane	124.89	126.47
10-Methylpentacosane	124.93	126.47
9-Methylpentacosane	125.01	126.47
8-Methylpentacosane	125.10	126.47
7-Methylpentacosane	125.23	126.47

6-Methylpentacosane	125.42	126.47
5-Methylpentacosane	125.67	126.47
4-Methylpentacosane	126.03	126.47
2-Methylpentacosane	126.26	126.47
3-Methylpentacosane	126.75	126.47
13-Methylhexacosane	129.65	131.23
12-Methylhexacosane	129.67	131.23
11-Methylhexacosane	129.69	131.23
10-Methylhexacosane	129.74	131.23
9-Methylhexacosane	129.82	131.23
8-Methylhexacosane	129.92	131.23
7-Methylhexacosane	130.05	131.23
6-Methylhexacosane	130.25	131.23
5-Methylhexacosane	130.50	131.23
4-Methylhexacosane	130.86	131.23
2-Methylhexacosane	131.09	131.23
3-Methylhexacosane	131.59	131.23
14-Methylheptacosane	134.45	135.99
13-Methylheptacosane	134.45	135.99
12-Methylheptacosane	134.47	135.99
11-Methylheptacosane	134.51	135.99
10-Methylheptacosane	134.56	135.99
9-Methylheptacosane	134.65	135.99
8-Methylheptacosane	134.74	135.99
7-Methylheptacosane	134.88	135.99
6-Methylheptacosane	135.07	135.99
5-Methylheptacosane	135.33	135.99
4-Methylheptacosane	135.70	135.99
2-Methylheptacosane	135.91	135.99
3-Methylheptacosane	136.43	135.99
14-Methyloctacosane	139.25	140.75
13-Methyloctacosane	139.25	140.75
12-Methyloctacosane	139.28	140.75
11-Methyloctacosane	139.32	140.75
10-Methyloctacosane	139.38	140.75
9-Methyloctacosane	139.47	140.75
8-Methyloctacosane	139.57	140.75
7-Methyloctacosane	139.71	140.75
6-Methyloctacosane	139.90	140.75
5-Methyloctacosane	140.16	140.75
4-Methyloctacosane	140.54	140.75
2-Methyloctacosane	140.76	140.75
3-Methyloctacosane	141.27	140.75
15-Methylnonacosane	144.04	145.51
14-Methylnonacosane	144.04	145.51
13-Methylnonacosane	144.07	145.51
12-Methylnonacosane	144.09	145.51
11-Methylnonacosane	144.13	145.51
10-Methylnonacosane	144.20	145.51
9-Methylnonacosane	144.29	145.51
8-Methylnonacosane	144.40	145.51
7-Methylnonacosane	144.53	145.51
6-Methylnonacosane	144.74	145.51
5-Methylnonacosane	144.99	145.51
4-Methylnonacosane	145.38	145.51
2-Methylnonacosane	145.58	145.51
3-Methylnonacosane	146.10	145.51

We are unable to find experimental $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ data in the published chemical literature to compare our calculated values against. What we offer in the way of a comparison is to compare our calculated values against the calculated values of a popular group-additivity method[73] that has been shown to predict $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ values for a wide range of organic and organometallic compounds to within standard deviations of SD = 4.30 kJ mol^{-1} (N = 3460 compounds) and SD = 10.33 kJ mol^{-1} (N = 1866 compounds), respectively. The basic method (Eqn. 9) sums the contributions that each atomic group makes to the given thermodynamic or physical property,

$$Property = \sum_i A_i a_i + \sum_j B_j b_j + C \qquad (9)$$

where A_i is the number of occurrences of the ith atom group, B_j is the number of times each special group occurs, a_i and b_j are the numerical values of each atom group and special group, and C is a constant. For both the $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ computations a C_nH_{2n+2} mono-methyl branched alkane would be fragmented into 3 sp^3 carbons (with an environment of 3 hydrogen atoms and 1 carbon), 1 sp^3 carbon atom (with an environment of 1 hydrogen atom and 3 carbon atoms), n-4 sp^3 carbon atoms (with an environment of 2 hydrogen atoms and 2 carbon atoms), and one special alkane group that is multiplied by the number of carbon atoms in the molecule. Numerical values of the groups values and constant are different for each property. In Eqns. (10) and (11) below we have filled in the numerical group values and constants for predicting $\Delta H_{vap,298K}$ (kJ mol^{-1}) and $\Delta H_{sub,298K}$(kJ mol^{-1}) of C_nH_{2n+2} mono-methyl branched alkanes:

$$\Delta H_{vap,298K} = 3\ x\ 3.07 + (n\text{-}4)\ x\ 4.67 + 3.57 + n\ x\ 0.09 + 8.61 \qquad (10)$$

$$\Delta H_{sub,298K} = 3\ x\ 5.99 + (n\text{-}4)\ x\ 6.88 + 2.28 - n\ x\ 0.53 + 21.03 \qquad (11)$$

Examination of the numerical entries in Tables 2 and 3 reveals that the predictions based on the Abraham model are similar to predictions based on the group-additivity model of Naef and Acree.[73] The group-additivity method though is not able to distinguish between the placement of the methyl group within the molecule, and gives the same predicted values for a given molecular formula. In other words, the predicted values of all methylheneicosane molecules are the same. This limitation is a common feature of most group-addivity and group contribution methods. The Abraham model, on the other hand, does provide different predicted values for a given molecular formula, and does not require

fragmentation of the molecule into atom groups or functional groups. Fragmentation of molecules into functional groups can be difficult at times, particularly in the case of more complex molecules having many different functional groups. Moreover, the solute descriptors for a given molecule can be used to predict many other properties of chemical and biological importance, such as vapour pressure, water-to-organic solvent partition coefficients, gas-to-water partition coefficients, solubility ratios and the infinite dilution activity coefficients of the compound in water.[74,75]

CONCLUSION

Numerical values of the Abraham model ***L*** solute descriptor have been reported for the first time for 174 different C_{12}-C_{30} mono-methyl branched alkanes. The numerical values were determined by regression analysis of published linear-programmed gas chromatographic retention indices versus known ***L*** solute descriptors of linear alkanes and smaller mono-methylated alkane molecules. Calculated ***L*** solute descriptors were used to predict the standard molar enthalpies of vaporization and standard molar enthalpies of sublimation of 174 mono-methyl alkanes at 298 K based on recently published Abraham model correlations.[11,12] The predicted values compare very favorably with calculated values based on an atom-group additivity model.[73] Unlike the additivity model the Abraham model gives different predicted values of $\Delta H_{vap,298K}$ and $\Delta H_{sub,298K}$ for each mono-methyl alkane having a given C_nH_{2n+2} molecular formula.

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