ESTIMATION OF STANDARD HEAT CAPACITY OF ALKANES IN GASEOUS STATE BY CALCULATING SIZE, STRUCTURAL AND ELECTRONIC PARAMETERS OF THE MOLECULES

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ABSTRACT

A quantitative analysis is made on the relationship of thermodynamic property, i.e., standard heat capacity (Cp^0) with size, structural and electronic parameters of the molecules, i.e., Kier's molecular connectivity index ($^1X^v$), Van der Waals' volume (Vw), electrotopological state index (E) and refractotopological state index (R) in gaseous state of alkanes. The regression analysis reveals a significant linear correlationships of standard heat capacity (Cp^o) with $^1X^v$, Vw, E and R. The equations obtained by regression analysis may be used to estimate standard heat Capacity (Cp^o) of alkanes in gaseous state.

Keywords: Kier's molecular connectivity index ($^1X^v$), Van der Waals' Volume (Vw), Electrotopological state index (E), Refractotopological state index (R).

INTRODUCTION

Heat capacity is an important and basic thermodynamic property. It is used in chemical engineering calculations to obtain the difference in thermodynamic functions between two different temperatures. Experimental measurements of standard heat capacity involve experimental difficulties and they are not always feasible, and the corresponding methods possess real drawbacks. Therefore, estimation methods are an obvious choice to provide heat capacities for compounds for which there is a complete lack of data or for which data are available only over a limited temperature interval.

The additive approach applied to the estimation of thermophysical properties was systematically developed by Benson and coworkers[1-3]. Many additive schemes that correlate standard heat capacity with molecular structure have become widely used for data

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estimation[4-8]. Because a molecular property is calculated by summing up atomic, bond or group contribution, the additive methods are purely empirical. Previously, in our laboratory, we have established a significant quantitative correlationships to estimate diamagnetic susceptibility and other physical properties of many organic compounds with structural and size parameters, i.e., first order valence connectivity ($^1X^v$), Van der Waals' volume (Vw)[9,10], electrotopological state index (E)[11-13] and refractotopological state index (R)[14,15] are also important parameters, which have been extensively used in quantitative correlationships with biological activities. In view of the above, it is thought that heat capacities, which depend upon the size, structure, electronic environment and complexity of the molecules, may be quantitatively correlated with size, structure and electronic parameters, i.e., first order valence connectivity ($^1X^v$), Van der Waals' volume (Vw), electrotopological state index (E) and refractotopological state index (R) in alkanes.

Calculation of Kier`s molecular connectivity ($^1X^v$)[16]

It is calculated by a hydrogen suppressed graph of the molecule[17]. The first order valence connectivity ($^1X^v$) is given by Eq. 1 :

$$^1X^v = \sum (\delta i^{\,v} . \delta j^{\,v})^{\,-1/2} \qquad ...(1)$$

Here, the sum is the overall connections or edges in such a graph, δi^v and δj^v are numbers assigned to each atom reflecting the numbers of atoms adjacent or connected to atom (i) and (j), which are formally bonded. The atom connectivity term (δi^v) is defined as -

$$\delta_i^{\,v} = \frac{Z_i^{\,v} - h_i}{Z - Z_i^{\,v} - 1} \qquad ...(2)$$

Where $Z_i^{\,v}$ = Number of valence electron of atom (i), Z = Atomic number of atom (i) and h_i = Number of hydrogen atoms attached to atom (i).

Calculation of Van der Waals' volume (Vw)

Another atomic parameter accounting for the size of a molecule, the Van der Waals' volume (Vw) may be calculated as suggested by Bondi[18]. The atoms are assumed to be spherical and necessary corrections for the overlap in the hydrogen chain are also incorporated[19].

$$Vw = \sum n_i\, a_i + [\sum \text{corrections for bonds} + \sum \text{corrections for no. of branching}] \qquad ...(3)$$

Where, Vw = Van der Waals' volume of the molecules, n_i = Number of atoms, a_i = Van der Waals'volume of atom i.

The values of Van der Waal's volume of different atoms and corrections for bonds and branching are taken from literature.[18]

Calculation of electrotopological state index (E-State)

This index is developed from chemical graph theory and uses the chemical graph (hydrogen -suppressed skeleton) for generation of atom -level structure indices. This index recognizes that every atom in a molecule is unique, and this uniqueness arises from differences in the electronic and topological environment of each atom. This descriptor is formulated as an intrinsic value I_i plus a perturbation given by the electronic influence of the topological environment of the molecule[20,21]. Intrinsic state valence I_i of each atom is calculated as follows:

$$I_i = [(2 / N)^2 \delta^v + 1] / \delta \qquad ...(4)$$

Where N is the principal quantum number of the atom i, δ^v is the number of valence electrons in the skeleton (Z^v-hi) and δ is the number of σ electrons in the skeleton ($\sigma - h$).

For a skeleton, Z^v is the total number of electrons on the atom, σ is the number of electrons in the σ orbitals and h is the number of bonded hydrogen atom.

E-state for an atom i in molecule (S_i) is given by

$$S_i = I_i + \sum \Delta I_i \qquad ...(5)$$

ΔI_i quantifies the perturbation effect on the intrinsic atom value. This perturbation is assumed to be a function of the difference in the intrinsic values I_i and I_j:

$$\Delta I_i = \sum (I_i - I_j) / r_{ij}^2 \qquad ...(6)$$

Where, r_{ij} is the number of atoms in the shortest path between atoms i and j including both i and j. The difference in intrinsic values ΔI_i, for a pair of skeletal atoms encode both electronic and topological attributes that arise from electronegativity differences and skeletal connectivity. Therefore, the total of sum of the differences in intrinsic values, $\sum \Delta I_i$, due to perturbation for a whole molecule is zero, i.e.. $\sum \Delta I_i = 0$ so,

$$S_i = I_i \qquad ...(7)$$

Therefore, E- state for a molecule = $\sum n_i\ S_i$ or $\sum n_i\ I_i$ ...(8)

Where n_i = Number of atom i, and I_i = Intrinsic state valence I_i of atom

Calculation of refractotopological state index (R- state)

The R state index is also developed from the chemical graph theory. This index is based on the influence of dispersive forces of each atom on the other atom in the molecule, modified by molecular topology. Crippen *et al* [22] reported the atomic refractivity values of the topological environment of each skeleton atom in the molecule. The evaluation of the individual atomic refractivity value (Calculated by Ghose and Crippen [22]) is based on the idea that the sum of the atomic values (α_i) being related to the molecular value of the molar refractivity :

$$R\ (molecule)_{calc.} = \sum n_i\ \alpha_i \qquad ...(9)$$

Where, n_i = Number of atoms, and α_i = Atomic refractivity value.

Molecular refractivity values of molecules are calculated by Eq. (9) and atomic refractivity values (α_i) are taken from literature.[22]

RESULTS AND DISCUSSION

The molecular connectivity ($^1X^v$), Van der Waals' volume (Vw), electrotopological state index (E) and refractotopological state index (R) of some alkanes have been calculated as described above and are listed in Table 1.

The standard heat capacity (Cp^o) of gases are taken from literature [23-28]. Standard heat capacity (Cp^o) are taken in cal / mol (1 cal = 4.184 J) at atmospheric pressure at 298.15 K. The correlations of Cp^o with first order valence connectivities ($^1X^v$), Van der Waals' volume (Vw) and electrotopological state index (E) have been found to be as Eqs. (10), (11), (12), respectively.

$$Cp^o = 10.576\ (\pm 0.131)\ ^1X^v + 5.022 \qquad ...(10)$$

N = 30, r = 0.998, s = 1.651, F (1, 28) = 6532.556

$$Cp^o = 34.609\ (\pm 0.371)\ Vw + 0.175 \qquad ...(11)$$

N = 30, r = 0.998, s = 1.432, F (1, 28) = 8691.481

$$Cp^o = 3.702 \, (\pm 0.035) \, E - 4.025 \qquad \qquad ...(12)$$

$N = 29$, $r = 0.999$, $s = 1.213$, $F \, (1, 27) = 11201.06$.

In regression analysis, the statistical parameters are -

N = Number of data points, r = Correlation coefficient, s = Standard deviation and F = Ratio between the variance of calculated and observed data.

In Eqs. (10), (11) and (12), the F values are significant at 99% level [F^1_{28} (0.01) = 7.64] and are accounting for 99.6% & 99.8% variance (r^2 = 0.996, 0.996 & 0.998), respectively. The correlation of standard heat capacities (Cp^o) with only refractotopological state index (R) shows very low level of significance but with the inclusion of indicator variable (I), i.e., I =0 for straight chain and I =1 for branched alkanes, shows high level of significance and is shown by Eq. (13).

$$Cp^o = 1.171 \, (\pm 0.003) \, R - 0.272 \, (\pm 0.133) \, I - 0.379 \qquad \qquad ...(13)$$

$N = 30$, $r = 0.999$, $s = 0.339$, $F \, (2, 27) = 77552.4$

Eq. (13) shows almost 100 % correlation, because F value is again significant at 99% level [F^2_{27} (0.01) = 5.45], 99.8% variance (r^2 = 0.998) and low value of standard deviation. It shows that refractotopological state (R) affects the standard heat capacities of the alkanes in branching. The standard heat capacities (Cp^o) calculated from Eq. (10), (11), (12) and (13) are found to be very close to the experimental values (Table 1).

Table 1: Experimental and theoretical calculated values of C_p by $1_X{}^v$, Vw, E and R parameters in alkanes

Name of compound	$^1X^v$	V_w	E	R	I	Exp. value	Cald. Eq. (10)	Cald. Eq. (11)	Cald. Eq. (12)	Cald. Eq. (13)
Methane	0.000	0.258	*	6.478	0	8.54	5.022	9.105	*	7.203
Ethane	1.000	0.412	4.000	11.125	0	12.540	15.599	14.434	10.784	12.643
Propane	1.414	0.566	5.500	15.771	0	17.590	19.977	19.764	16.337	18.081
n-Butane	1.914	0.720	7.000	20.418	0	23.290	25.265	25.094	21.890	23.521

Cont...

Name of compound	$^1X^v$	V_w	E	R	I	C_p^0				
						Exp. value	Cald. Eq. (10)	Cald. Eq. (11)	Cald. Eq. (12)	Cald. Eq. (13)
2-Methyl propane	1.731	0.670	7.333	20.418	1	23.140	23.330	23.363	23.123	23.249
n-Pentane	2.414	0.874	8.500	25.065	0	28.730	30.554	30.424	27.443	28.960
2-Methyl butane	2.269	0.824	8.833	25.065	1	28.390	29.020	28.693	28.676	28.688
2,2-Dimethyl propane	2.000	0.774	9.250	25.065	1	29..070	26.175	26.963	30.220	28.688
n-Hexane	2.914	1.028	10.000	29.712	0	34.200	35.842	35.753	32.997	34.400
2-Methyl pentane	2.769	0.978	10.333	29.712	1	34.460	34.308	34.023	34.229	34.128
3-Methyl pentane	2.807	0.978	10.333	29.712	1	34.200	34.710	34.023	34.229	34.128
2,2-Dimethyl butane	2.560	0.928	10.750	29.712	1	33.910	32.098	32.293	35.773	34.128
2,3-Dimethyl butane	2.641	0.928	10.666	29.712	1	33.590	32.944	32.293	35.462	34.128
Heptane	3.414	1.182	11.500	34.359	0	39.670	41.130	41.083	38.550	39.839
2-Meyhyl hexane	3.269	1.132	11.833	34.359	1	39.670	39.596	39.353	39.783	39.567
3-Mehtyl hexane	3.307	1.132	11.833	34.359	1	39.670	39.998	39.353	39.783	39.567
2,2-Dimethyl pentane	3.061	1.082	12.250	34.359	1	39.670	37.386	37.622	41.326	39.567
2,3-Dimethy pentane	3.179	1.082	12.166	34.359	1	39.670	38.645	37.622	41.015	39.567
2,4-Dimethyl pentane	3.124	1.082	12.166	34.359	1	39.670	38.063	37.622	41.015	39.567
2,2,3-Trimethyl butane	2.942	1.032	12.583	34.359	1	39.330	36.138	35.892	42.559	39.567
Octane	3.914	1.336	13.000	39.005	0	45.140	46.418	46.413	44.103	45,278
Nonane	4.414	1.490	14.500	43.652	0	50.600	51.706	51.743	49.656	50.717
3-Ethyl pentane	3.345	1.132	11.833	34.359	1	39.670	40.400	39.353	39.783	39.567
Undecane	5.414	1.798	17.500	52.946	0	61.530	62,283	62.402	60.763	61.596
Hexadecane	7.914	2.568	25.000	76.180	0	88.860	88.723	89.051	88.529	88.792
Nonadecane	9.914	3.030	29.500	90.120	0	105.260	104.588	105.040	105.189	105.110
Octadecane	8.914	2.876	28.000	85.473	0	99.800	99.300	99.711	99.635	99.670
Pentadecane	7.414	2.414	23.500	71.533	0	83.400	83.435	83.721	82.976	83.353
Tetradecane	6.914	2.260	22.000	66.886	0	77.930	78.147	78.392	77.422	77.913
Tridecane	6.414	2.106	20.500	62.239	0	72.470	72.859	73.062	71.869	72.474

C_p^0 values are taken in cal / mol (1 cal = 4.184 J)

CONCLUSIONS

Therefore, these equations can be used to predict the standard heat capacities of any alkane by simply calculating $^1X^v$, Vw, E and R. These equations are the simplest and provide accurate methods to estimate standard heat capacities (Cp^o) of alkanes in gaseous state at one atmospheric pressure and 298.15 K.

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