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QSPR modeling of heat capacity, thermal energy and entropy of aliphatic Aldehydes by using Topological Indices and MLR method

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ABSTRACT Quantitative Structure-Property Relationship (QSPR) models are useful in understanding how chemical structure relates to the physicochemical properties of natural and synthetic chemicals. In the present investigation the applicability of various topological indices are tested for the QSPR study on 24 aldehydes. The topological indices used for the QSPR analysis were Randić ($^1\chi$) (the first order molecular connectivity), Balaban (J), Wiener (W) and Harary (H) indices. In this study, the relationship between the topological indices to the thermal energy (Eth), heat capacity (Cv) and entropy(S) of 24 aldehydes are established. The thermodynamic properties are taken from HF level using the ab initio 6-31 G basis sets from the program package Gussian 98. For obtaining appropriate QSPR model we have used multiple linear regression (MLR) techniques and followed Back ward regression analysis. The results have shown that combining the three descriptors (J, W, $^1\chi$) could be used successfully for modeling and predicting the heat capacity (C_V), two descriptors (J, 1χ) could be efficiently used for estimating the entropy (S) and one descriptors ($^1\chi$) could be predict the thermal energy of compounds.

KEYWORDS Topological indices • Aldehydes • QSPR • MLR method.

1. INTRODUCTION

Graph theory has been found to be a useful tool in Quantitative Structure- Activity Relationship (QSAR) and Quantitative Structure- Property Relationship (QSPR) [1–6]. A QSPR is a mathematical description of a property in terms of other properties (descriptors) that are of three broad classes hydrophobic, electronic, and steric. Numerous studies have been made related to the various fields by using what are called topological indices (TI) [7–12]. Topological indices are the digital value combined with chemical constitution purporting for correlation of chemical structures with various chemical and physical

properties that have constructed the effective and useful mathematical methods for finding good relationship between several data of the properties in these materials [13–16]. The use of the effective mathematical methods for making good correlations between several data properties of chemicals is important.

Recent years have seen the publication of a plethora of QSPR methods for the prediction of the normal boiling point, heat capacity, standard Gibbs energy of formation, vaporization enthalpy. Many of the studies deal with specific classes of compounds, especially alkanes [17,18], alcohols [19,20], aldehydes and ketones [21,22,23].

This method is useful when there is not any interaction between descriptors and their relation with linear defined activity. Heat capacity, thermal energy and entropy are applied in reactions for modification of reactants evaluation. In addition, they are useful for heat - energy balance design calculation. On the other hand, the tests for determining these properties are expensive and expense much more time. Therefore, we need the models to predict the heat capacity and other physico – chemical properties of molecules.

Ivanova and Gakh give a model for evaluation the heat capacity of alkanes by using artificial neural network (ANN) [23]. Yao proposed a general nonlinear model for evaluation of heat capacity that can be used for the prediction of liquid heat capacity of all organic compounds [24]. Lailong proposed model for predicting standard absolute entropy (S°_{298}) of inorganic compounds by using multivariate linear regression (MLR) and (ANN) methods [25].

In the present study, the multiple linear regression (MLR) techniques and back ward methods are used for modeling the thermal energy (E_{th}), heat capacity (C_V) and entropy (S) of 24 aldehydes. The proposed QSPR models were based on molecular descriptors (topological indices) that can be calculated for any compound utilizing only the knowledge of its molecular structure (molecular graph).

The topological indices (Tis) used for the QSPR analysis were Wiener (W) [16], first order molecular connectivity ($^1\chi$) [18], Balaban (J) [19] and Harary(H) [22] indices.

The aim of this study is to provide reliable QSPR models for predicting physicochemical properties of aldehydes.

2. MATERIALS AND METHODS

2.1. QUANTUM CHEMISTRY CALCULATIONS

The thermal energy (E_{th}), heat capacity (C_V), entropy (S) and lumo energy (E_{lumo}) of 24 aldehydes are taken from the quantum mechanics methodology with Hartree- Fock (HF) level using the ab initio 6-31G basis sets. The quantum chemistry data of the 24 congeners are listed in Table 1.

2.2. TOPOLOGICAL INDICES

All the used topological indices were calculated using all hydrogen suppressed graph by deleting all the carbon hydrogen from the structure of the aldehydes. The descriptors were calculated with chemicalize program [23]. Four topological indices tested in the present study are recorded in Table 2.

2.3. STATISTICAL ANALYSIS

Structure- Property models (MLR models) are generated using the multi linear regression procedure of SPSS version 16. The thermal energy (E_{th} *kcal/mol*), heat capacity (*Cv cal/molK* and entropy (*S cal/molk*) are used as the dependent variable and $^1\chi$, J, H, and W indices as the independent variables. The models are assessed with R value (correlation coefficient), the R^2 (coefficient of determination), the R^2- adjusted, the SD value (root of the mean square of errors), the F value (Fischer statistic), the D value (Durbin-Watson) and the Sig (significant).

3. RESULTS

Several linear QSPR models involving three-eight descriptors are established and strongest multivariable correlations are identified by the back ward method are significant at the 0.05 level and regression analysis of the SPSS program. In the first of this study we drown scattering plots of C_V, S and E_{th} versus the four topological indices ($^1\chi$, J, W, H). Some of these plots are given in Fig. (1-3), respectively.

Distribution of the dependent variable against the independent variable for 41 chemicals employed in developing quantitative structure- Properties relationship. For obtaining appropriate QSPR model we have used maximum R^2 method and followed Back ward regression analysis. The predictive ability of the model is discussed on the basis of predictive correlation coefficient.

3.1. QSPR MODELS FOR HEAT CAPACITY (C_V)

Initial regression analysis indicated that combination of seven topological indices and E_{lumo} plays a dominating role in modeling the heat capacity. In Table 3 are given the regression parameters and quality of correlation of the proposed models for heat capacity of 24 aldehydes.

It turns out that the heat capacity (C_V) has a highly correlation with a combination of the three parameters, namely, Balaban (J), Randić ($^1\chi$) and Wiener (W) indices. Fig 4 shows the linear correlation between the observed and the predicted heat capacity values obtained using Eq. (1).

Model 3.1.1

$C_V = 0.817 - 1.034J + 0.0001W + 9.182^1\chi$

N= 24 R= 1 R^2 =1 $R^2_{adj} = 1$ SD=0.267 F=1.083×10^5 Sig=0.000 D=2.033(1)

3.2. QSPR MODELS FOR THERMAL ENERGY (ETH)

In Table 4 are given the regression parameters and quality of correlation of the proposed models for the thermal energy of 24 aldehydes.

Statistically significant models are obtained when one descriptors are used and that the quality of the model goes on improving with higher parameteric modeling (Table 4),the model (3) containing one descriptors (1χ) is found as below:

Model 3.2.3

$E_{th} = -14.763 + 39.829^1\chi$

N= 24 R= 1 R^2 =1 $R^2_{adj} = 1$ SD=2.609 F= 6.701×10^4 Sig = 0.000 D=2.129 (2)

Figure 5 shows the linear correlation between the observed and the predicted thermal energy values obtained using Eq. (2).

3.3. QSPR MODELS FOR ENTROPY (S)

In Table 5 are given the regression parameters and quality of correlation of the proposed models for the entropy of 24 aldehydes.

It turns out that the entropy(S) has a good correlation with all descriptorsas well as with a combination of the two parameters, namely, Balaban(J) and Randic (1χ) indices. Fig 6 shows the linear correlation between the observed and the predicted entropy obtained using Eq. (3).

Model 3.3.2

$S = 44.647\text{-}1.835J\text{+}14.7811\chi$

N= 24 R= 1 R^2 =1 R^2_{adj} =1 SD=0.236 F= 5.517×10^5 D=2.310 Sig = 0.000(3)

4. DISCUSSION

We studied the relationship between topological indices to the thermal energy (E_{th}), heat capacity (C_v) and entropy (S) of 24 aldehydes**.**

In this study, to find the best model for predict the properties mentioned,we will use the following sections.

4.1. VERIFICATION AND VALIDITY OF MODELS

In this section for verification and validity of the regression models, we will focus on the Durbin-Watson (D) statistic, unstandardized predicted and residual values.

4.1.1. TEST FOR AUTOCORRELATION BY USING THE DURBIN-WATSON STATISTIC

The Durbin-Watson statistic ranges in value from 0 to 4. A value near 2 indicates non-autocorrelation; a value toward 0 indicates positive autocorrelation; a value toward 4 indicates negative autocorrelation. Therefore the value of Durbin–Watson statistic is close to 2 if the errors are uncorrelated. In our all models, the value of Durbin–Watson statistic is close to 2 (See Eq. 1–3) and hence the errors are uncorrelated.

4.2. REGULAR RESIDUALS

The residual is difference between the observed value of the dependent variable (y) and the predicted value (ŷ). Plot the residuals, and use other diagnostic statistics, to determine whether our model is adequate and the assumptions of regression are met. The residuals can also identify how much a model explains the variation in the observed data. The residuals values of heat capacity, thermal energy and entropy expressed by Eqs. (1–3) are shown in Table 6. The residual plots, Figures 7–9, show a fairly random pattern. This random pattern indicates that a linear model provides a decent fit to the data.

4.3. QSPR MODELS

The QSPR model (3.1.1) reveals that the heat capacity of the aldehydes could be explained by three parameters. This model can explain about 100% of the experimental

variance of the dependent variable C_V. The combination of the three parameters (J, $^1\chi$, W) increases remarkably the predictive power of the QSPR model given by Eq. (1) (R^2 =1 R^2_{adj} =1 SD=0.267 F=1.083×10^5 Sig=0.000 D=2.033).

The Back ward method values of the thermal energy shows that all of models (3.2.1-3.2.3) can explain about 100% of the variance of the thermal energy. The QSPR model given by Eq. (2) (R^2 =1 R^2_{adj} =1 SD=2.609 F= 6.701×10^4 Sig = 0.000 D=2.129). As can be seen from the statistical parameters of the above equation, a considerable improvement is achieved by one descriptor ($^1\chi$).This model has a minimum of independent variables and maximum of F, compared with another models.

Similarity, this method for the entropy shows that all of models (3.3.1, 3.3.2) can explain about 100% of the variance of the entropy and according to statistical parameters of the below equation, a considerable improvement is achieved by combining the two descriptors ($^1\chi$, J). The QSPR model given by Eq. (3) (R^2 =1 R^2_{adj} =1 SD=0.236 F= 5.517×10^5 D=2.310 Sig = 0.000).

This model has a minimum of independent variables and maximum of F, compared with another model.

5. CONCLUSION

Graph theory has provided the chemist with a variety of very useful tools. Tis contain valuable structural information as evidenced by the success of their widespread applications in QSAR/QSPR. In this work, the relationship between topological indices (J, W, H, $^1\chi$) and the heat capacity (C_V), entropy (S), thermal energy (E_{th}) of 24 aldehydes were studied.

The aforementioned results and discussion lead us to conclude that combining the three descriptors (J, W, $^1\chi$) could be used successfully for modeling and predicting the heat capacity (C_V), two descriptors (J, $^1\chi$)could be efficiently used for estimating the entropy (S) and one descriptors ($^1\chi$) could be predict the thermal energy of compounds. The training set models established by MLR method have good correlation of physicochemical properties, which means QSPR models could be used for prediction of the heat capacity (C_v), entropy (S), thermal energy (E_{th}) for a set of 24 aldehydes.

Table 1. Structural details and their thermal energy (E_{th}), heat capacity (C_V) and entropy (S) for the aldehydes used in present study.

Compound	Formula	No.	E_{th} $kcal/mol$	Cv $cal/molK$	S $cal/molK$
Ethanal	C_2H_4O	1	40.074	10.472	62.483
Propanal	C_3H_6O	2	60.162	14.719	69.255
Butanal	C_4H_8O	3	80.131	19.195	76.521
Pentanal	$C_5H_{10}O$	4	100.175	23.569	83.11
Hexanal	$C_6H_{12}O$	5	132.672	26.877	90.594
Heptanal	$C_7H_{14}O$	6	139.94	32.586	97.626
Octanal	$C_8H_{16}O$	7	159.879	37.083	104.813
Nonanal	$C_9H_{18}O$	8	179.812	41.597	112.474
Decanal	$C_{10}H_{20}O$	9	199.764	46.095	119.946
Undecanal	$C_{11}H_{22}O$	10	219.717	50.587	127.356
Dodecanal	$C_{12}H_{24}O$	11	239.673	55.061	134.061
Tridecanal	$C_{13}H_{26}O$	12	259.626	59.553	141.197
Tetradecanal	$C_{14}H_{28}O$	13	279.545	64.08	149.267
Pentadecanal	$C_{15}H_{30}O$	14	299.493	68.575	156.6
Hexadecanal	$C_{16}H_{32}O$	15	319.434	73.07	163.611
Heptadecanal	$C_{17}H_{34}O$	16	339.444	77.48	171.456
Octadecanal	$C_{18}H_{36}O$	17	360.034	81.825	178.205
Nonadecanal	$C_{19}H_{38}O$	18	380.088	86.245	185.815
Eicosanal	$C_{20}H_{40}O$	19	400.07	90.739	193.172
Heneicosanal	$C_{21}H_{42}O$	20	420.055	95.226	200.52
Docosanal	$C_{22}H_{44}O$	21	440.039	99.715	207.846
Tricosanal	$C_{23}H_{46}O$	22	460.024	104.206	215.418
Tetracosanal	$C_{24}H_{48}O$	23	480.006	108.692	222.462
Pentacosanal	$C_{25}H_{50}O$	24	499.992	113.185	230.223

Table 2. Topological indices values used in present study.

Comp.No	$^1\chi$	J	H	W
1	1.41	1.63	2.5	4
2	1.91	1.97	4.33	10
3	2.41	2.19	6.42	20
4	2.91	2.34	8.7	35
5	3.41	2.45	11.15	56
6	3.91	2.53	13.74	84
7	4.41	2.6	16.46	120
8	4.91	2.65	19.26	165
9	5.41	2.69	22.22	220
10	5.91	2.73	25.24	286
11	6.41	2.76	28.34	364
12	6.91	2.78	31.52	455
13	7.41	2.81	34.77	560
14	7.91	2.83	38.09	680
15	8.41	2.85	41.47	816
16	8.91	2.86	44.91	969
17	9.41	2.88	48.41	1140
18	9.91	2.89	51.95	1330
19	10.41	2.9	55.55	1540
20	10.91	2.91	59.2	1771
21	11.41	2.92	62.89	2024
22	11.91	2.93	66.62	2300
23	12.41	2.94	70.4	2600
24	12.91	2.95	74.21	2925

Table 3. Regression parameters and quality of correlation of the proposed models for the heat capacity.

Model	independent variables	R	R^2	R^2_{adj}	SD	F
1	J, $^1\chi$,W	1	1	1	0.267	1.083×10^5

Table 4. Regression parameters and quality of correlation of the proposed models for the thermal energy.

Model	Independent variables	R	R^2	R^2_{adj}	F	SD
1	J, W, $^1\chi$	1	1	1	2.232×10^4	2.610
2	W, $^1\chi$	1	1	1	3.256×10^4	2.647
3	$^1\chi$	1	1	1	6.701×10^4	2.609

Table 5. Regression parameters and quality of correlation of the proposed models for the entropy.

Model	Independent variables	R	R^2	R^2_{adj}	SD	F	Sig
1	J, 1χ, W	1	1	1	0.242	3.507×10^5	0.000
2	J, 1χ	1	1	1	0.236	5.517×10^5	0.000

Table 6. Comparison between predicted and observed values of thermal energy, heat capacity and entropy of respect aldehydes.

Comp No	Observed (Cv)	Predicted (Cv)	Residual	Observed (Eth)	Predicted (Eth)	Residual	Observed (S)	Predicted (S)	Residual
1	10.472	10.442	0.030	40.074	39.731	0.343	62.483	61.826	0.657
2	14.719	14.678	0.041	60.162	61.152	-0.990	69.255	69.634	-0.379
3	19.195	19.036	0.159	80.131	81.808	-1.677	76.521	76.877	-0.356
4	23.569	23.463	0.106	100.175	102.028	-1.853	83.11	83.864	-0.754
5	26.877	27.928	-1.051	132.672	132.011	0.661	90.594	90.833	-0.239
6	32.586	32.421	0.165	139.945	141.827	-1.882	97.626	97.800	-0.174
7	37.083	36.919	0.164	159.879	161.609	-1.730	104.813	104.929	-0.116
8	41.597	41.432	0.165	179.812	181.295	-1.483	112.474	111.990	0.484
9	46.095	45.951	0.144	199.764	200.956	-1.192	119.946	119.271	0.675
10	50.587	50.463	0.124	219.717	220.659	-0.942	127.356	126.617	0.739
11	55.061	54.979	0.082	239.673	240.343	-0.670	134.061	133.970	0.091
12	59.553	59.497	0.056	259.626	260.013	-0.387	141.197	141.323	-0.126
13	64.08	63.998	0.082	279.545	279.802	-0.257	149.267	148.840	0.427
14	68.575	68.500	0.075	299.493	299.585	-0.092	156.6	156.317	0.283
15	73.07	72.993	0.077	319.434	319.429	0.005	163.611	163.820	-0.209
16	77.48	77.487	-0.007	339.444	339.274	0.170	171.456	171.242	0.214
17	81.825	81.960	-0.135	360.034	359.254	0.780	178.205	178.773	-0.568
18	86.245	86.433	-0.188	380.088	379.243	0.845	185.815	186.159	-0.344
19	90.739	90.895	-0.156	400.07	399.309	0.761	193.172	193.541	-0.369
20	95.226	95.344	-0.118	420.055	419.457	0.598	200.52	200.884	-0.364
21	99.715	99.781	-0.066	440.039	439.690	0.349	207.846	208.159	-0.313
22	104.206	104.206	0.000	460.024	460.012	0.012	215.418	215.356	0.062
23	108.692	108.616	0.076	480.006	480.427	-0.421	222.462	222.492	-0.030
24	113.185	113.013	0.172	499.992	500.940	-0.948	230.223	229.512	0.711

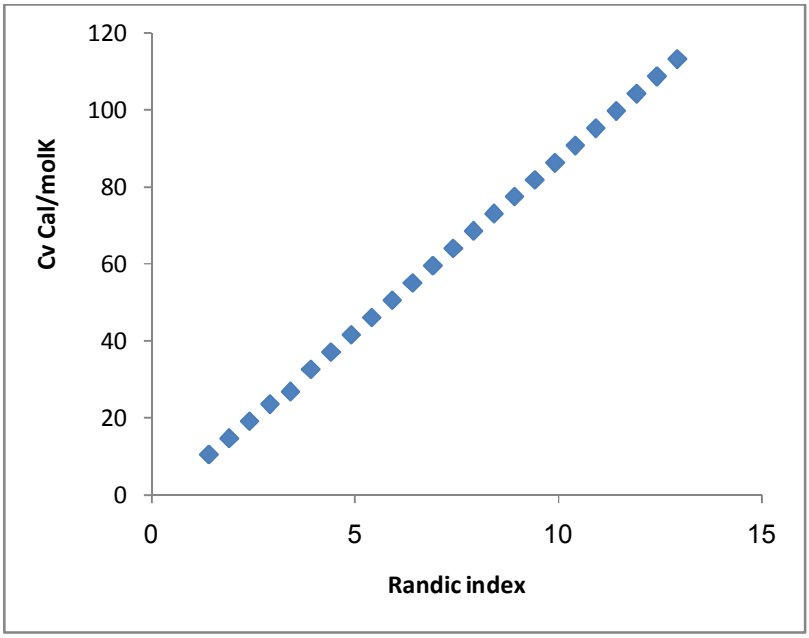

Figure 1. Plots of the Randić index ($^1\chi$) versusheat capacity (C_v) of 24 aldehydes.

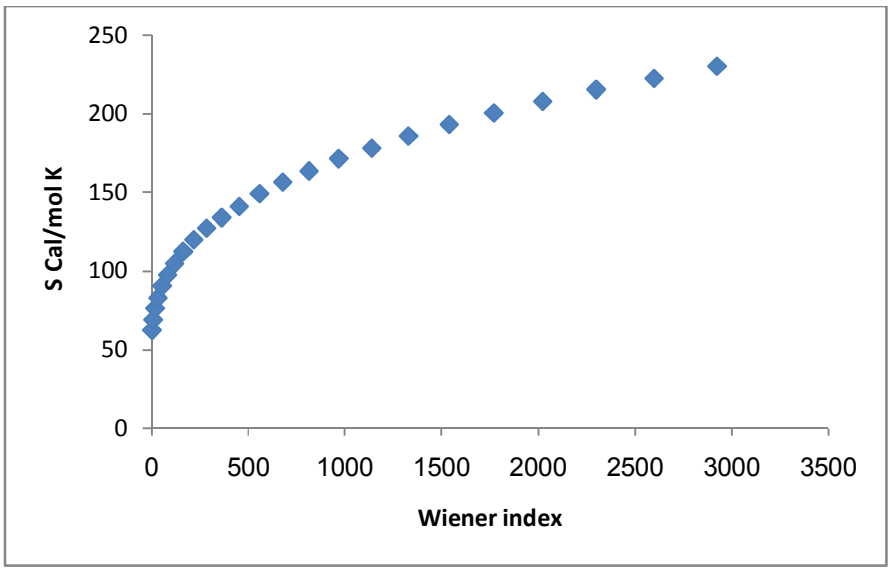

Figure 2. Plots of the Wiener index (W) versus entropy (S) of 24 aldehydes.

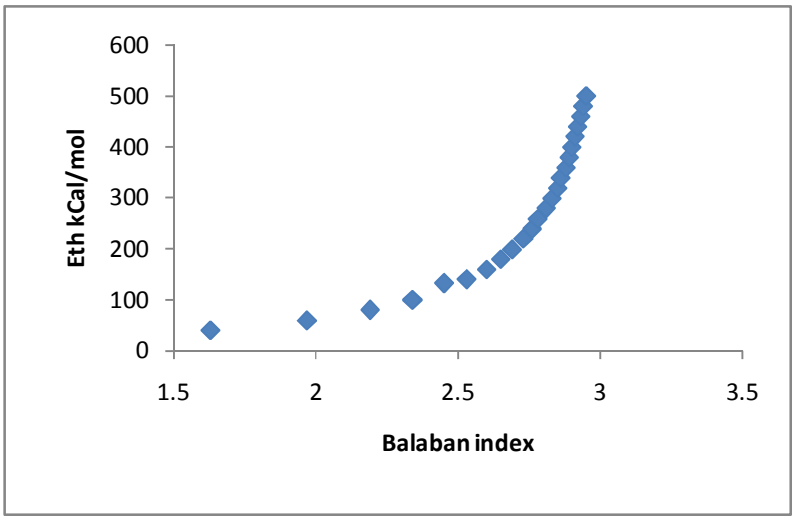

Figure 3. Plots of the Balaban index (J) versus thermal energy (E_{th}) of 24 aldehydes.

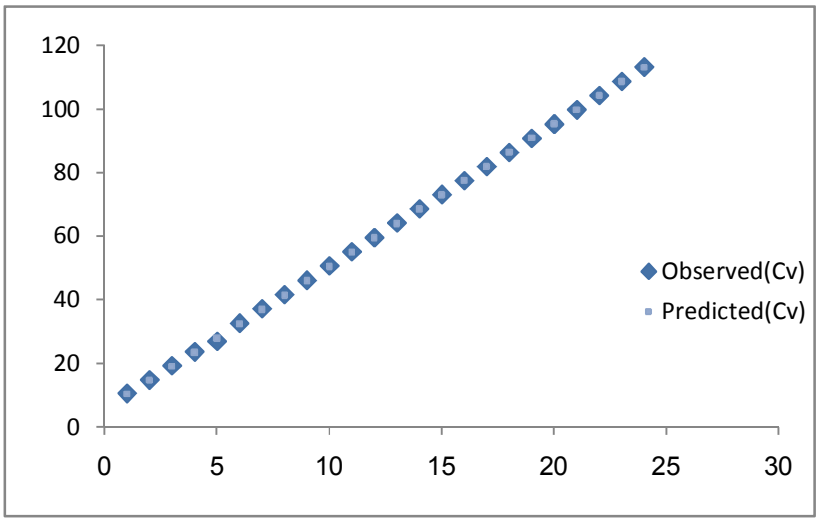

Figure 4. Comparison between the predicted and observed values of heat capacity by MLR.

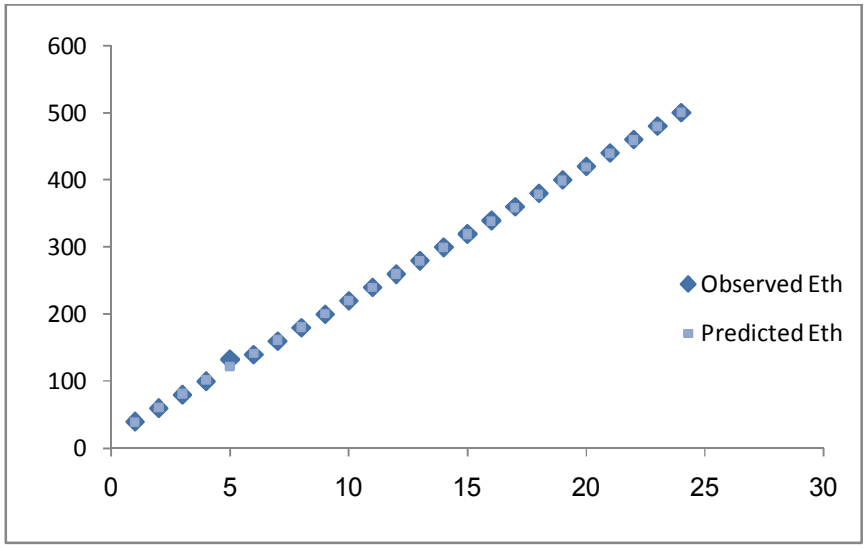

Figure 5. Comparison between the predicted and observed values of thermal energy by MLR.

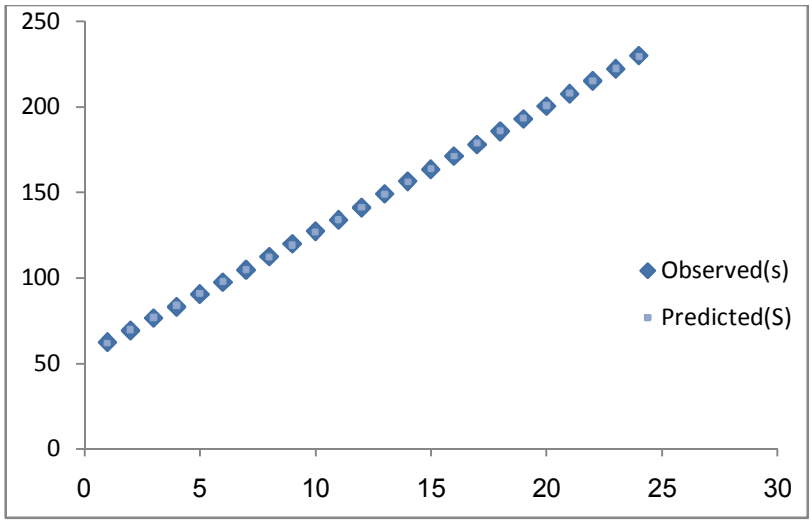

Figure 6. Comparison between the predicted and observed values of entropy(S) by MLR.

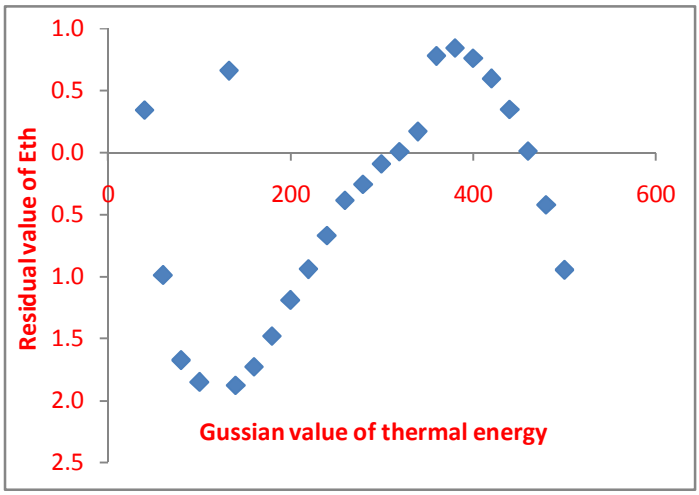

Figure 7. Plot of residuals against experimental value with Eq. (2) for the thermal energy of 24 aldehydes.

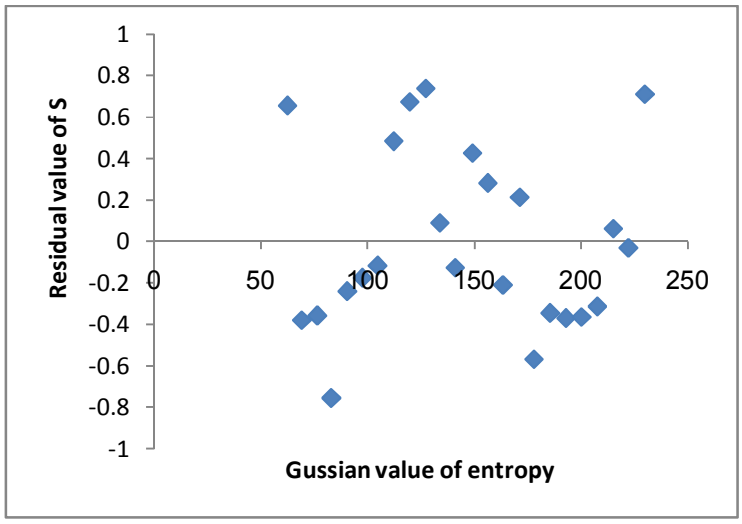

Figure 8. Plot of residuals against experimental value(Gussian value) with Eq. (3) for the entropy of 24 aldehydes.

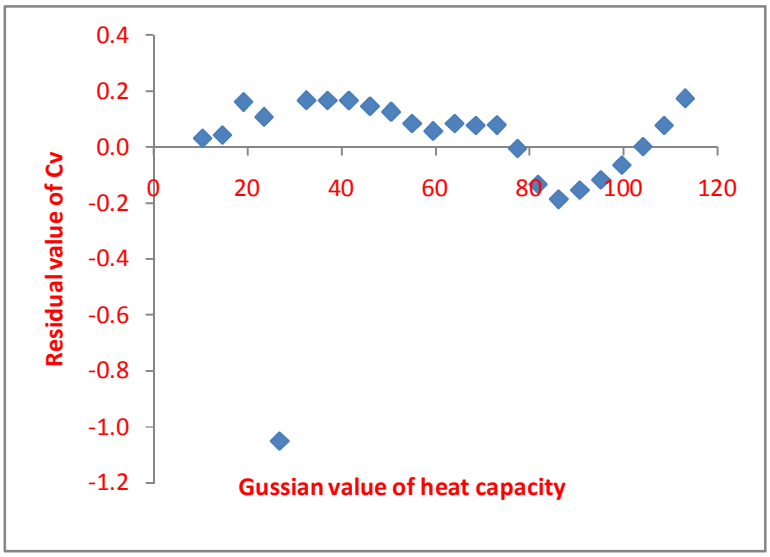

Figure 9. Plot of residuals against experimental value with Eq. (1) for the heat capacity of 24 aldehydes.

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