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QSPR model of Intrinsic Viscosity For Poly(isobutylene)

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ABSTRACT

The critical relationship between quantitative structure-property relationships (QSPRs) and the quality of the experimental data is discussed by using multiple linear regression (MLR) analysis and describe the activities and influences of the vibrational frequency (stretching & bending) for groups C=C and =CH_2 to predicated intrinsic viscosity by semiemperical molecular orbital methods AM1&PM3. Three models with R^2 ranges from 0.830-0.991by using MLR based on descriptors calculated from PM3 semiemperircal. A highly significant two-parameter correlation (R^2 = 0.991, F = 57.685 and low S =10.541), employs just two molecular parameters C=C str and =CH_2 bending was eq 3., these parameters which indicate play an important role in effect on intrinsic viscosity of polymer. The capability to predict by these techniques for intrinsic viscosity, set a successful example for applying a similar approach in building QSPR models for intrinsic viscosity and that could potentially offer a new opportunity in the design of novel properties of polymers or extended to other polymer composite.

Keywords. *Intrinsic Viscosity, Organic Solvents, Recomputed QSPR model.*

INTRODUCTION

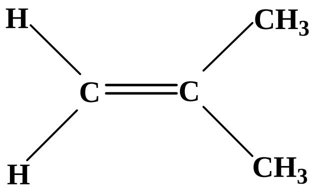
Intrinsic viscosity, [η], is extensively used for analysis or characterization of synthetic polymers [1–3], biological macromolecules[4,5], nanoparticles, and colloids [6]. Indeed, [η] provides information about fundamental properties of the solute and its interaction with the solvent [7–8] . The variation of the viscosity number with concentration depends on the type of molecule as well as the solvent. The intrinsic viscosity [η] is a widely used measure of molecular weight, M, and size (dimensions) of macro-molecules in dilute solution. [9]. The viscosity study of polymers has been of continuing interest, mainly due to its simplicity and its importance in the characterization of the intermolecular interaction between the two different polymers.[10].

Many approaches for the prediction of chemical and physical properties such as poling point transition temperature TG, biological activities, performed by using the a Quantitative structure–property/activity relationships(QSPR/QSAR)[11-14]. QSAR/QSPR studies constitute an attempt to reduce the trial-and-error element in the design of compounds with desired activity/properties by establishing mathematical relationships between the activity/property of interest and measurable or computable parameters, such as topological, physicochemical, stereochemistry, or electronic indices [15]. Computational methods aids is not only the design and interpretation of hypothesis-driven experiments in the field of cancer research but also in the rapid generation of new hypotheses[16] This research tries to get prediction equation (QSPR model) of intrinsic viscosity of polymer by computational chemistry approach. This research use vibrational frequency as function of intrinsic viscosity based on Hansch Analysis. Previous modeling efforts [17] for prediction of intrinsic viscosity in polymer solutions. The model was produced by using the multiple linear regression (MLR) technique on a database that consists of 65 polymer–solvent combinations involving 10 different polymer. While in this paper we re-report a QSPR model for the prediction of intrinsic viscosity for one polymer compound(N of polymer=1) in four organic solvent, In this work we demonstrate the usefulness and focus of some of the descriptors in deriving predictive QSPR models. according to

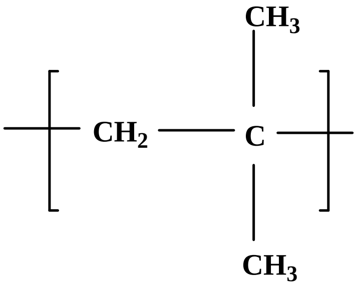
QSPR models similar in our work which were previously published[18], to know descriptor effect of the vibrational frequency (stretching & bending) for groups C=C and =CH_2 which calculated by AM1 and PM3 to predicated intrinsic viscosity of polyisobutylene by using QSPR model.

Modeling & Geometry Optimization

Theoretical calculations were performed on MOPAC program version 11.052w, MOPAC 2009[19], running on a Pentium V PC-CPU 3400GHz. The geometries of the four compounds were optaimization first at level (MM+) by molecular mechanics force field theory and then at calculation done by the AM1 and PM3 Hamiltonion to be used calculated from the composition series consisting of 5 monomer units from the (isobutylene) in deferent solvents [[BENZENE, CCL4, CYCLOHEXANE and TOLUENE] [20]. no imaginary frequencies was found in the calculation of the studied compounds usingAM1 and PM3 Hamiltonion. The experimental data of the intrinsic viscosity of polyisobutylene has been taken from reference[17] .The Structures of these compounds and shown in Figure.1.



Isobutylene



Poly(isobutylene)

Figure 1. Molecular structure of the compound used in the present study

RESULTS AND DISCUSSION

The prediction model of QSPR study has been make up with assist of the next descriptors C=C str, =CH_2 asym.str, =CH_2 sym.str and =CH_2 bending(scissoring). The values of these descriptors for the studied chain including five unit from isobutylene, table 1 reports the values of PM3 and AM1 calculation based descriptors[21-23]. The statistical parameters of the predictive model of QSPR which contain values of PM3 & AM1 based descriptors in tables 2&3 are summarized. From tables 2 and 3 the statistical parameters for the predictive model of QSPR which including descriptors calculated by PM3 method are often best than predictive model of QSPR which has been construct up with aid values of AM1 method based descriptors. .

Table 1. The values of AM1 & PM3 based descriptors.

PM3 Method				
Descriptors				*SOLVENT*
υ_1	υ_2	υ_3	υ_4	
3138.32	*3134.12*	*1324.4*	*1870.2*	*BENZENE*
3138.19	*3133.49*	*1324.76*	*1870.2*	*CCL4*
3138.25	*3133.4*	*1325.14*	*1870.2*	*CYCLOHEXANE*
3138.25	*3133.33*	*1324.8*	*1870.2*	*TOLUENE*

AM1 Method				
Descriptors				*SOLVENT*
υ_1	υ_2	υ_3	υ_4	
3214.16	*3176.56*	*1411.61*	*1875.74*	*BENZENE*
3214.33	*3176.71*	*1411.91*	*1875.7*	*CCL4*
3214.27	*3176.59*	*1411.7*	*1875.7*	*CYCLOHEXANE*
3213.99	*3176.47*	*1411.52*	*1875.7*	*TOLUENE*

***Definition of Descriptors Used in This Study*.**
υ_1= =CH_2 STR, asym υ_2= =CH_2 STR. sym υ_3= =CH_2 BEND, scissoring υ_4= C=C STR, The all values in cm^{-1}.

Table 2. Statistical parameters of the linear regressions models obtained by using one descriptor.

METHOD	AM1			PM3		
DISCRIPTOR	R^2	F	S	R^2	F	S
υ_4	0.415	1.423	61.460	0.771	6.752	38.436
υ_3	0.200	0.501	71.898	0.830	9.789	33.117
υ_1	0.154	0.364	73.951	0.347	64.946	1.065
υ_2	0.361	1.131	64.263	0.246	0.653	69.808

Table 3. Statistical parameters of the linear regressions models obtained by using two descriptor.

METHOD	AM1			PM3		
DISCRIPTOR	R^2	F	S	R^2	F	S
υ_3 & υ_4	0.487	0.474	81.441	0.890	4.059	37.655
υ_1 & υ_3	0.299	0.213	95.177	0.919	5.685	32.331
υ_2 & υ_1	0.602	0.758	71.680	0.354	0.274	91.343
υ_4 & υ_2	0.692	1.124	63.078	0.991	57.685	10.541
υ_3 & υ_2	0.416	0.356	86.879	0.830	2.454	46.777
υ_4 & υ_1	0.504	0.509	80.016	0.867	3.264	41.445

Definition of Statistical parameters Used in This Study.
R^2= correlation coefficient.
S= standard of error.
F= sequential Fischer test.

The resulting parametric models are depicted in eqs. 1-3, along with statistical parameters of the regression. Several equations were generated by using all the variables and the best statistically model that we have obtained is one-descriptor equation, was by using PM3 method, which is as follows:

One descriptor; The model when depend on only one parameter [υ_3] gave good model with correlation coefficient R^2 values for this model of 0.830, as eq 1. .

η =197.706 υ_3-261794.246 **..........Eq 1.**
$R^2 = 0.830$ S = 33.117 F =9.789

From eq 1. positive value for υ_3 suggest a positive relationship between υ_3 and the intrinsic viscosity which indicated that any increase in the value of υ_3 lead to increasing the value of viscosity. Figure 2 shows Graph of experimental verses the predicted values for the intrinsic viscosity by using eq 1 .

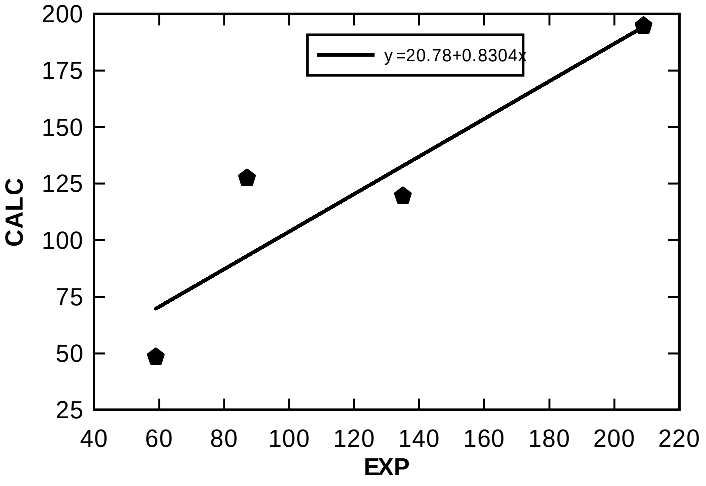


Figure 2. Plot of intrinsic viscosity prediction vs intrinsic viscosity experimental using Eq 1.

Tow descriptors; We have the best tow model when depend on only two descriptor eq 2 and eq 3. The correlation coefficient R^2 of eq 2., when included the υ_3 and υ_1 obtained very good model with correlation coefficient R^2 values for this model of 0.919, as equation 2. The positive value of υ_1 and υ_3 in the eq 2, refers to a positive correlation with the intrinsic viscosity.

η = -691826.664 +293.766 υ_3 + 96.6225 υ_1**......Eq 2.**

$R^2 = 0.919$ S = 32.331 F =5.685

The statistical quality of the above equation very good as evident from its correlation coefficient R^2 value = 0.919. The intrinsic viscosity of the compounds is given in Table 3 by using Eq 2. The graph of experimental verses the predicted values for the intrinsic viscosity by using eq 2. shown in Figure 3.

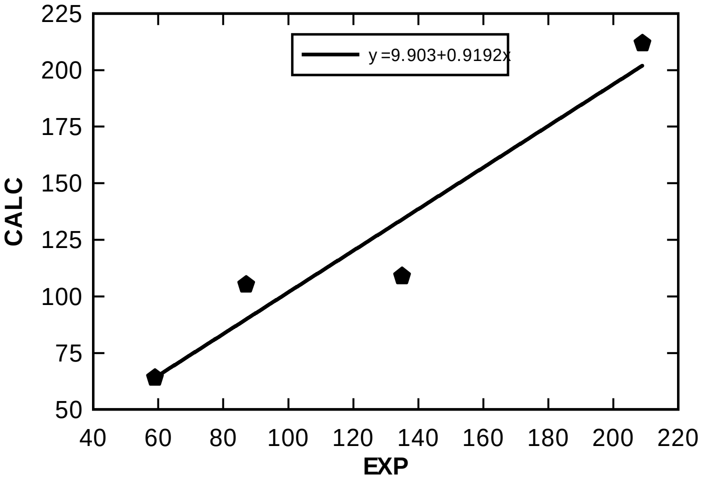


Figure 3. Plot of intrinsic viscosity prediction vs intrinsic viscosity experimental using Eq 2.

The second best equation was eq 3. included this descriptor υ_4 and υ_2 gave excellent model with correlation coefficient R^2 values for this model of 0.961, as equation 3. From eq 3. The positive value of υ_4 points to an increase in viscosity values increase the values of the vibration model, while negative reference of υ_2 stretching refers to the inverse relationship with viscosity.

η= -302038.291+1134.0157 υ_4 -579.527 υ_2……**Eq 3.**
$R^2 = 0.991$ S = 10.541 F =57.685

Statistical characteristics of the eq 3. very excellent comparable with eq 1 & eq 2. This indicated the big influences of these parameters on intrinsic viscosity of polymer. These results show that this model have a high correlation with experimental data shown in Figure 4.

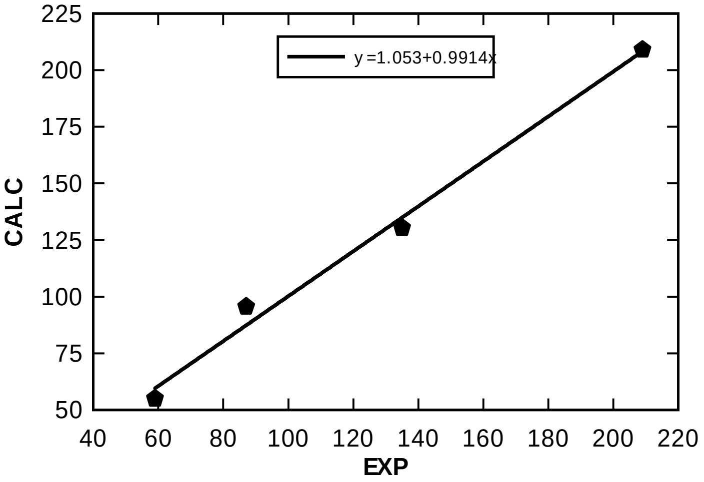


Figure 4. Plot of intrinsic viscosity prediction vs intrinsic viscosity experimental using Eq 3.

The predicted intrinsic viscosity values obtain from eqs. 1-3 which depicted in table 4., It is obvious from this table that the relations between descriptors which calculations in this study and experimental intrinsic viscosity values are excellent eq 3.

Table 4. Experimental and predicated of intrinsic viscosit of poly(isobutylene) by using Eqs 1-3.

SOLVENT	Exp	Calc		
		Eq.1	Eq.2	Eq.3
BENZENE	59	48.36	64.03	55.03
CCL4	135	119.53	108.91	130.37
CYCLOHEXANE	209	194.66	211.84	209
TOLUENE	87	127.44	105.2	95.59

CONCLUSION

The quantum chemical have been shown to provide very good QSPR models for the estimation of intrinsic viscosity of poly (isobutylene) by using values descriptors calculated by PM3 method, comparable with values descriptors calculated by AM1 method. . The predictive of the values of the correlation coefficient (R^2), standard error (SE) and F values for all the descriptors (mono & di descriptors) and models are predictive from the PM3 method are often best than the one from the AM1 method. From these results.. The model depending on the eq. 3. is the excellent produced model with very good statistical fit as evident from its $R^2 = 0.991$, $F = 57.685$ and $S = 10.541$ this model including vibration frequency of υ_4 and υ_2 showed insignificant role in the intrinsic viscosity in polymer. Through the present results exemplified here, we can apply a similar approach to build other QSPR models for intrinsic viscosity of poly(isobutylene) of those models will likely provide more effective means in designing novel polymer compounds with improved profiles.

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