QSPR Study of the Intrinsic Viscosity[η] of Polyisobutylene Solution

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Abstract: Quantitative structure-property relationship (QSPR) analysis to intrinsic viscosity [η] of polyisobutylene solution have been conducted. The study was done by using molecular modelling. The calculation was performed by the PBE method at 6-31G(d) basis set. The relationship analysis between intrinsic viscosity [η] and physicochemical properties of four solvents (benzene, toluene, cyclohexane, and CCl_4) under study was done by MLR analysis to generate the equation that relates the structural features to the intrinsic viscosity [η] properties. The results show good models with two parameters linear equations. The best model using theoretical parameters was the Eq. 1a, that including LUMOs and T.Es parameters. While the best model using experimental parameters was Eq.1b, that involving Ɛs and S parameters, with excellent statistical fit as evident from its R^2 = 0.999, F= 1413.035 and SE=2.138.

Introduction

Experimental measurements of some thermodynamic parameters involve experimental difficulties and they are not always feasible, and the corresponding methods possess real drawbacks[1]. Intrinsic viscosity, [η], is extensively used for analysis or characterization of synthetic polymers[2-4], biological macromolecules[5-6], nanoparticles, and colloids[7]. Consequently, it is necessary to resort to a theoretical calculation of these parameters. This option is now accessible because an important, fruitful and current field of research in contemporary chemistry is the model and prediction of physical-chemistry properties of molecules[8].

Quantitative structure–property/activity relationships (QSPR/QSAR) are tools to estimate physicochemical and biochemical parameters and reduce the coast, time and efforts[9-15]. QSPR/QSAR study is an important section in computational chemistry and uses frequently for predicting physicochemical and biological activity of organic compounds. To establish the relation between structural characteristics of molecule and its properties the mathematical methods can be used. The basic strategy of QSPR is to find the optimum quantitative relationship, which can then be used for the predication of the properties of

molecular structures including those unmeasured or even unknown[16-18]. Antreas *et al.*, have been investigated QSPR model for prediction of intrinsic viscosity in polymer solution by using the multiple liner regression technique on a database that consists of 65 polymer-solvent combination involving 10 different polymer[19]. The aim of this study is to investigate QSPR model for prediction of intrinsic viscosity of polyisobutylene solution by using two methods the first method using theoretical descriptors represents the solvents properties, while the second method using experimental properties of organic solvents to drive QSPR model.

Experimental

Geometry Optimization

Full geometric optimization calculations for four solvents (benzene, toluene, cyclohexane and CCl_4) were performed using PC Gamess[20]. Geometry optimizations were performed using 6-31G(d) basis set and PBE method[21]. Physical properties calculated involve total energy, LUMO energy and HOMO energy. The experimental values of viscosity and dielectric constant of four solvent taken from reference[19]. The structure of polyisoprene understudy shown in Scheme 1.
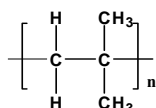
Scheme 1. Molecular structure of polyisobutylene used in the present study

Results and Discussion

The relationship between intrinsic viscosity[η] of polyisobutylene and various descriptors of organic solvents (Physiochemical and alignment-independent) were established by sequential multiple regression analysis (MLR) in order to obtain QSPR models. The best multilinear regression (BMLR) procedure[13-14] was used to find the best correlation models from the selected noncollinear descriptors. To establish the statistical correlation, the physicochemical parameters were taken as independent variables and intrinsic viscosity as dependent variable. The best model was selected on the basis of statistical parameters *viz* observed with high correlation coefficient (R), sequential Fischer test (F) and low standard error of estimate (SE), were employed to judge the validity of regression equation and evaluate the obtained QSPR models[22-25]. The model of QSPR study has been build up with help of the theoretical descriptors and experimental descriptors Table 1 and 2. The best model derived from the (MLR) analysis was used to intrinsic viscosity polymer in the 4 organic solvents which using in this study (benzene, toluene, cyclohexane and CCl_4). Several equations were generated by using all the variables and the best statistically model that we have obtained is two descriptor equations.

Table 1. Calculated physicochemical descriptors of the solvents

No	Solvent	*Exp [η]	HOMO	LUMO	T.E	Vander Waals volume A^3
					Theoretical descriptor	
1	Benzene	58	-0.2574	0.009	-231.964141	83.122
2		87	-0.2457	0.0093	-271.23345	99.806
3		135	-0.2314	-0.1859	-1878.045474	88.868
4		209	-0.3002	0.0999	-235.588135	101.13

*Ref=19 Definition of Descriptors Used in This Study *Exp[η]=Experimental viscosity of polymer, T.E= Totol Energy in hartree, HOMO=The energy of Highest Occupied Molecular Orbital in Hartree, LUMO= The energy of Lowest Unoccupied Molecular Orbital in Hartree

Table 2. Experimental physicochemical descriptors of the solvents

No	Solvent	*Exp [η]	*η	*Cp. J.deg⁻¹. mol⁻¹	*S. J.deg⁻¹. mol⁻¹	*εs
1	benzene	59	0.649	136	173.4	2.283
2	toluene	87	0.632	157	221	2.385
3	CCl4	135	0.908	130.7	216.2	2.24
4	cyclohexane	209	0.98	148.3	214.6	2.02

Ref=26 Ɛs=Dielectric constsntcontant ,Cp= Capacity heat in J.deg⁻¹.mol⁻¹=, S= Entropy in J.deg⁻¹.mol⁻¹ η= Viscosity of organic solvents

From Table 1, The model of QSPR study has been build up with help of the theoretical descriptors T. E, LUMO, HOMO and Vander Waals volume. The several QSPR model depends on the two theoretical descriptors, Table 3.
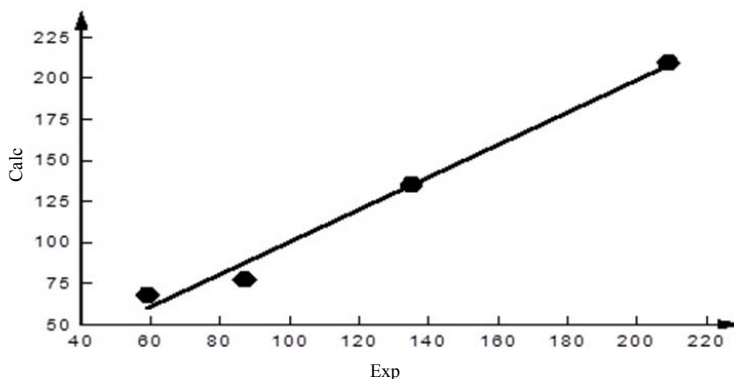
Table 3. Statistical parameters of the linear regressions models obtained by using two descriptor

Descriptor	R^2	F	SE
HOMO$_s$&LUMO$_s$	0.79	1.884	52.074
LUMO$_s$&T.E$_s$	0.986	36.218	13.269
T.E$_s$&HOMO$_s$	0.874	3.473	40.337
HOMO$_s$&V. W. V	0.532	0.569	77.76
LUMO$_s$& V. W. V	0.374	0.298	89.962
T.E$_s$& V. W. V	0.479	0.46	82.052

The best model was chosen, from Table 3 as the excellent model which it has less standard error (SE) and high R^2 and F values. The model when depend on two theoretical descriptors LUMO and T.E$_s$, gave good model with correlation coefficient R^2 values for this model of 0.98, as equation 1a.

Theoretical descriptor: [η]=2.0562-0.2241LUMO+1548.1752 T.E$_s$ (1a)

In Eq. 1a the positive sign of T.E$_s$ descriptor refers to a positive correlation with the intrinsic viscosity while negative signs of LUMO$_s$ descriptor suggest that the intrinsic viscosity decreases with increasing value of this descriptor. The relationship between the experimental and predicted data is represented in the Figure 1.

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

While the model of QSPR study has been build up depends on the experimental descriptors, (Table 2). Several equations were generated by using all the variables and the best statistically model that we have obtained is two descriptor equations (Table 4).

Table 4. Statistical parameters of the linear regressions models obtained by using two descriptor

Descriptor	R^2	F	SE
Cp**&**η	0.992	9.79	66.957
ε_s&Cp	0.828	2.412	47.114
Cp&S	0.332	0.248	92.918
η**&**S	0.889	4.017	37.831
η**&**ε_s	0.89	4.069	37.614
S**&**ε_s	0.999	1413.035	2.138

From Table 4, the best model when depend on only two experimental descriptor was eq 1b. This model build up by using the descriptors [ε_s and **S**] gave the best model with high correlation coefficient R^2, sequential Fischer test (F) and very low standard error (SE).

Experimental descriptor: $[\eta]=636.9807-357.4398\ \varepsilon_s+1.3733S$ (1b)

In Eq 2, the negative sign of E_s descriptor refers to inverse correlation between Ɛs with the intrinsic viscosity and on the other hand in this model Entropy have negative sign which suggests that the intrinsic viscosity increases with decreasing value of this parameter. The relationship between the experimental and predicted data Figure 2.
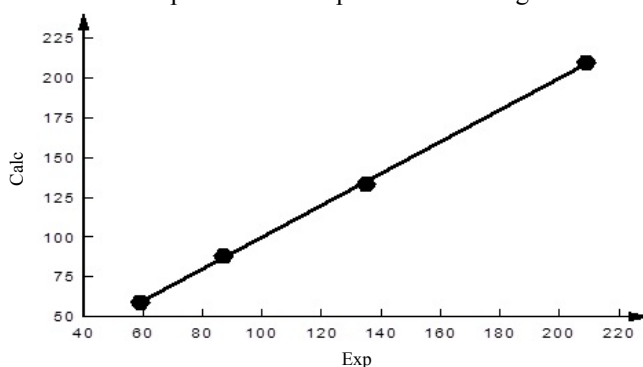

Figure 2. Plot of intrinsic viscosity prediction *vs*. experimental intrinsic viscosity using Eq.1b

The predicted intrinsic viscosity of polyisobutylene and experimental intrinsic viscosity can be seen in Table 5.

Table 5. Experimental and predicated of intrinsic viscosity of polyisobutylene

Solvent	Expintrinsic polymer	Calcd. Eq. 1a	Calcd. Eq. 1b
Benzene	59	59.08	53.6
Toluene	87	88	90.95
CCl$_4$	135	133.23	140.72
Cyclohexane	209	209.67	204.72

Conclusion

The present study have been shown to provide very good QSPR models for the estimation of intrinsic viscosity of poly(isobutylene) solution by using values theoretical descriptors

calculated and experimental descriptors. The study indicated that intrinsic viscosity [η]of polyisobutylene solution parameters of organic solvents can be modeled. The best model when depends on theoretical descriptors [LUMO and T.E] was Eq.1a, while the best model when depends on experimental descriptor[ε_s and S]was eq1b. From all the results, the QSPR models, Eq. 1a. which depends on theoretical descriptors [LUMO and T.E$_s$] give results close to QSPR models Eq. 1b, that have been used experimental descriptor organic solvents. And this showed insignificant role in predict the QSPR model of the intrinsic viscosity [η] of polyisobutylene solution. This result encourages the application of QSPR techniques to a wider selection of polymer properties.

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