مجلة المثنى للعلوم الصرفة
AL-Muthanna Journal of Pure Sciences (MJPS)
VOL.(3)...NO.(1) 2016

Quantum Chemical QSPR Study of The Best Parameters Influences on Intrinsic Viscosity of Polyisoprene Solution

Sadiq M-H. Ismael, Kawkab A. Hussain, Hawraa K. Dhaef
Department of Chemistry– College of Education Pure Science
University of Basrah

Abstract

Quantitative Structure-Property Relationship (QSPR) analysis for intrinsic viscosity [η] of Polyisoprene solution have been conducted. The study was done by using molecular modeling. The calculation was performed by the (PBE)exchange-correlation functional method for (Perdew, Burke, and Ernzerhof) at 6-31G(d) basis set. The relationship analysis between intrinsic viscosity [η] of polyisoprene solution and physicochemical properties of four solvents [Benzene, Toluene, Hexane, and Isooctane] under study was done by multiple linear regression (MLR) analysis to produce the equation that relates the structural features to the intrinsic viscosity [η] properties. The results show good models with one and two parameters linear equations. The best model predicted in this study was the eq.3, with excellent statistical fit as evident from its R2=0.99, F=218144 and S=0.129, the model including the descriptors [LUMOs and HOMOs], which showed insignificant role in the intrinsic viscosity [η] of polyisoprene solution. And this could potentially offer a new opportunity in the design of novel properties of polymers or extended to other polymer composite.

Keywords: Intrinsic Viscosity, QSPR model.

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 physico-chemical and biochemical parameters and reduce the coast, time and efforts [9,12]. (QSPR/QSAR) study is an important section in computational chemistry and uses frequently for predicting physico-chemical and biological activity of organic compounds.

To establish the relation between the structural characteristics of molecule and its properties the mathematical methods can be used. The basic strategy of QSPR is employed to find the optimum quantitative relationship, that can then be used for the predication of the properties of molecular structures including those unmeasured or even unknown [13,15]. Antreaset 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 [16]. In this research the QSPR model was produced by using the multiple linear regression (MLR) technique on a database that consists of one polymer in four organic solvent for the prediction of intrinsic viscosity of polyisoprene solution, and focus of some of the descriptors in deriving predictive QSPR models,[17,19]. The descriptors used in the composition of models represents the solvent properties are two types theoretically such as $HOMO_s$, $LUMO_s$ and Total Energy ($T.E_s$), and practically such as the viscosity of the solvent and the dielectric constant (Ɛ) of the solvent.

Geometry Optimization& Experimental

Full geometric optimization calculations for four solvents(benzene, toluene, hexane and isooctane) 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, $LUMO_s$ energy and $HOMO_s$ energy.

Results and Discussion

The relationship between intrinsic viscosity of polyisoprene solution 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. The descriptors Table 1, which were significant for experimental data, were selected by QSPR-contingency module. 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 (S), were employed to judge the validity of regression equation and evaluate the obtained QSPR models [22,25].

Table 1.Physic-chemical descriptors of the solvents.

NO	Solvent	[1*]Exp, [η]	$T.E_s$	$LUMO_s$	$HOMO_s$	[2*] η	[3*]Ɛs
1	benzene	186	-231.964	0.009	-0.2574	0.649	2.283
2	toluene	184	-271.233	0.0093	-0.2457	0.632	2.385
3	hexane	91	-276.044	0.1037	-0.309	0.313	1.89
4	isooctane	110	-315.306	0.0856	-0.3037	0.502	1.94

[1*]Exp[η]=Ref=16, [2*]η&[3*]Ɛs= Ref = 26

Definition of Descriptors Used in This Study.

$T.E_s$=Totol Energy in hartree of solvent,$HOMO_s$=The energy of Highest Occupied Molecular Orbital in hartree, $LUMO_s$=The energy of Lowest Unoccupied Molecular Orbital in hartree,Ɛs=Dielectric constsnt of solvent.[1*]Exp[η]=intrinsic viscosityof polyisoprene solution.[2*]η=Viscosity of solvent

The model of QSPR study has been build up with help of the descriptors $T.E_s$, $LUMO_s$, $HOMO_s$, Viscosity and Ɛswas investigated. The predictive model of QSPR study has been built up with the help of the following descriptors in Table 1. The best model derived from the (MLR) analysis was used to intrinsic viscosity polymer in the 4 organic solvents which using in the study [Benzene, Toluene, Hexane, and Isooctane]. Several equations were generated by using all the variables and the best statistically model that have obtained is one-two descriptor equation, table. 2 and 3, when depend on only one descriptor such as $HOMO_s$, $LUMO_s$, $\eta_s$andε_s. From table 2,The correlation between [η] and $LUMO_s$gave good correlation coefficient R^2 values and low standerd error.

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

descriptor	R^2	F	S
$T.E_s$	0.450	1.640	44.8513
η_s	0.873	13.779	21.542
ε_s	0.960	48.548	12.0359
$HOMO_s$	0.964	55.008	11.333
$LUMO_s$	0.999	7125.924	1.0135

the best second model when depend on only two descriptor Table 3. That gave good model with high correlation coefficient R^2 values.

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

descriptor	R2	F	S
$T.E_s$&η_S	0.960	12.019	17.101
ε_s&$T.E_s$	0.968	15.137	15.301
$HOMO_s$&$T.E_s$	0.968	15.484	15.134
$HOMO_s$&ε_S	0.970	16.578	14.641
ε_s&η_s	0.981	26.342	11.679
$HOMO_s$&η_s	0.997	203.799	3.482
$LUMO_s$&η_S	0.999	2992.857	1.105
$T.E_s$&$LUMO_s$	0.999	1803.275	1.424
$LUMO_s$&ε_s	0.999	37786	0.311
$HOMO_s$& $LUMO_s$	0.999	218144	0.129

The best model was chosen, whose specifications are presented in Table 3, we have chosen three equations as the excellent model which it has less standard error (SE) and high $R^2$and F values. The resulting parametric models are depicted in Eq. 1 to 3, and figures 1to 3. The model when depend on descriptors [$LUMO_s$ and $T.E_s$], these gave good model with correlation coefficient R^2 values for this model of 0.99, as equation 1.

$[\eta]$=195.013(+/-)522.009-988.039(+/-)1413.101$LUMO_s$+3.595(+/-)2.069$T.E_s$ ------ Eq.1

From eq 1, the positive sign of $T.E_s$ descriptor refers to a positive correlation with the intrinsic viscosity. In this model $LUMO_s$ have negative sign which suggest that intrinsic viscosity decreases with increasing value of this parameter. The relationship between the experimental and predicted data shows in Fig 1.

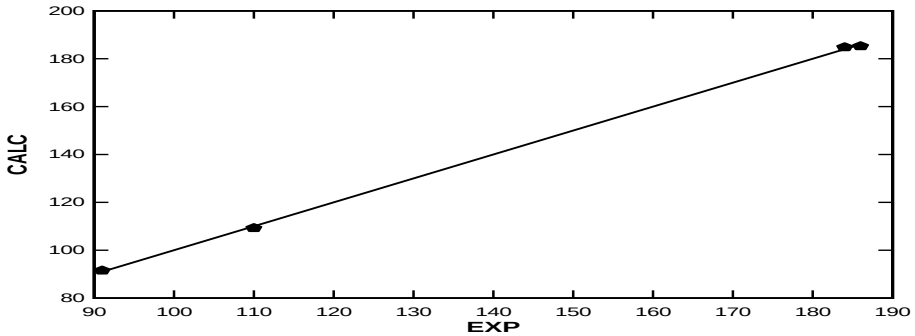

Figure 1.Plot of intrinsic viscosity prediction vsexperimental intrinsic viscosity using eq.1.

While when replace the descriptor$T.E_s$ in eq 1, by the descriptor Ɛs this lead to generated the eq 2. That gave model with correlation coefficient R^2 values for this model of 0.99, with low less standard error (SE) comparable with eq.1.

.$[\eta]$=236.741- 1076.715(+/-)1253.646LUMOs-17.938(+/-)254.040Ɛs……Eq.2

In eq 2, the negative sign of these descriptors refers to inverse correlation between LUMOs and Ɛs with the intrinsic viscosity. The relationship between the experimental and predicted data, Fig (2).

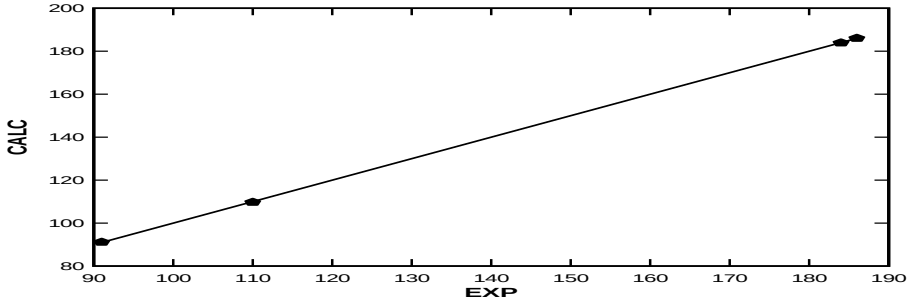

Figure 2.Plot of intrinsic viscosity prediction vs experimental intrinsic viscosity using eq2.

In equation 3.These build up by using the descriptors [$LUMO_s$ and $HOMO_s$]. This model generated by replace the descriptor Ɛs in eq 2, by descriptor $HOMO_s$ gave the best model

with correlation coefficient R^2 values for this model of 0.99,and very low standard error (SE) 0.129.

[η] =157.104(+/-)213.910-150(+/-)868.827$HOMO_s$-1084.892(+/-)$LUMO_s$ ----**Eq.3**

Also in eq 3, the negative sign of $HOMO_s$ and $LUMO_s$ descriptors refers to inverse correlation between the intrinsic viscosity and these parameters.

The relationship between the experimental and predicted data was showed in Fig 3.

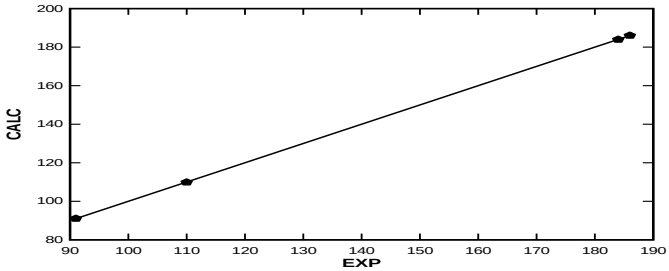

Figure 3.Plot of intrinsic viscosity prediction vs experimental intrinsic viscosity using eq 3.

The predicted intrinsic viscosity of polyisoprene and experimental intrinsic viscosit can be seen in table 4.

Table 4.Experimental and predicated of intrinsic viscosity of Polyisoprene by usingEqs 1-3.

Solvent	Exp [η]	Calc eq.1	Calc eq.2	Calc eq.3
benzene	**186**	**185.28**	**186.09**	**186.05**
toluene	**184**	**184.84**	**183.94**	**183.96**
hexane	**91**	**91.56**	**91.18**	**91.07**
isooctane	**110**	**109.3**	**109.77**	**109.91**

Conclusion

The linear model and multiple regressions were performed between intrinsic viscosity [η] of polyisoprene solution and some chemical parameters/descriptors of organic solvents. The study indicated that intrinsic viscosity for polymer can be modeled. The values of R^2, S and F suggest that the QSPR models in Eqs from1 to 3 are predicted and validated. From all the results the Eq 3.have small value of S and large the values of F and R^2 that regard as better in QSPR model. The experimental and the predicted values using MLR model was excellent, and this model including [$LUMO_s$ and $HOMO_s$] showed significant role in the intrinsic viscosity [η] of polyisoprene solution. This study may be helpful for the chemists and researcher to understanding parameters intrinsic viscosity of polyisoprene solution understudy.

References

1-Stull D R., Westrum E F., andSinke G C., *The Chemical Thermodynamics of Organic Compounds*., Wiley, New York, (1969).

2-Elias HG., Macromolecules., vol. 1. Wiley Interscience, New York,(1977).

3-Billmeyer FW., *Textbook of polymer science*., 3rded, Wiley Interscience, New York, (1984).

4-Munk P., and Aminabhavi TM., *Introduction to macromolecular science*., 2nded,Wiley, New York,(2002).

5- Harding S.E., *ProgBiophys MolBiol* ., 68:207–262,(1997).

6- Van Holde K.E., Johnson W., and Ho P., *Principles of physical biochemistry*., 2nded, Prentice Hall, Upper Saddle River, New jersey, USA,(1998).

7- Hunter R.H., *Foundations of colloid science*., Oxford University Press, Oxford. Uk,2001.

8-Yefim B., *Encyclopedia of Chromatography*., 2rded, CRC Press., Taylor & Francis Group, USA, (2009).

9-Bahjat A S., Rita S E., Sadiq M-H I., and Kawkab A.H .,*American Journal of Applied Sciences*., 8 (8), 773-776,(2011).

10-Andrés M, Eduardo A. C., and Andrey A. T., *Int. J. Mol. Sci*., 2, 121-132,(2001).

11-Rita S E., Sadiq M-H I., and Bahjat A. S.,*International Journal of PharmTech Research.*,3,(4), 2183-2189,(2011).

12-Kawkab A. H, Wisam A-H R., and Sadiq M-H I., *J. Chem. Pharm. Res*.,4(3),1702-1707.(2012).

13-Uzma M., Sitara R., Ishrat A S.,Rasheeda P., Zaheer-ul-H., Nida A., Khalid M K., Shahnaz P.,
and Wolfgang V., *Int. J. Mol. Sci.*,12,8862-8877,(2011).

14-Antreas A., Georgia M., Kalliopi M., Alex A., Haralambos S., and Olga Iglessi-M., *Journal of Molecular Structure: Theochem*., 716, 193–198,(2005).

15- Irina R., Victor K., Olga O., Eugeniy M., Anatoliy A., and Sergei A., *Chemistry& Chemical Technology*., 3,4,255-261,(2009).

16-Antreas A., Georgia M., Haralambos S., Panayiotis A. K., John M., and Olga Igglessi-M.,*Polymer*.,47,3240-3248,(2006).

17-Sadiq M-H I., *Journal of Computational Methods in Molecular Design*.,2(4):130-135,(2012).

18-Kawkab A. H. A., Methem N. A., andSadiq M-H.I.,*Journal of Basrah Researches ((Sciences))*, 37. 4 A/ 111-115,(2011).

19-Sadiq M-H. I., Kawkab A. H., and Hasanain A S. A M., *Der Pharmacia Lettre*.,4 (6):1826-1831,(2012).

20. Schmidt M.W., Baldridge K. K., BoatzJ. A., Elbert S.T., Gordon M. S., Jensen J. H., Koseki S., Matsunaga N., NguyenK. A.,Su S. J., Windus T. L., Dupuis M., and MontgomeryJ. A., *J. Comput.Chem.*,14, 1347-1363,(1993).

21-PBE exchange/correlation functional: Perdew J. P., Burke K., and Ernzerhof M., *Phys. Rev. Lett*., 77, 3865-8,(1996). Ernzerhof M., and Scuseria G. E., *J. Chem. Phys*., 110, 5029-5036,(1999).

22- Cardoso S. P., Gomes J. A. C. P., Borges L. E. P., and Hollauer E., *Brazilian Journal of Chemical Engineering*.,24,4, 547-559,October-December, (2007).

23-Satish K. S., Kalpna T., Jitendra B., Parul M., Pathak A.K., and Mukul T., *International Journal of Advances in Pharmaceutical Sciences.*,1.309-318, (2010).

24-LIU T-B.,PENY Y-F., and WU X-M., *Chinese J. Struct. Chem*., 26, 12, 1466-1470,(2007).

25- Lorentz J., *Leonardo Journal of Sciences*.,4, January-June,68-85,(2004).

26- John A. D., *Lange's Handbook OF Chemistry*.,15th ed.CRC Press, USA,(1999).

دراسة نظرية وكمية بتقنيات QSPR لأفضل تأثير للمتغيرات على اللزوجة الجوهرية [η] لمحلول البولي ايزوبرين

صادق محمد حسن اسماعيل كوكب علي حسين حوراء كريم ضايف
جامعة البصرة –كلية التربية للعلوم الصرفة- قسم الكيمياء.

الخلاصة

وصفت اللزوجة الجوهرية لمحلول البولي ازوبرين باستخدام تقنيات العلاقة التركيبية الخصائصية الكمية QSPR. انجزت الحسابات بطريقة دالة العلاقة الاستبدالية exchange-correlation functional (PBE) ل (Perdew, Burke, and Ernzerhof) وعند المستوى النظري 6-31G(d). وتم تحليل العلاقة بين اللزوجة الجوهرية [η] لمحلول البوليمر والخواص الفيزوكيميائية للمذيبات [Benzene, Toluene, Hexane, and Isooctane] تحت الدراسة بأستخدام تحليل الخطي المتعدد MLR لتكوين معادلة تربط مميزات التركيب بخواص اللزوجة الجوهرية [η].أظهرت النتائج موديلات جيدة ذات علاقة خطية مع اثنين من المتغيرات. وكان افضل موديل للتنبأ في هذه الدراسة معادلة رقم 3، مع وسائط احصائية R^2=0.99, F=218144 and S= 0.129, الموديل تضمن الموصوفات [$LUMO_s$, $HOMO_s$] والتي اظهرت دور مميز في التأثير على اللزوجة الجوهرية لمحلول البولي أيزوبرين. وهذه الدراسات ممكن أن تقدم فرص حديثة لتصميم خواص جديدة للبوليمرات او التوسع لمكونات بوليمرية اخرى.