Theoretical study of Optimum conditions of intrinsic viscosity of polyethylene oxide solution using QSPR model

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(NJC)
(Received on 13/6/2013) (Accepted for publication 25/11/2013)

Abstract

Quantitative Structure–Property Relationship (QSPR) models method have been used for the prediction intrinsic viscosity of (poly ethylene oxide) in solution. Several models for the prediction of intrinsic viscosity have been drawn up by using the multiple regression technique. Penta models with R^2 ranges from 0.87-0.99 by using MLR based on descriptors calculated from molecular structure have been developed present in this study. The results show excellent model with high correlation coefficient, minimum standard of error by using five parameters, which indicate that these parameters Total Energy T.E, capacity heat of organic solvent Cp(s), Van Der Waals Area V.W.AREA, The energy of Highest Occupied Molecular Orbital HOMO and The energy of Lowest Unoccupied Molecular Orbital LUMO, play an important role in effect on intrinsic viscosity of polymer in these solvents .

Keywords. Intrinsic Viscosity, Organic Solvents, Redesign QSPR Model.

الخلاصة

العلاقة التركيبية الخصائصية الكمية استخدمت للتنبأ باللزوجة الجوهرية ل(بولي اثليين اوكسيد) في المحلول. عدة موديلات للتنبأ باللزوجة الجوهرية وضعت بأستخدام تحليل MLR . خمسة موديلات تملك معامل احصائي ضمن المدى R=0.87-0.99 باستعمال MLR اعتمادا على الموصوفات المحسوبه من التركيب الجزيئي . النتائج اظهرت أن أفضل موديل ممتاز والتي لها أفضل الوسائط الاحصائية (اعلى قيمه لمعامل الارتباط واقل خطأ) باستخدام خمس متغيرات , HOMO, LUMO, T.E, Cp(s) and V.W.AREA والتي اكدت بأن هذه المتغيرات تلعب دورا مهما في التأثير على اللزوجة الجوهرية [η] لمحلول بولي أثلين اوكسيد في المذيبات المختارة .

Introduction

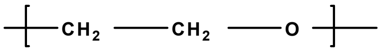
Intrinsic viscosity [η] is the ratio of a solution's specific viscosity to the concentration of the solute, extrapolated to zero concentration. Intrinsic viscosity reflects the capability of a polymer in solution to enhance the viscosity of the solution. The intrinsic viscosity number is defined as the limiting value of the specific viscosity/concentration ratio at zero concentration. Intrinsic viscosity is dependent on the salinity of the solvent, temperature, molecular weight and the percentage of polymer hydrolysis [1-2]. The variation of the viscosity number with concentration depends on the type of molecule as well as the solvent. In general, the intrinsic viscosity of linear macromolecular substances is related to the molecular weight or degree of polymerization [3-6]. The different approaches for the prediction of intrinsic viscosity such as quantitative-structure-property relationships (QSPR) [7-8]. This approach, based on molecular structure, is important not only from a fundamental physical point of view, since it allows a more transparent interpretation of the phenomenon on physical ground, but it is also technologically useful for the efficient production of materials with specific properties for a given application [9-12]. Thus, predictive models based on molecular structure are important for the design of novel chemicals since properties can be thus predicted prior to synthesis. In this way, the design of novel compounds may be guided by the calculation results [13]. Sarimvies et al., have been investigated Quantitative Structure–Property Relationship (QSPR) model for prediction of intrinsic viscosity in polymer solution by using the multiple linear regression techniques on a database that consists of 65 polymer-solvent combination involving 10 different polymer (14). On the other hand we previously reported the QSPR model for prediction of intrinsic viscosity of polyethylene oxide (15). In this paper we re-report a QSPR model for the prediction of intrinsic viscosity of polyethylene by combination polymeric chain parameters with experimental organic solvents properties such as capacity heat and enthalpy of sublimation.

Geometry Optimization

Theoretical calculations were performed on MOPAC program version 11.052w [15], running on a Pentium V PC-CPU 3.400GHz. The geometries of the compound were optaimized first at level (MM+) by molecular mechanics force field theory and then at calculation done by the RM1 Hamiltonion to be used calculated from the composition series consisting of 14 monomer units [16].

Experimental

The experimental intrinsic viscosity data of polyethylene oxide under study has been taken from reference[14]. Structure of this compound shown in Figure.1.



Polyethers

Poly(ethylene oxide)

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

Results and Discussion

QSPR model for prediction and recomputed of the intrinsic viscosity in polymer–solvent combinations. The eight organic solvents have been used in the study [BENZENE, ACETONE, CARBON TETRACHLORIDE, CHLOROFORM, CYCLOHEXANE, DIOXANE, DIMETHYLFORMAMIDE and METHANOL] using MLR based on descriptors calculated from molecular structure,Table1.

Table 1. Calculated physico-chemical parameters of the polymeric chain and observed parameters of the organic solvents.

EXP[η] Intrinsic viscosity	SOLVENT	LUMO	HOMO	ELEC.E	V.W.A	DIELEC.E	H.F	T.E	CP (s)	ΔHs (s)
120	BENZENE	1.386	9.517-	40837.5-	1692.67	0.43935-	2116.49-	9009.75631-	136	33.8
78	ACETONE	1.354	9.569-	14889-	1545.91	0.99624-	2166.61-	9010.27575-	126.3	31
135	CARBON TETRACHLORIDE	1.376	9.535-	41880-	1786.53	0.41976-	2109.35-	9009.68226-	130.7	32.4
102	CHLOROFORM	1.397	9.509-	26933.7-	1635.99	0.65649-	2142.76-	9010.02858-	114.2	31.3
186	CYCLOHEXANE	1.438	9.457-	44811.8-	1818.78	0.23194-	2104.74-	9009.63455-	148.3	33
127	DIOXANE	1.417	9.483-	42075.1-	1671.96	0.40054-	2118.88-	9009.78104-	153.6	38.6
209	DIMETHYLFORMAMIDE	1.374	9.539-	13259.2-	1565.52	0.98741-	2170.06-	9010.31155-	150.6	46.9
257	METHANOL	1.366	9.55-	13442.8-	1164.18	1.08735-	2178.95-	9010.40362-	81.2	37.4

CP(S =(capacity heat of organic solvent ,ΔHs(S =(Enthalpy sublimation of organic solvent =Ref [17] =and] η =[Ref.[14] =
Ref= [17] and [η]= Ref= [14].

include number of variables as small as possible relatively, checking the highest of correlation coefficient R, minimum standard of error S and significantly by F parameter. The best model derived from the (MLR) analysis was used to intrinsic viscosity polymer in the Eight organic solvents which using in the study [BENZENE, ACETONE,CARBON TETRACHLORIDE, CHLOROFORM, CYCLOHEXANE, DIOXANE, DIMETHYLFORMAMIDE and METHANOL]. The resulting parametric models are depicted in Eq. 1-4, along with statistical parameters of the regression[19-22]. The first model when depend on only five parameter

Definition of Descriptors Used in This Study.
LUMO= The energy of Lowest Unoccupied Molecular Orbital in eV, HOMO= The energy of Highest Occupied Molecular Orbital in eV, ELE.E= Electronic Energy eV., V.W.AREA= VAN DER WAALS AREA Ang^2, DIELE=Dielectric Energy eV, H. F= Heat of Energy in KJ/mol, T.E = Total Energy in eV, ΔHs(S)= Enthalpy sublimation of organic solvent in KJ mol $^{-1}$ and CP(S)= capacity heat of organic solvent in J. K^{-1}. Mol^{-1}.

The correlation analysis to find the best QSPR model was carried out using the best multi linear regression analysis method. Evaluating the best QSPR model is looking for the model

[ΔHs(S), LUMO,T.E, HOMO and H.F] gave good model with correlation coefficient R^2 values for this model of 0.874, as equation1.

$$[\eta]=47844368.603T.E-495872.701H.F-12.144\Delta Hs(S)+15081.286LUMO-12127.598HOMO\ldots\ldots\ldots Eq1.$$

$$R^2 = 0.874 \quad F = 2.793 \quad S = 39.838$$

In this model H.F, ΔHs(S) and HOMO have negative sign which suggests that the intrinsic viscosity decreases with increasing values of these parameters, while it increase with increasing values of both T.E and LUMO. The relationship between the experimental and predicted data in this model, Fig.2

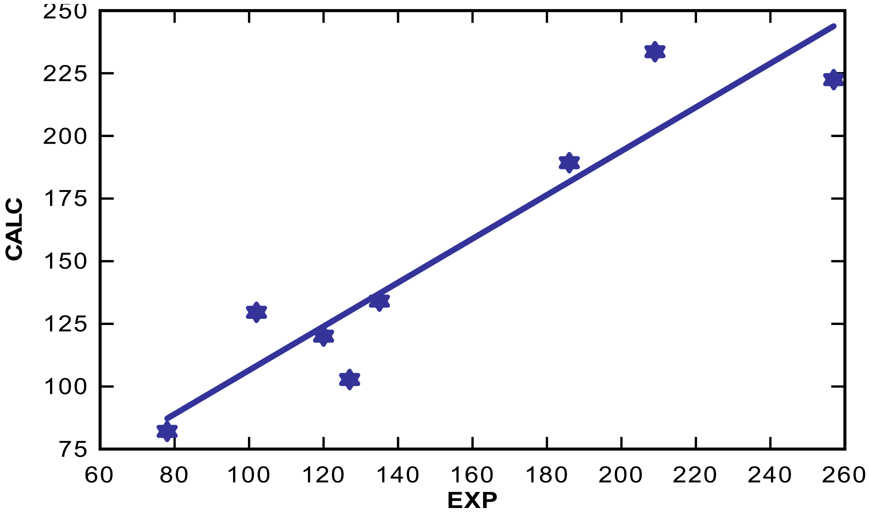


Figure 2. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq1.

On the other hand the the correlation coefficient R^2 increase when using the parameters [H.F, LUMO, HOMO and ΔHs(S)] and become 0.942 , Eq 2.

$$[\eta] = 29617924.798T.E-306967.414H.F-1.682CP(S)+15475.476LUMO-12241.214HOMO+266200453735.401\ldots\ldots\ldots\ldots Eq\ 2.$$

$$R^2 = 0.942 \quad F=6.582 \quad S = 26.942$$

From eq 2. Positive sign of T.E and LUMO descriptor refers to a positive correlation with the intrinsic viscosity, while negative sign of H.F, ΔHs(S) and HOMO refers to a negative correlation with intrinsic viscosity. The relationship between the experimental and predicted data ,Fig.3

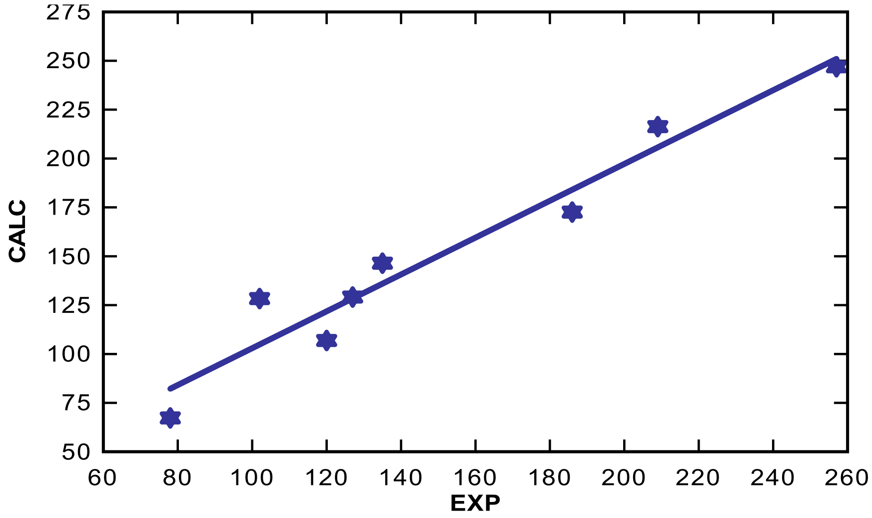


Figure 3. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq2.

While the correlation coefficient R^2 increase when using the parameters [H.F, T.E, CP(S), ELECT.E, and LUMO]. the correlation coefficient R^2 value rised to 0.983 , Eq. 3.

$$[\eta] = 17305401.568T.E-179334.636H.F-1.387Cp(S)+6526.438LUMO-2542.446ELECT.E+155537881131.341 \ldots\ldots\text{Eq 3.}$$

$R^2= 0.983$ $F =23.604$ $S = 14.531$

Eq 3. negative sign of H.F, Cp(S) and ELECT.E descriptor refers to a negative correlation with the intrinsic viscosity, while positive sign of T.E and LUMO refers to a positive correlation with intrinsic viscosity. The relationship between the experimental and predicted data ,Fig.3

The relationship between the experimental and predicted data in this model, Fig.4.

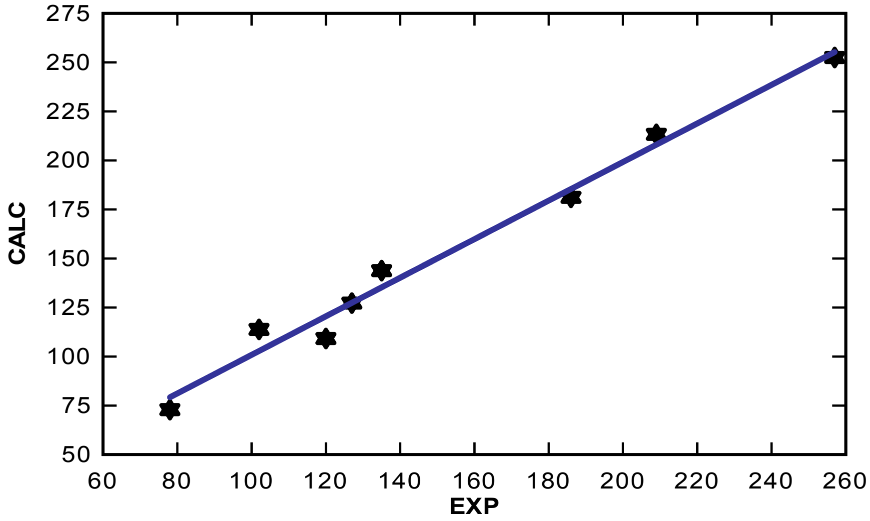


Figure 4. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq3.

In Eq 4. The correlation coefficient R^2 increase when using the parameters [CP(S), H.F, Di ELEC.E, HOMO and LUMO] and become 0.999.

$$[\eta] = 17723.997\text{HOMO} + 50.125\text{H.F} - 0.925\text{Cp(S)} - 7862.150\text{LUMO} - 5622.654\text{DIELEC.E} + 283443.989 \quad \text{........ Eq 4.}$$

$$R^2 = 0.9996 \quad F = 1177.185 \quad S = 2.074$$

Positive sign of H.F and HOMO descriptor refers to a positive correlation with the intrinsic viscosity, while negative sign of Cp(S), LUMO and DIELEC.E refers to a negative correlation with intrinsic viscosity in eq 4. The relationship between the experimental and predicted data ,Fig.5.

The relationship between the experimental and predicted data in this model, Fig.5

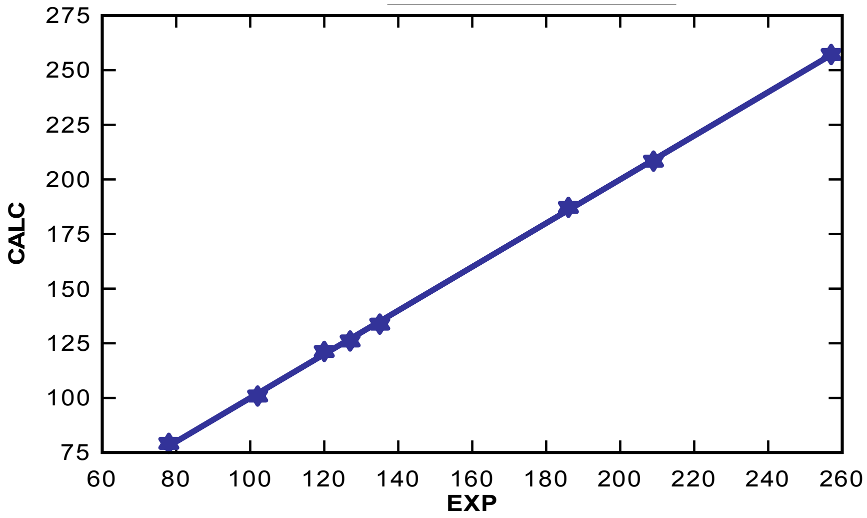


Figure 5. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq 4.

When replacement the parameters DiElec and H.F in eq 4. By the parameters V. W.AREA and T.E, this lead us to best F value with R^2 constant in the eq 5. by using the parameters [T. E, HOMO, CP(S), LUMO and V.W.AREA].

$$[\eta]=4835.719T.E+17719.297HOMO-0.925Cp(S)-7858.362LUMO-5621.829\,V.W.AREA+43745958.260 \ldots\ldots\ldots\ldots \text{Eq 5.}$$

$R^2 = 0.9996$ F = 1181.958 S = 2.070

From eq 5, the positive sign of HOMO descriptor refers to a positive correlation with the intrinsic viscosity, while negative sign of Cp(S), LUMO and V.W.AREA refers to a negative correlation with intrinsic viscosity in eq 5. Compared with the previous study (22) we notes that F and S values in this study improved with constant values R^2. The relationship between the experimental and predicted data, Fig.6.

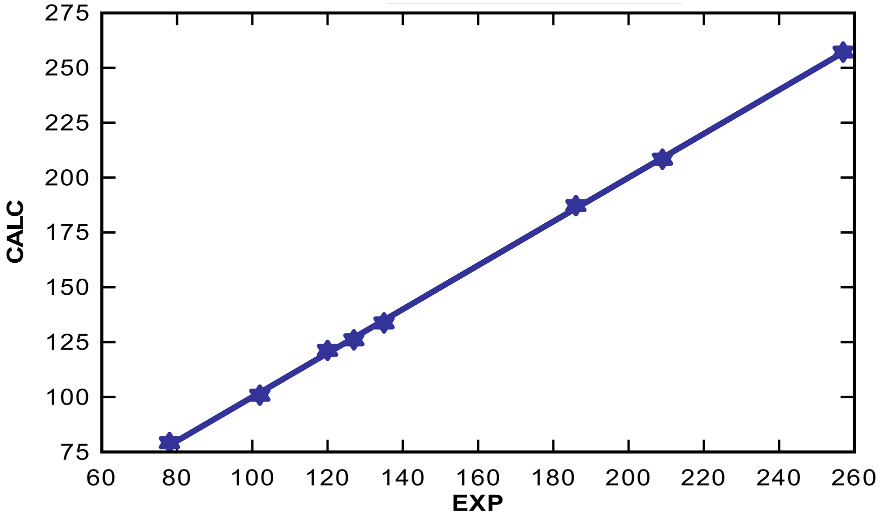


Figure 6. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq 5

In the Table 2 The predicted intrinsic viscosity values obtain from Eq. 1-5 in this study and It is obvious from Table 2 that the relations between descriptors which calculations in this study and experimental intrinsic viscosity values are excellent [20], compared with the previous study found that the equations 4 and 5 have the F and SE values are better than those obtained in the previous study [15].

Table 2. Predicated Experimental Data

Exp[η] Intrinsic viscosity	Calc F=1181	Calc F=1177	Calc F=23.604	Calc F=6.582	Calc F=2.79	*Previous Study
120	121.29	121.29	109.2	106.9	120.08	118.68
78	79.2	79.2	72.94	67.3	82.07	77.14
135	133.78	133.78	143.8	146.46	134.07	136.13
102	100.87	100.87	113.84	128.35	129.59	103.24
186	187.2	187.21	181.17	172.58	189.31	185.16
127	126.08	126.08	127.25	129.13	102.79	127.50
209	208.37	208.37	213.3	216.32	233.6	209.04
257	257.16	257.16	252.47	246.92	222.46	257.67

*=Ref [15], F= 672.6164, SE= 2.5056, R= 0.9997

Conclusion

In the present study we investigated and recomputed descriptors for intrinsic viscosity in polymer–solvent combinations. The excellent regression coefficients R, depends on Eq 4. & Eq 5 and the best of model which depends on the parameters in Eq 4. & Eq 5; have a significant role in the intrinsic viscosity of the polyethylene oxide. We have improving the value of R^2 and compared QAPR results of the intrinsic viscosity with previously study, and attempt to build the best successful QSPR models. In Eq 5. descriptors understudy including [T.E, CP(S), VW.AREA, HOMO and LUMO], with the values of **R^2= 0.999, F=1181.958 and S=2.070.**

The observed and the predicted values was excellent. QSPR techniques are of considerable importance, because it can offer faster(50 minute for optimization and 10-11days the predicted values of QSPR), precise, and cheaper means to interpret and assess the structural parameters that determine the physical property and to predict the property for new compounds without the necessity to synthesize them, and this may be helpful for the industrial chemists in understanding intrinsic viscosity in polymer.

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