Investigation Of The Best Parameters Influences On Intrinsic Viscosity In Polymer And Recomputed QSPR Model

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Abstract: Quantitative Structure – Property Relationship (QSPR) models based on molecular descriptors derived from molecular structures have been used for the prediction , improving and for recomputed intrinsic viscosity of polymer compound (poly ethylene oxide) in eight organic solvents[BENZENE, ACETONE, CCL_4, $CHCL_3$, CYCLOHEXANE, DIOXANE DMF and METHANOL]. QSPR model includes some molecular descriptors, regression quality indicates that these descriptors provide valuable information and have significant role in the assessment of the intrinsic viscosity of poly ethylene oxide. Several models for the prediction of intrinsic viscosity have been drawn up by using the multiple regression technique. Seven models with R^2 ranges from 0.98-0.99 by using MLR based on descriptors calculated from molecular structure have been developed. present in this study. The results show excellent model by Eq 5. & Eq 6. With high correlation coefficient, minimum standard of error by using six parameters, which indicate that these parameters T.E, DIELEC.E, VW.AREA, ELEC.E, HOMO, H.Fand LUMO, play an important role in effect on intrinsic viscosity of polymer in these solvents .
*Keyword*s. *Intrinsic Viscosity, Organic Solvents, Recomputed QSPR model.*

Introduction

Intrinsic viscosity [ ] 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].

In this paper we re-report a QSPR model for the prediction of intrinsic viscosity of polymer compounds in six organic solvent and based on six molecular descriptors having definite physical meaning corresponding to the different intermolecular interactions occurring

in the solution. The QSPR shall reduce the coast, time and efforts. we demonstrate the usefulness some of the parameters in deriving predictive QSPR models. To know parameters effect of the intrinsic viscosity behavior of polymer in organic solvents, and to find out the effect of various the structural, chemical, physical and other properties Ref[14]. 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].

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 compounds were

Experimental

The experimental intrinsic viscosity data of compounds under study has been taken from

reference[14]. Structure of this compound shown in Figure.1.
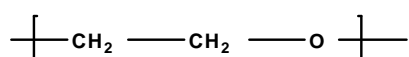
Polyethers

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 8 organic solvents which using in the study [BENZENE, ACETONE,

CCL$_4$, CHCL$_3$,CYCLOHEXANE, DIOXANE DMF and METHANOL] using MLR based on descriptors calculated from molecular structure, Table 1.

Table 1. Calculated physico-chemical parameters of the compounds

T.E	H.F	DIELE.E	V.W.AREA	ELE.E	HOMO	LUMO	SOLVENT	No
-9009.7563	-2116	-0.439	1692.67	-40837.54	-9.517	1.386	BENZEN	1
-9010.2758	-2167	-0.996	1545.91	-14888.98	-9.569	1.354	ACETONE	2
-9009.6823	-2109	-0.42	1786.53	-41879.97	-9.535	1.376	CCL4	3
-9010.0286	-2143	-0.656	1635.99	-26933.65	-9.509	1.397	CHCL3	4
-9009.6346	-2105	-0.232	1818.78	-44811.79	-9.457	1.438	CYCLOHEXANE	5
-9009.781	-2119	-0.401	1671.96	-42075.06	-9.483	1.417	DIOXANE	6
-9010.3116	-2170	-0.987	1565.52	-13259.17	-9.539	1.374	DMF	7
-9010.4036	-2179	-1.087	1164.18	-13442.83	-9.55	1.366	METHANOL	8

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.

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 include a 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 8 organic solvents which using in the study [BENZENE, ACETONE, CCL$_4$, CHCL$_3$, CYCLOHEXANE, DIOXANE DMF and METHANOL] understudy. The resulting parametric models are depicted in Eq. 1-4, along with statistical parameters of the regression[17-20]. The first model when

depend on only five parameters [DIELEC.E, VW.AREA, T.E, HOMO and H.F] gave good model with correlation coefficient R^2 values for this model of 0.961, as equation1.

=-3752.883+/-9615.616DIELEC.E-0.1841+/-0.7782VW.AREA+6545431.0286+/-696888.042T.E+7558.0777+/-18217.705HOMO-67804.226+/-7224.326H.F+58829302250.56+/-6263500075.16 -----Eq 1.

S = 21.9605   F =10.1102   R^2 = 0.9619

The relationship between the experimental and predicted data in this model, Fig.2
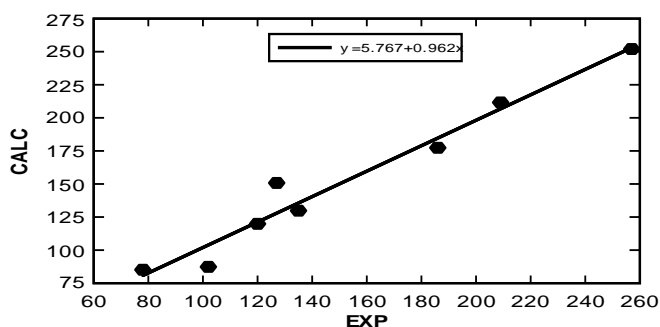

Figure 2. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq 1.

On the other hand the the correlation coefficient   R^2 increase when using the parameters [DIELEC.E, VW.AREA, ELEC.E, HOMO and T.E,] and become 0.9619 , Eq 2.

= -3752.883+/-9615.616 DIELEC.E - 0.1841+/-0.7782VW.AREA+6545431.0286+/-696888.042ELEC.E+7558.0777+/-

18217.705HOMO-67804.226+/-7224.3261T.E+58829302250.56+/-6263500075.1694   -------Eq 2.
S = 21.9605   R^2 = 0.9619   F=10.1102

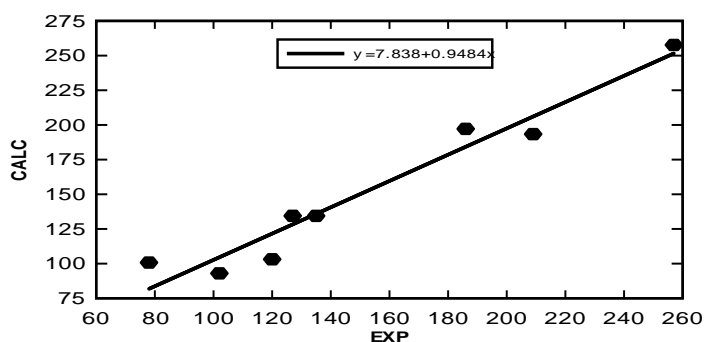The relationship between the experimental and predicted data ,Fig.3

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

While the correlation coefficient R^2 increase when using the parameters [H.F, DIELEC.E, VW.AREA, ELEC.E, HOMO and LUMO]. the correlation coefficient R^2 value rised to 0.994 , Eq. 3.

= 47.609+/-309.544H.F-4640.76+/-35050.76DIELEC.E-0.3039+/-5.392VW.AREA+1.097E-02+/-0.313ELEC.E +15342.67+/-143927.6677127.323HOMO-7127.323+/-155486.66LUMO+255707.96+/-1939806.68 -------- Eq 3.

S = 11.735161 R^2= 0.9945   F =30.5049

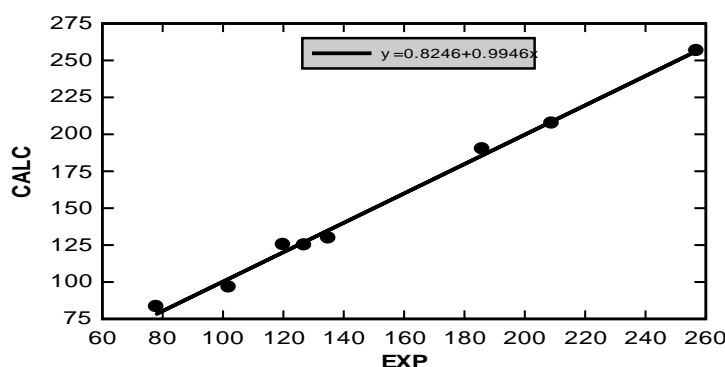The relationship between the experimental and predicted data in this model, Fig.4.

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

In Eq 4. The correlation coefficient R^2 increase when using the parameters [T.E, H.F, VW.AREA, ELEC.E, HOMO and LUMO]. and become 0.995

= 22429081.809+/-3538836.87T.E-232450.227+/-36678 H.F-0.52529+/-4.66VW.AREA+1.746E-02+/-0.2761ELEC.E-8904.398+/-115501.692HOMO+11605.448+/-143956.74LUMO+201588483639.583+/-31806404011.546 ------ Eq 4.

S = 10.8931 R^2 = 0.9953   F =35.4301

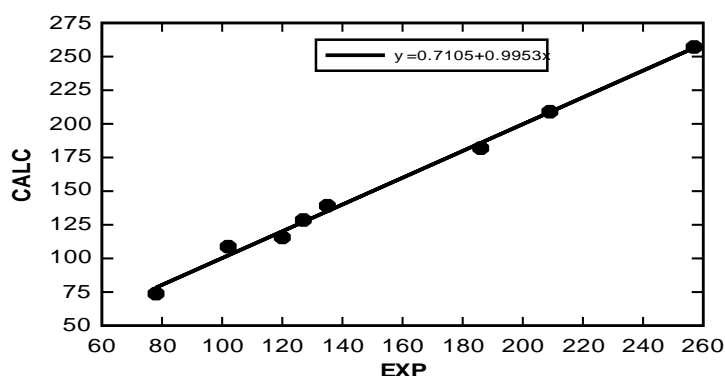The relationship between the experimental and predicted data in this model, Fig.5.

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

When replacement the parameters HOMO in eq 4. By the parameters DiElec, this lead us to best correlation coefficient with 0.999 . in the eq 5. by using the parameters[T. E, DIELEC.E, VW.AREA, ELEC.E, H.F and LUMO].

= 14253524.089+/-813875.793T.E-1754.474+/-6469.029DIELEC.E-0.44103+/-1.1347VW.AREA+1.488+/-6.696E-02ELEC.E-147702.669+/-8435.802H.F+4835.431+/-14830.358LUMO+128108161368.752+/-7314968956.291 ------- Eq 5.

$R^2 = 0.9997$ S = 2.5056 F = 672.6164
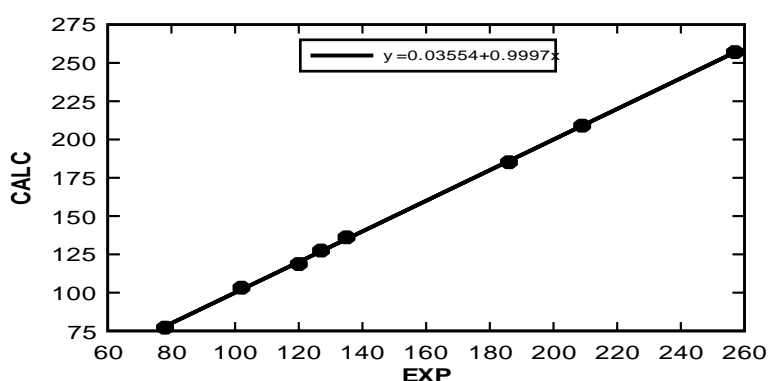The relationship between the experimental and predicted data in this model, Fig.6

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

On the other hand the replacement the parameters LUMO in eq 5. By the parameters HOMO , gave excellent equation 6. with correlation coefficient with 0.999, a significant F-value, and a low standard deviation, depends on the parameters[T.E, DIELEC.E, VW.AREA, ELEC.E, HOMO and H.F].
While the Eq 7**.,** shows decrease in the value of correlation coefficient with 0.994 comparable with eq 6.,this happens whether the replacement the parameter H.F in eq 6. by the parameter LUMO in eq 7. Which become depends on the parameters [T.E, DIELEC.E, VW.AREA, ELEC.E, HOMO and LUMO],[19].

= 8739151.264+/-1013687.105T.E-2880.138+/-9295.649DIELEC.E-0.3874+/-1.4322VW.AREA+1.342+/-8.248E-02ELEC.E+6117.85+/-17098.128HOMO-90541.267+/-10507.875H.F+78546051840.488+/-9110831107.0443 ----- Eq 6.

S = 3.1201 R^2= 0.9996   F = 433.6952
The relationship between the experimental and predicted data in this model, Fig.7.
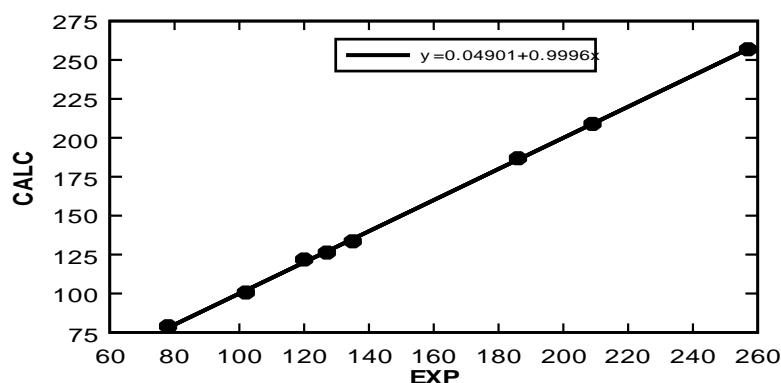
Figure 7. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq 6.

= 4592.89+/-29849.33T.E-4639.856+/-35031.131DIELEC.E-0.3039+/-5.39VW.AREA+1.097E-02+/-0.3136ELEC.E+15337.8007+/-143854.692HOMO-7123.506+/-155423.125LUMO+41535714.65+/-269628931.144 ----- Eq 7.

$S = 11.7305$ $R^2 = 0.9945$ $F = 30.5289$

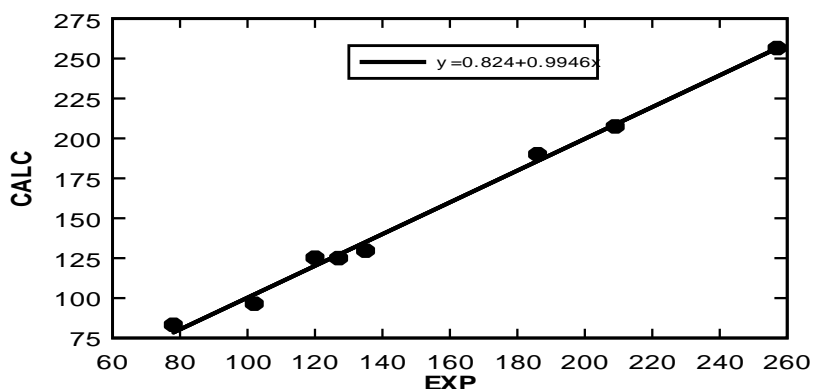The relationship between the experimental and predicted data in this model, Fig.8.

Figure 8. Plot of intrinsic viscosity prediction versus intrinsic viscosity experimental using Eq 7.

Consequently, among different models, the best model was chosen, whose specifications are presented in Table 3. It is obvious that the best model derived from the (MLR) analysis was Eq 5. & Eq 6.with the highest of correlation coefficient R^2, cross validated correlation coefficient (training set) Q^2 , minimum standard of error S and significantly by F parameter[20].

Table 3. Statistical parameters of the lineal regressions models obtained for the 7 kinds of equation.

S	F	Q^2	R^2	No eq
21.96	10.110	0.960	0.961	1
21.960	10.110	0.960	0.961	2
11.735	30.504	0.945	0.994	3
10.893	35.430	0.9915	0.995	4
2.505	672.616	0.9997	0.9997	5
3.120	433.695	0.9996	0.9996	6
11.730	30.528	0.9945	0.994	7

The resulting parametric models are depicted with correlation coefficient R^2 in Eq. 1-7, Fig .

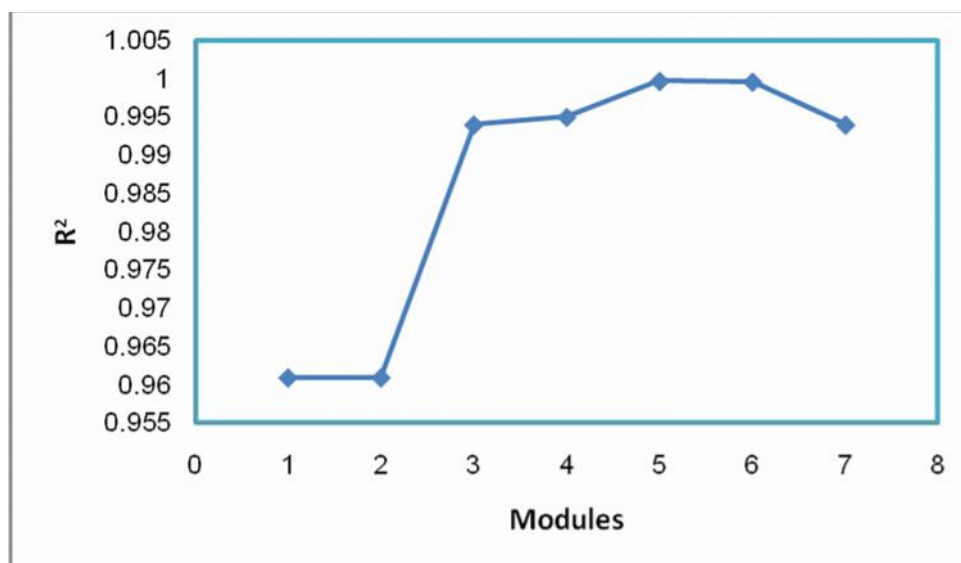9., shows the change dramatically of increasing the number of descriptors on R^2 values.

Fig. 9. Plot of number of Models vs R^2 of MLR models

In the Table 5. The predicted intrinsic viscosity values obtain from Eq. 1-7 in this study and It is obvious from Table 5. that the relations

between descriptors which calculations in this study and experimental intrinsic viscosity values are excellent[20].

Table 5. Predicated Experimental data

CALC BY eq 7	*CALC BY eq 6	*CALC BY eq 5	CALC BY eq 4	CALC BY eq 3	CALC BY eq 2	CALC BY eq 1	*Intrinsic Viscosity (EXP)	Solvent
Correlation coefficient R^2								
0.994	0.9996	0.9997	0.995	0.994	0.961	0.961		
Predication of Intrinsic Viscosity								
125.31	121.85	118.68	115.59	125.31	103.12	119.87	120	BENZENE
83.29	78.98	77.14	73.82	83.3	100.75	85.14	78	ACETONE
129.7	133.52	136.13	139.16	129.7	134.43	129.81	135	CCL₄
96.49	100.65	103.24	108.74	96.49	92.98	87.35	102	CHCL₃
190.07	186.89	185.16	181.93	190.07	197.17	177.35	186	CYCLOHEXA
125.02	126.28	127.5	128.56	125.02	134.46	150.78	127	DIOXANE
207.49	208.92	209.04	209.03	207.49	193.38	211.63	209	DMF
256.59	256.87	257.07	257.13	256.59	257.67	252.03	257	METHANOL

*= Ref [14]

*= best correlation coefficient

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 5. & Eq 6. And the best of model which depends on the parameters in Eq 5. & Eq 6, have a significant role in the intrinsic viscosity of the polymers compounds. 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. & Eq 6.,the 7 descriptors understudy including [T.E, DIELEC.E, VW.AREA, ELEC.E, HOMO, H.F and LUMO], showed insignificant role in the intrinsic viscosity in polymer and become the model was used to improving a predict the data the intrinsic viscosity, shown it a better predictive equations, with the values of R^2 =0.9997, F=672.616 and S=2.505, from Eq.5, as well as the values of R^2 =0.9996, F=433.695 and S=3.120, from Eq 6. the observed and the predicted values was excellent. QSPR techniques are of considerable importance, because it can offer faster, 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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