Prediction of Viscosity for Plasticizers using a QSPR model

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Abstract

In this work, a linear quantitative structure–property relationship (QSPR) model is presented for the prediction of Viscosity[η] for Plasticizers. Structural parameters were derived from the structures of minimum energy obtained by molecular mechanics(MM+) and the semi- empirical molecular orbital (AM1) calculations. QSPR model includes some molecular properties, regression quality indicates that these descriptors provide valuable information and have significant role in the assessment of the Viscosity of Plasticizers. This model provides good results, when the model depends on eight parameters [T.E, V.W.V, Mass, H.E, LUMO,V, ΔE and HOMO], with correlation coefficient $R^2 = 0.905$ for 21 Plasticizers.

Keywords*:* Prediction, QSPR model, Viscosity , Plasticizers.

Chemistry classification : QD 450-801

Introduction

In 1951, the International Union of Pure and Applied Chemistry (IUPAC) developed a universally accepted definition for a plasticizer as a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or distensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product. In 2003, the worldwide market for plasticizers was more than 4.6 million metric tons(10 billion pounds), with approximately 90% applied as plasticizers for PVC[(1)].

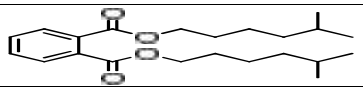
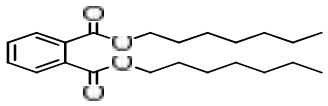
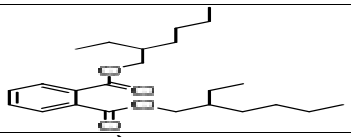
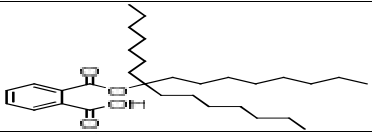
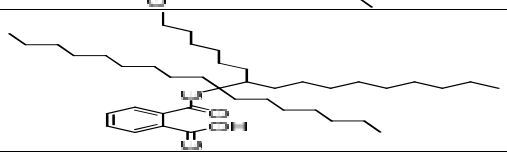
The design of new materials with optimal thermo physical, mechanical and optical properties is a challenge for computational chemistry. Novel materials are typically developed using a trial and error approach, which is costly and time consuming [(2)]. An alternative strategy is to model the material properties as functions of the molecular structure using the so called quantitative structure–property relationships (QSPR) [(3,4)]. Application of QSPR methodologies in material design has the potential to decrease considerably the time and effort required to improve material properties in terms of their efficacy or to discover new materials with desired properties [(5)]. The QSPR approach is based on the assumption that the variation of the behavior of the compounds, as expressed by any measured physicochemical properties, can be

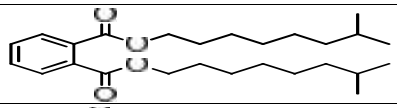
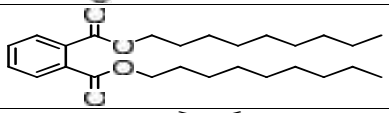
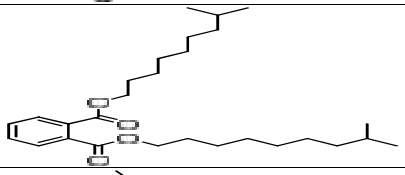
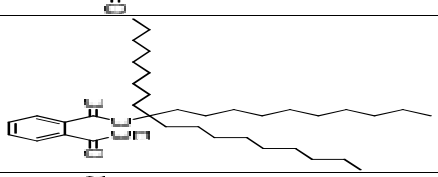
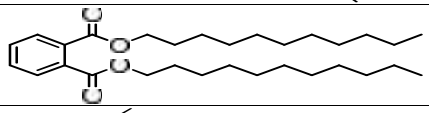
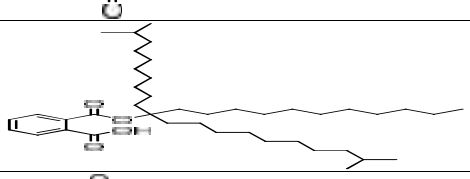
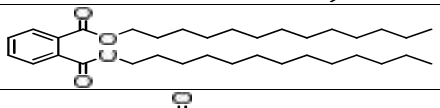
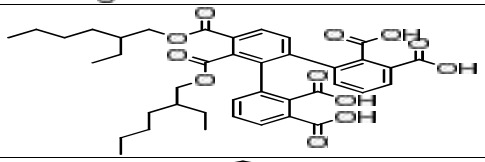
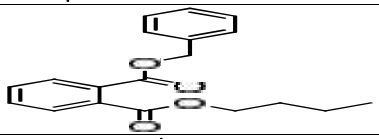
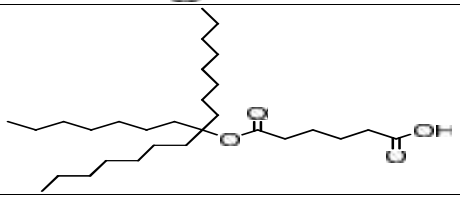
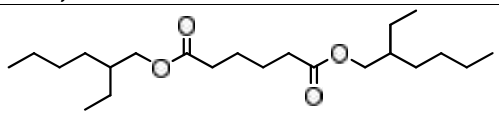
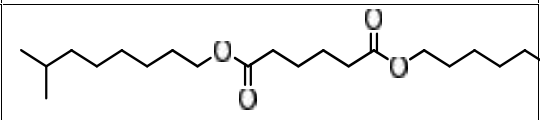
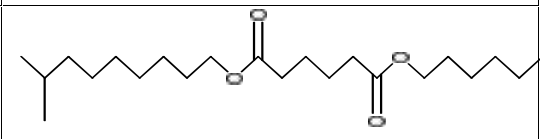
correlated with changes in molecular features of the compounds termed descriptors [6,7]. The advantage of this approach lies in the fact that it requires only the knowledge of the chemical structure and is not dependent on any experimental properties. The QSPR approach has been successfully used to predict many polymeric properties, such as refractive index [8–13], glass transition temperature [10,14–20], intrinsic viscosity [21,22], solubility parameters [23] and conformational property [24]. In this work we demonstrate the usefulness and focus of some of the parameters in deriving predictive QSPR models. The relation between viscosity for Plasticizers and quantum chemical calculated parameters, Different between HOMO and LUMO is energy gaps (Δ E), The energy of Lowest Unoccupied Molecular Orbital (LUMO), The energy of Highest Occupied Molecular Orbital in (HOMO), Hydration Energy (H.E) , Heat of formation (H.F), Mass, Total Energy (T.E), VANDER WALES Volume (V.W.V) and Volume(V) investigated theoretically.

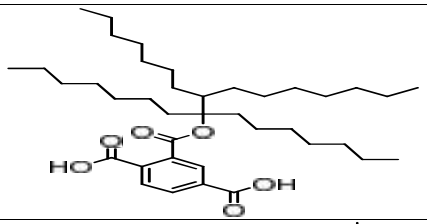
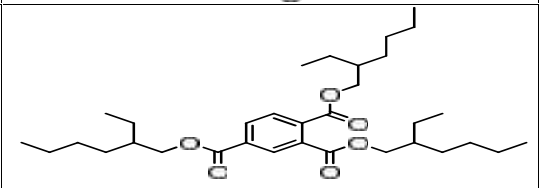
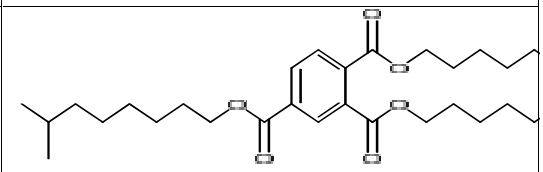
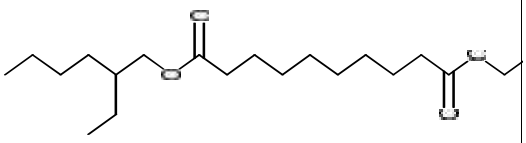
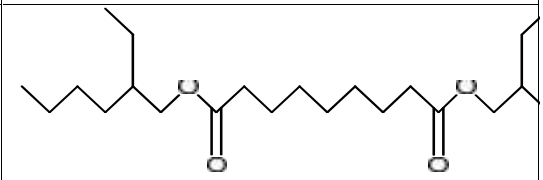
Modeling and computational Method

The calculations were performed using Gaussian 03 program[25]. The full geometry of the compounds were optimized first at level (MM+) by molecular mechanics force field theory and then at level (AM1) by semi- empirical theory [26]. The predictive model of QSPR study has been built up with the help of the following descriptors in Table 2. These descriptors for the Plasticizers under study were calculated. The Viscosity data of Plasticizers have been taken from reference [27]. The structures of Plasticizers are shown in Table 1.

Table 1: The list of chemical structures of Plasticizers

No. of molecule	Name of molecule	structures
1	Diisoheptyl phthalate	
2	Di heptyl phthalate	
3	Di(2-ethylhexyl) phthalate	
4	Di heptylnonyl phthalate	
5	Di heptylnonylundecyl phthalate	

6	Di isononyl phthalate	
7	Di nonyl phthalate	
8	Di isodecyl phthalate	
9	Di nonylundecyl phthalate	
10	Diundecyl phthalate	
11	Diisoundecyldodecyl phthalate	
12	Ditridecyl phthalate	
13	Di(2-ethylhexyl) teraphthalate	
14	Butyl benzyl phthalate	
15	Di heptylnonyl adipate	
16	Di(2-ethylhexyl) adipate	
17	Di isononyl adipate	
18	Di isodecyl adipate	

19	Tri heptylnonyl trimellitate	
20	Tri(2-ethylhexyl) trimellitate	
21	Tri isononyl trimellitate	
22	Di(2-ethylhexyl) sebacate	
23	Di(2-ethylhexyl) azelate	

Results and Discussion

In this study we used parameters in Table 2. to establish the related correlation, the physicochemical parameters were taken as independent variables and viscosity as dependent variable. The data were transferred to statistical program data fit (version9.0.59) to generate the statistically significant QSPR models. The predictive model of QSPR study has been built up with the help of the following descriptors in Table 2. These descriptors for the Plasticizers under study were calculate.

Table 2: Calculated physico-chemical descriptors of the Plasticizers

No. of molecule	LUMO (eV)	HOMO (eV)	Δ E (eV)	T.E (a.u)	V.W.V (Ang^3)	Mass (a.m.u)	H.E (Kcal/mol)	V (Ang^3)
1	-0.54722	-10.1488	9.599436	-0.31666	344.194	334.46	0.97	1122

2	-0.88193	-10.5521	9.670186	-0.21678	306.311	306.4	0.87	1029
3	-0.41987	-9.01221	8.592335	-0.35331	412.197	390.56	2.23	1299.56
4	-0.7622	-10.3159	9.553721	-0.43675	530.131	488.78	2.03	1655.04
5	-0.67975	-10.3086	9.628825	-0.54628	716.92	643.05	4.29	2198.9
6	-0.62804	-10.2759	9.647873	-0.38218	445.958	418.62	3.57	1442.49
7	-0.62886	-10.2767	9.647873	-0.3905	445.801	418.62	3.3	1469.51
8	-0.62832	-10.2765	9.648145	-0.40405	479.878	446.67	3.72	1554.99
9	-0.76383	-10.3173	9.553449	-0.5024	631.89	572.91	2.92	1975.09
10	-0.6294	-10.2773	9.647873	-0.43426	513.641	474.72	4.75	1682.22
11	-0.7562	-10.3202	9.564061	-0.54784	716.861	643.05	4.28	2220.87
12	-0.62968	-10.2775	9.647873	-0.47802	581.48	530.83	6.08	1897.85
13	-1.01771	-10.1687	9.150989	-0.79803	666.208	718.8	-16.37	1901.94
14	-0.71757	-9.59835	8.880778	-0.21807	296.276	312.37	-7.67	956.36
15	0.93744	-10.6563	11.59377	-0.54324	526.211	468.76	1.08	1669.14
16	1.094995	-11.0525	12.14753	-0.45452	408.36	370.57	4.94	1309.85
17	1.091729	-11.1638	12.22454	-0.48357	442.117	398.63	5.73	1448.54
18	1.091185	-11.1108	12.20195	-0.50545	476.037	426.68	6.43	1555.25
19	-1.33174	-10.5676	9.235889	-0.64389	676.673	630.95	0.15	2041.78
20	-1.18153	-10.5459	9.364328	-0.55152	576.6	546.79	4.65	1749.27
21	-1.29037	-10.4678	9.177384	-0.58647	627.358	588.87	5.89	2005.15
22	1.173092	-11.027	12.20005	-0.49859	476.205	426.68	6.25	1523.55
23	1.163568	-11.0286	12.19189	-0.48754	459.248	412.65	6.01	1471.62

All descriptors are in Table 2. examinant to build the best model, the best model were selected on the basis of statistical parameters viz., Standard error of estimate (s), sequential Fischer value (F), and correlation coefficient(R), were used to evaluate the obtained QSPR. Acceptability of the regression model was judged by examining the correlation coefficient (R), Fischer value (F) and standard error of estimate (s), performing multiple liner regression analysis results in statistically significant QSPR models viscosity for Plasticizers**.** 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.

Where n is the number of compounds used for regression.
The two- , three-, four-, five-,six- and seven- descriptors correlations of the viscosity for Plasticizers were given correlation coefficient (R^2= 0.266, 0.299, 0.613, 0.676, 0.691 and 0.699) , while Fischer value (F=3.640, 2.713, 7.130, 7.097, 5.988 and 4.983) and values of Standard error of estimate (s =68.802, 68.978, 52.686, 49.601, 49.866 and 50.878) respectively.
The two - and three - descriptor correlations of Viscosity for Plasticizers were given in eq. (1 and 2) respectively.

[η]=-76.371T.E +185.507 V.W.V +0.467…….(1)

n= 23 R^2=0.266, s=68.802, F =3.640

[η] = 269.73 T.E + 9.104 V.W.V + 0. 588 MASS- 82.720.....(2)

n= 23 R^2= 0.299, s= 68.978, F = 2.713

The relationship between the experimental and predicted data in these model, Figures (1and 2).

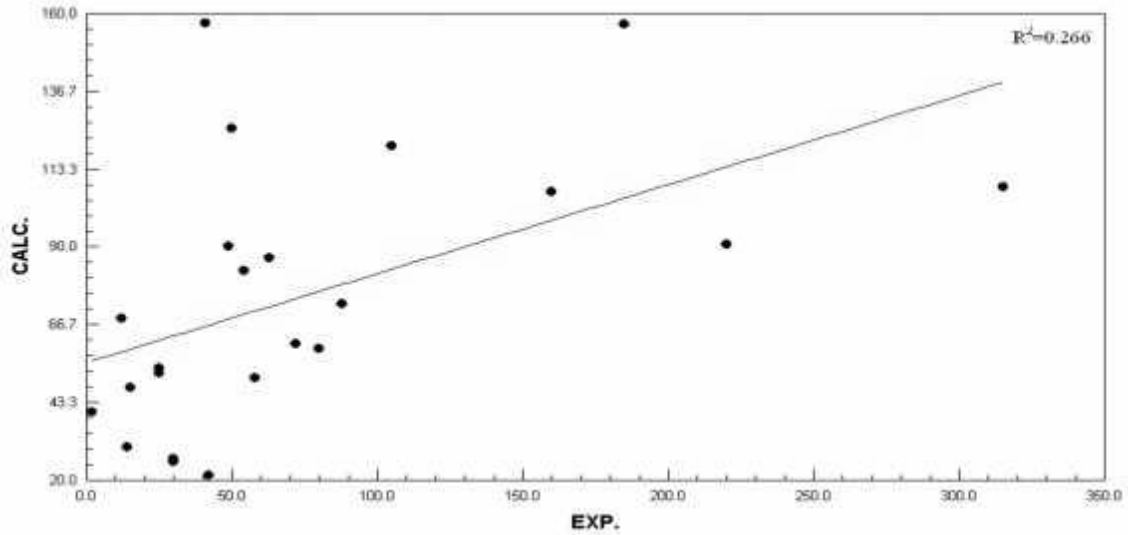


Fig.1. Observed vs. predicted viscosity of Plasticizers calculated by Eq.1

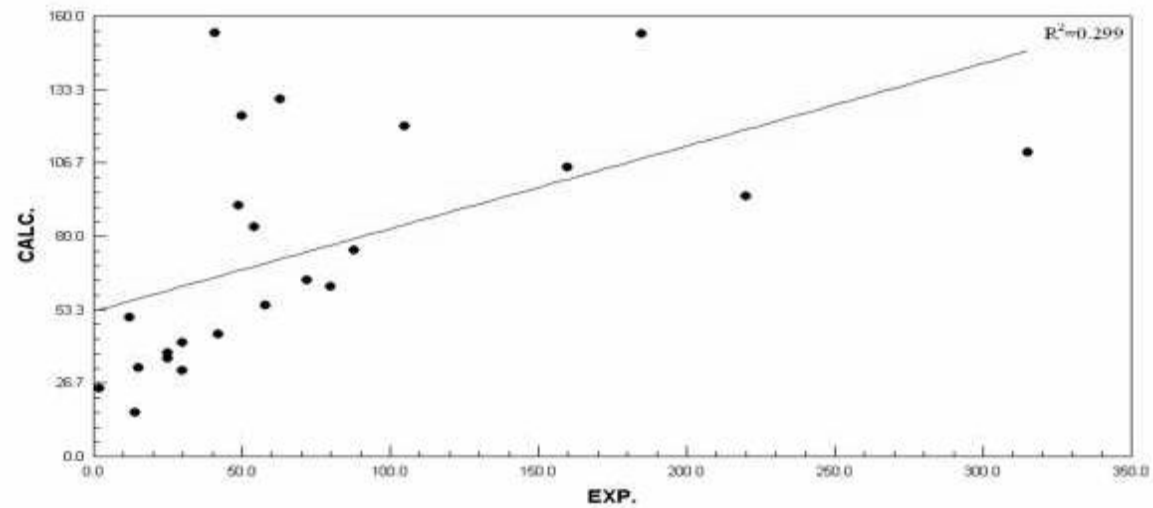


Fig.2. Observed vs. predicted viscosity of Plasticizers calculated by Eq.2

[η]= -329.676 T.E -2.359 V.W.V +1. 338 MASS +10.797 H.E. -63.944LUMO-0.357V-134.440

The four - and five – descriptors correlations of Viscosity for Plasticizers were respectively. given in equations (3 and 4)

n=23 R^2=0.613, s= 52.686, F = 7.130

[η]= -246.150 T.E -1.393 V.W.V +1. 478 MASS +13.605 H.E. -60.206LUMO-84.027

n=23 R^2= 0.676, s= 49.601, F =7.097

The relationship between the experimental and predicted data , Figures (3 and 4) respectively.

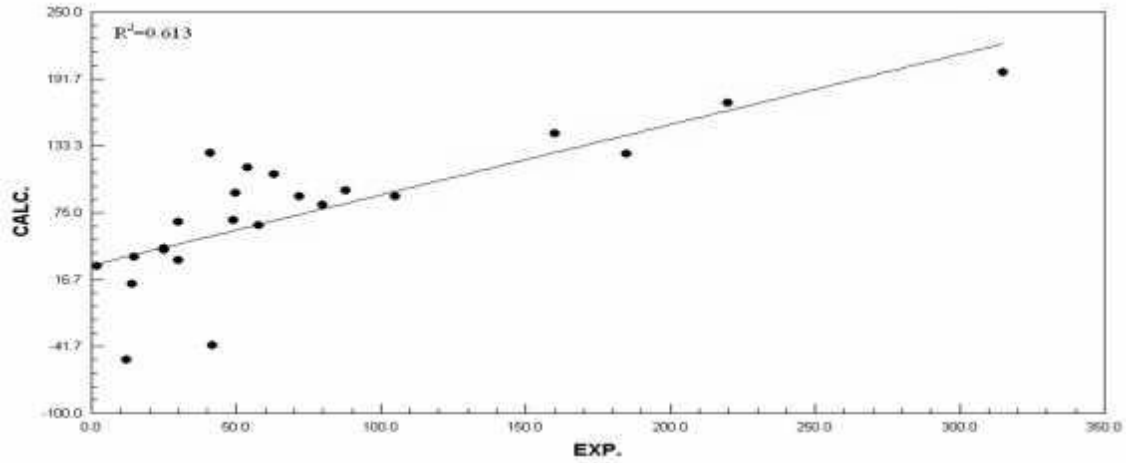


Fig.3. Observed vs. predicted viscosity of Plasticizers calculated by Eq.3

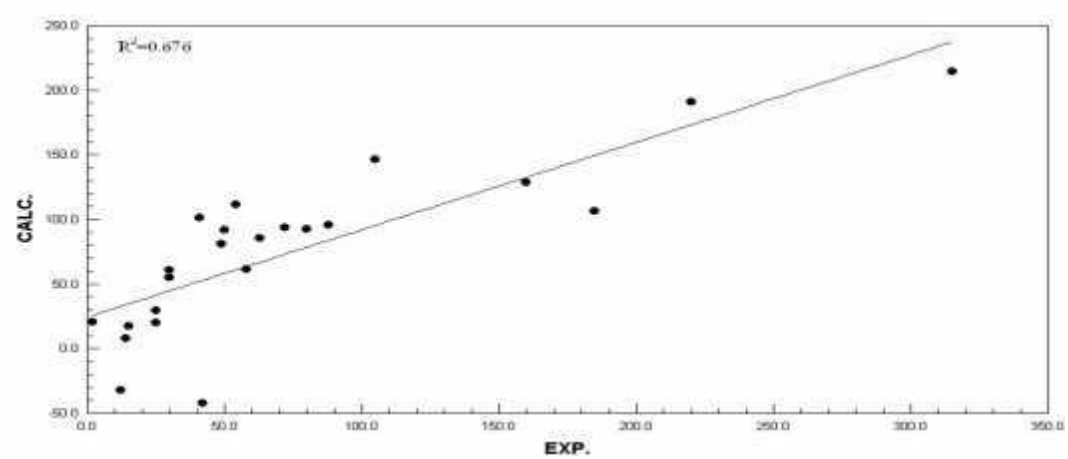


Fig.4. Observed vs. predicted viscosity of Plasticizers calculated by Eq.4

On the other hand the correlation coefficient R^2 increase when using the six- and seven- descriptors equations (5 and 6) respectively. while The relationship between the experimental and predicted data ,Figures(5 and 6)

n=23 R^2= 0.691, s= 49.866, F = 5.988

[η] = -408.088T.E -2.433V.W.V +1. 285 MASS +11.409 H.E. -

39.794LUMO+0.380V-21.426 Δ E+76.478 .....(6)

n=23 R^2= 0.699, s= 50.878, F = 4.983

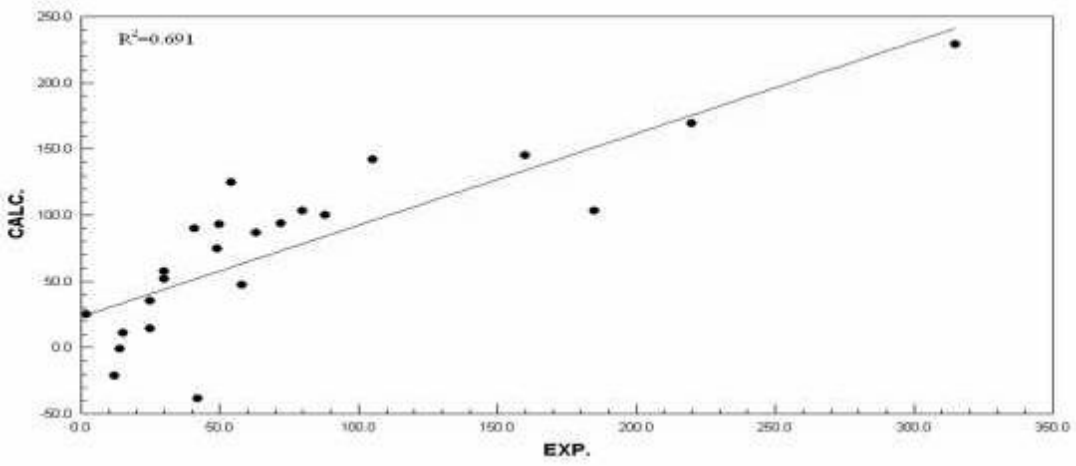


Fig.5. Observed vs. predicted viscosity of Plasticizers calculated by Eq.5

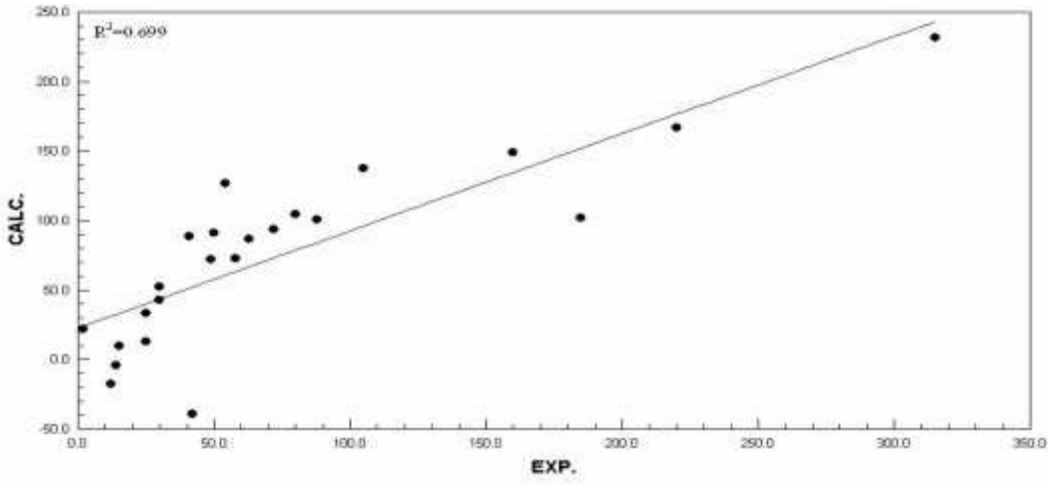


Fig.6. Observed vs. predicted viscosity of Plasticizers calculated by Eq.6

when depend on eight parameters [T.E, V.W.V, Mass, H.E, LUMO,V, Δ E and HOMO] regression equation (7) is the good produced model with good statistical fit (R^2= 0.70) while depicted in Figure (7).

[η]= -419.57T.E-2.498 V.W.V +1.2863 MASS+11.361H.E-
896.141LUMO+0.3980V+835.719 Δ E +855.413 HOMO+59.379 ……(7)

n= 23 R^2= 0.703, s= 52.276, F = 4.156

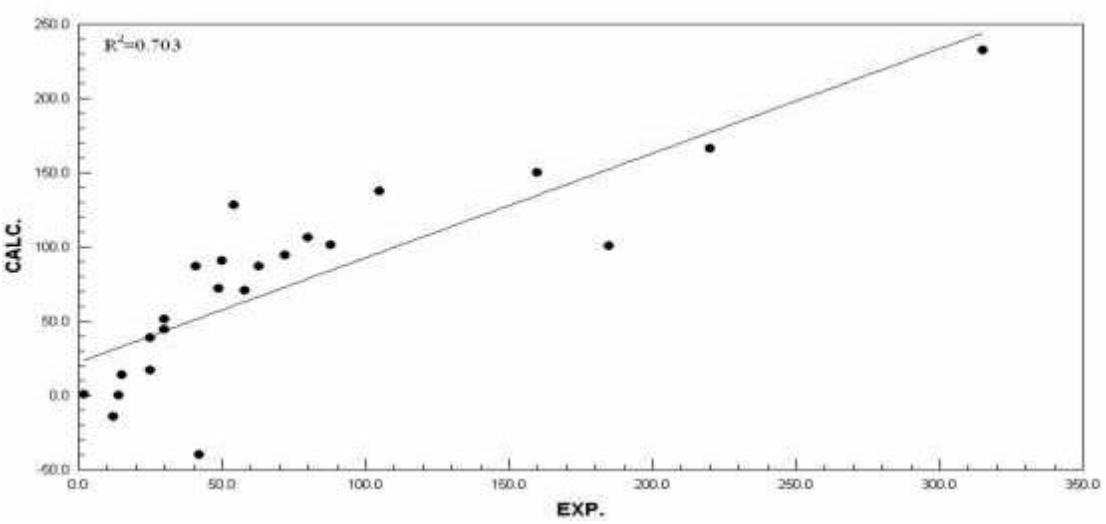


Fig.7. Observed vs. predicted viscosity of Plasticizers calculated by Eq.7

While in the equation(8), eight parameters, the excellent correlation coefficient R^2=0.905 obtained when compounds 11 and 13 outlier, on the other hand in the equation(8). It can be seen decrease the standard error comparable with equation(7). while depicted in Figure (8).

[η] = -291.295 T.E-9.1074 V.W.V +8.4737MASS+12.994H.E-1100.24LUMO+0.6423V+ 1137.5987ΔE+1165.2083 HOMO-192.3890 ...(8)

n=21 R^2= 0.905, s= 30.241, F = 14.426

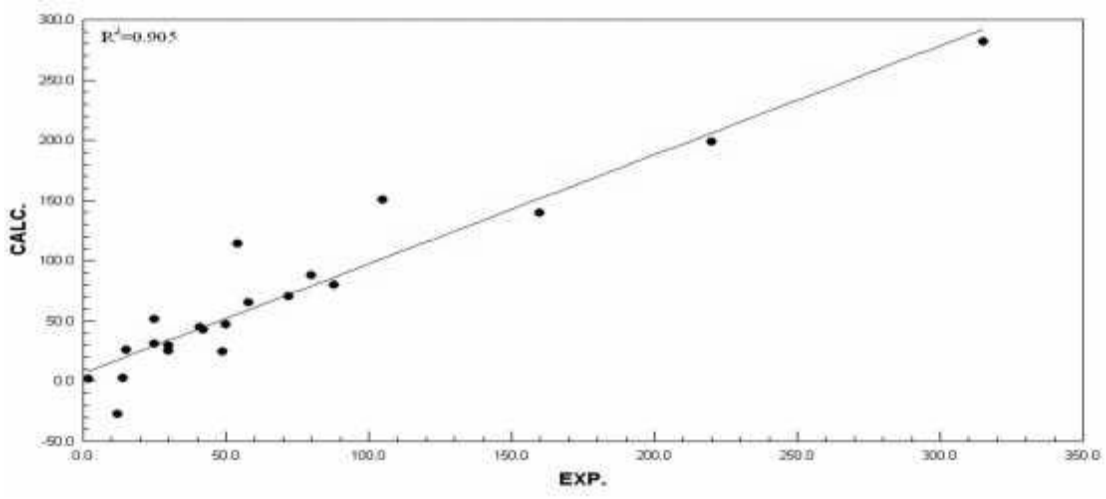


Fig.8. Observed vs. predicted viscosity of Plasticizers calculated by Eq.8

According to the best equations (7 and 8), the negative signal for each T.E , V.W.V and LUMO of the shows on the existence of an inverse relationship between these variables and viscosity. While the

positive signal for Mass, H.E, V, ΔE and HOMO both indicate the presence of a direct correlation between these variables and viscosity.The good relationship between the experimental data and predicted viscosity is reported in Table 3.

Table3. Experimental and predicated of viscosity by using Eq 1,Eq2, Eq 3, Eq4, Eq 5, Eq 6, Eq 7 and Eq 8.

*Exp of viscosity [η]	Calc. by Eq1	Calc. by Eq2	Calc. by Eq3	Calc. by Eq4	Calc. by Eq5	Calc. by Eq6	Calc. by Eq7	Calc. by Eq8
30	25.65	31.28	33.23	54.80	51.70	52.38	51.54	29.41
30	26.48	41.41	66.89	60.32	57.70	42.99	44.09	25.36
58	50.61	54.94	63.55	61.46	47.30	72.45	70.68	65.16
49	90.22	91.15	68.27	80.72	74.70	71.85	71.61	24.63
41	157.15	153.84	126.67	101.21	89.96	88.27	86.64	44.59
72	61.03	63.92	89.34	93.76	93.54	93.52	94.34	70.42
80	59.41	61.68	81.95	92.40	103.45	104.53	105.95	88.07
88	72.81	74.80	94.52	95.39	100.08	100.50	101.34	79.74
50	125.57	123.74	92.01	91.64	92.88	91.24	90.71	46.93
54	82.98	83.42	113.97	111.32	124.56	126.97	128.14	113.78
185	156.83	153.42	126.14	106.14	103.24	101.73	100.47	-
160	106.55	105.16	143.77	128.61	145.42	149.15	150.14	139.92
63	86.76	129.93	108.13	85.08	86.43	86.70	86.76	-
42	21.56	44.47	-40.40	-42.63	-38.87	-39.10	-39.68	42.56
12	68.63	50.64	-53.09	-32.44	-21.62	-17.70	-14.14	-27.47
14	30.05	15.87	12.76	7.83	-0.959	-4.21	0.29	2.287
2	40.42	24.81	28.13	20.36	24.80	21.85	0.49	1.94
25	52.21	35.68	43.67	29.50	35.23	33.41	38.44	51.45
105	120.24	120.04	89.12	146.36	141.77	137.80	137.33	150.82
220	90.63	94.66	170.63	190.86	169.30	166.70	166.38	198.97
315	107.86	110.39	197.19	214.36	229.12	231.43	232.41	282.01
25	53.56	37.53	42.06	20.20	14.07	12.86	17.18	30.59
15	47.69	32.12	36.37	17.68	11.12	9.63	13.78	25.74

***= The experimental of viscosity reference (26)**

Conclusion

The QSPR mathematical models consist of multiple regressions taking into account only the influential descriptors. Using the linear model, multiple regressions were performed between some viscosity of Plasticizers and some quantum chemical parameters/descriptors. The model depending on the Equation(8) is the best produced model with a better predictive statistical fit as evident from its R^2 = 0.905, F = 14.426 and S = 30.241 by using eight descriptors and n=21, comparable with the previously study R^2 = 0.703, F = 4.156 and S = 52.276, by using eight descriptors and n=23. .The study indicated that viscosity of Plasticizers can be modeled by using eight parameters. The good correlation coefficients R^2, depends on Equation(8) . And the best of model which depend on the parameters T.E, V.W.V, Mass, H.E, LUMO,V, ΔE and HOMO.

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التنبؤ بآللزوجة للملدنات باستخدام موديل QSPR

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الخلاصة

في هذا العمل، تم تقديم نموذج خطي لعلاقة التركيب الخاصية الكمية (QSPR) للتنبؤ باللزوجة للملدنات . استخدم كيمياء الكم لحساب الموصوفات لتنبأ بخواص QSPR للملدنات . تم حساب المتغيرات التركيبية من التراكيب الجزيئية عند الطاقة الدنيا بطريقة (AM1) شبه التجريبية. حيث تضمن موديل QSPR بعض الخواص الالكترونية والجزيئية للتنبئ بلزوجة الملدنات. حيث أعطت المعادلة 8 التي تضمنت ثمان متغيرات [T.E, V.W.V, Mass, H.E, LUMO,V, ΔE and HOMO] قيمة معامل ارتداد مقداره $R^2 = 0.905$ وهي أفضل قيمة بالمقارنة مع المعادلة السابقة وبالتالي يمكن استخدم المعادلة 8 للتنبؤ بقيم لزوجة الملدنات.

الكلمات المفتاحية: التنبؤ، موديل QSPR،اللزوجة، الملدنات