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Recomputed model (QSPR) of Plasticization and Structure Properties for PVC Using Molecular Modeling Techniques

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ABSTRACT

25 plasticizers compounds of PVC can be recomputed and modeled by using quantum chemical calculations. The geometries of the compounds were optimized first at level (MM+) by molecular mechanics force field theory and then at level (PM3) by semi- empirical method. Quantitative Structure – Property Relationship (QSPR) have been recomputed and established of 25 plasticizater compounds to correlate and predict low temperature flex point(T_f) and improving it. In addition to compare this values with the original study. Linear multiple regression analysis were used to generate the equation that relates the structural features to the Plasticization properties. The results show good models with three and four descriptors linear equation with R^2 value of 0.889, which indicate that these descriptors Mass, V.W.V, H.F and H. E play an important role in effect on Plasticization properties. All Eqs 1-7 give better statistical values than those found in the Ref [14].

Keywords. Polyvinyl Chloride (PVC), Plasticization Properties, (QSPR) Model.

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 tonnes(10 billion pounds), with approximately 90% applied as plasticizers for PVC[1]. Polyvinyl chloride (PVC) is used as an all purpose plastic in a wide variety of fields ranging from industrial materials such as pipes and wire coating materials to general consumable materials such as film and sheets. One characteristic that makes PVC different from other polymers is the ability to greatly adjust the elasticity and hardness of end products through the addition of plasticizer[2-3].

The quantitative structure-activity/property relationship (QSAR/QSPR) is a successful strategy for prediction of surfactant properties based on modeling between calculated descriptors from molecular structures of the surfactants and chemical or physical properties of the solution[4-8]. QSPR has also become a well-established and proven technique to correlate diverse physicochemical properties of compounds, ranging from simple to complex, with molecular structure, through a variety of descriptors of the chemical structures. Most QSAR/QSPR treatments utilize a program to calculate descriptors and then try to select a small number of descriptors in a purely empirical fashion to form an equation. This is derived from a so-called “training set” of compounds for which a property of interest has been measured[9-13]. QSPR methodology has been aided by new software tools, which allow chemists to elucidate and to understand how molecular structure influences properties. Very importantly, this helps researchers to predict and prepare structures with optimum properties. The software is also of great assistance for chemical and physical interpretation.

we present numerical results and discuss them, making suitable comparisons with previous published data. Finally, we give the conclusions on the proposed procedure and the evident advantages in resorting to this rather simple and direct method. results and discuss them,. In this paper we have chosen the same molecular set comprising 25molecules as described in Ref [14]and identical molecular descriptors to calculate R, S and F in order to be able to perform a comparison analysis between present results and those previously published.

Modeling and Geometry Optimization

Theoretical calculations were performed by Gamess-US [15] version 22nd February 2006 compiled with CygWin gcc 3. 4. 4. ., running on a Pentium V PC-CPU 3.4GHz. The geometries of the compounds were optaimized first at level (MM+) by molecular mechanics force field theory and then by (PM3) semi- empirical method[16]**.**

MATERIALS AND METHODS

The experimental low temperature flex point(T_f) of 25 and compounds under study which use as plasticization of PVC has been taken from reference[14]. Structures of PVC and vinyl chloride compound shown in Figure.1

Monomer : Vinyl chloride **Poly (Vinyl chloride) (PVC)**

Figure 1. Molecular structure of PVC

Table 1. Calculated physico-chemical descriptors of the compounds

No of molecule	Name of molecule	H.E	Mass	T. E	H.F	D.M	V. W.V
1	Dipropylene glycol dibenzoate	-3.92	342.39	-153.4655706	-145.38	0.603026	322.645
2	Diethylene glycol dibenzoate	-6.17	314.34	-142.4834436	-140.058	4.827077	288.845
3	2,2,4-Trimethyl-1,3-pentane diolisobutyrate benzoate	-0.3	320.43	-141.8088158	-176.968	3.793732	326.221
4	Tris(2-ethylhexyl)trimellitate	4.99	546.79	-239.1885759	-324.61	1.258892	573.815
5	Acetyl tris-n-butyl citrate	-1.84	402.48	-192.7742512	-373.405	4.171497	395.587
6	Diisodecyl phthalate	3.92	446.67	-191.2793563	-232.9	1.142734	477.484
7	Diisononyl phthalate	3.19	418.62	-180.288432	-222.057	1.045518	443.707
8	Ditridecyl phthalate	6.42	530.83	-224.2290182	-250.923	2.866395	579.1
9	Tri-n-butyl citrate	-2.16	360.45	-172.154243	-344.952	1.898259	358.984
10	Bis(2-ethylhexyl) phthalate	2.67	390.56	-169.2896598	-206.291	1.617515	410.197
11	Heptyl nonyl trimellitate	-2.22	434.57	-195.2535925	-299.261	1.140108	437.29
12	Diisohexyl phthalate	1.11	334.46	-147.3143994	-188.741	2.487178	342.462
13	Bis(2-butoxyethyl)phthalate	-2.64	366.45	-168.8393002	-232.057	5.273248	361.126
14	Butyl octyl phthalate	1.25	334.46	-147.2969294	-177.778	3.460698	342.623
15	Dibutyl phthalate	-0.23	278.35	-125.3147323	-155.875	3.267177	275.023
16	Bis(2-ethylhexyl) terephthalate	-13.28	718.8	-329.7607157	-445.623	7.504899	659.38
17	Heptyl nonyl phthalate	2.78	390.56	-169.2787473	-199.443	3.449544	410.177
18	Diundecyl phthalate	4.97	474.72	-202.2481082	-229.828	2.899259	511.526
19	Butyl acetoxystearate	5.68	398.63	-173.9025256	-272.306	2.480789	437.794
20	Diisodecyl adipate	6.56	426.68	-184.8927682	-282.72	0.185585	473.704
21	Bis(2-ethylhexyl) adipate	4.93	370.57	-162.907927	-259.158	2.540719	406.382
22	Bis(2-ethylhexyl) azelate	5.64	412.65	-179.3954956	-276.163	0.270457	457.043
23	Bis(2-ethylhexyl) sebacate	5.96	426.68	-184.8899803	-280.971	2.900822	473.938
24	Tris(2-ethylhexyl) phosphate	3.44	434.64	-181.2879701	-343.123	5.008266	473.314
25	Heptyl nonyl adipate	5.39	370.57	-162.9106566	-260.871	0.031543	406.033

***Definition of Descriptors Used in This Study*.**

H.E= Hydration Energy in Kcal/mol D.M= Dipole moment in debyes, H.F= Heat of formation in Kcal/mol, Mass in a.m.u, T.E= Tatal Energy in Kcal/ml, V.W.V=VANDER WALES Volume in Ang^3 according the Facio program version 14.2.4.[17]

RESULTS AND DISCUSSION

Multiple linear regression (MLR) is one of the mathematical methods which have an extent application. Seven QSPR models were produced in this study. The predictive model of QSPR study has been built up with the help of the following descriptors in Table 1. These descriptors for the pvc plasticizers under study were calculated.

The best model derived from the (MLR) analysis was used to predict the plasticization efficiency of pvc plasticizers of compounds understudy which represent by low temperature flex point(T_f). The resulting parametric models are depicted in Eq. 1-7, along with statistical parameters of the regression. These parameters are the number of descriptors, correlation coefficient (R^2) for training and prediction sets, standard error (SE) for training and prediction sets, and F statistic. A reliable MLR model is one that has high R^2 and F values, low SE and least number of descriptors. the model should have a high predictive ability[18]. the best model was chosen, whose specifications are presented in Table 2.

Table 2. Statistical parameters of the linear regressions models obtained for the 3&4 kinds of descriptors.

MODEL	Descriptors				R^2	S	F	N	Outlier
1	D.M	Mass	V. W. V	-------	0.763	8.455	20.401	23	6,16
2	H.F	V. W. V	T.E	------	0.850	6.722	35.963	23	6,16
3	H.F	Mass	V. W. V	-------	0.878	6.043	45.997	23	6,16
4	T.E	H.F	V. W. V	H .E	0.858	6.704	27.370	23	6,16
5	H.F	Mass	V. W. V	T.E	0.882	6.111	33.884	23	6,16
6	H.F	Mass	V. W. V	D. M	0.888	5.950	35.988	23	6,16
7	H.F	Mass	V. W. V	H .E	0.889	5.942	36.099	23	6,16

From Table 2. When replace descriptor Mass, D.M, T.E and H.F, this lead to improving of the statistical data of R^2, F and S, and this gave the best model. Where n is the number of compounds used for regression, R^2 is the squared correlation coefficient, S is the standard error of the regression, and F is the Fisher ratio for the regression[19-21].

The three- and four- descriptor correlations of the plasticization were given in eq. (1-7) respectively and the resulting parametric models are depicted in figures. 2-6, along with statistical parameters of the regression[22-28].

Three descriptors, the first Eq 1. when depends on three descriptor D.M, Mass and V. W. V, gave model with correlation coefficient R^2 values for this model of 0.722 .Table 2.

Y =(-0.7616+/- 3.9206) D.M+(0.8870+/-0.1451)MASS-(0.7842+/- 0.1179)V.W.V+(204.0804+/-15.2618).....Eq 1.

n = 23 R^2= 0.722 F= 16.502 S= 9.456

While in the Eq. 2 the good correlation coefficient R^2 increase when using the descriptors H.F, V.W. V and T.E.

Y =(0.1964+/- 8.258) H.F+(-0.4151+/-0.1361)V.W. V+(-1.4434+/- 0.4594)T.E+(196.4209+/-31.0174).....Eq 2.

n = 23 R^2= 0.850 F= 35.963 S= 6.722

In Eq 2. Negative value of V.W.V and T.E refer to reversible relation with T_f while increase in T_f with increasing H.F**.** Fig. 2, show the relationship between the experimental T_f data and predicted $T._f$ by this model.

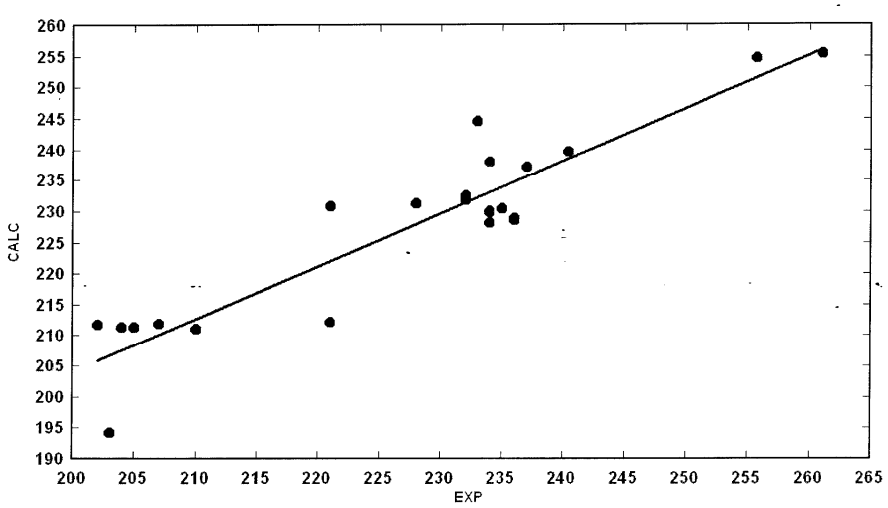

Fig. 2. Plot of experimental T_f vs. predicted T_f calculated by Eq 2.

When replace the total energy in Eq 2. by heat of formation this gave best statistical data R^2, F and S,as show in Eq 3. The Eq 3. of the plasticization of compounds are best predicated by the depends on the H.F, Mass and V.W.V descriptors gave good model with correlation coefficient R^2 value for this model equal 0.878.

Y=(0.1082+/-6.7817*10^{-2}H.F)+(0.9387+/-0.2627MASS)+(-0.7563+/-0.2098v.W.V)+(196.2504+/-27.6327)
……..…Eq 3.

n = 23 R^2= 0.878 F= 6.043 S= 45.997

According to Eq 3. the T_f. increases with increases H.F, while the decrease in the V.W.V and T.E and T.E will increase the T_f. The relationship between the experimental data and predicted plasticization in this model, Fig.3

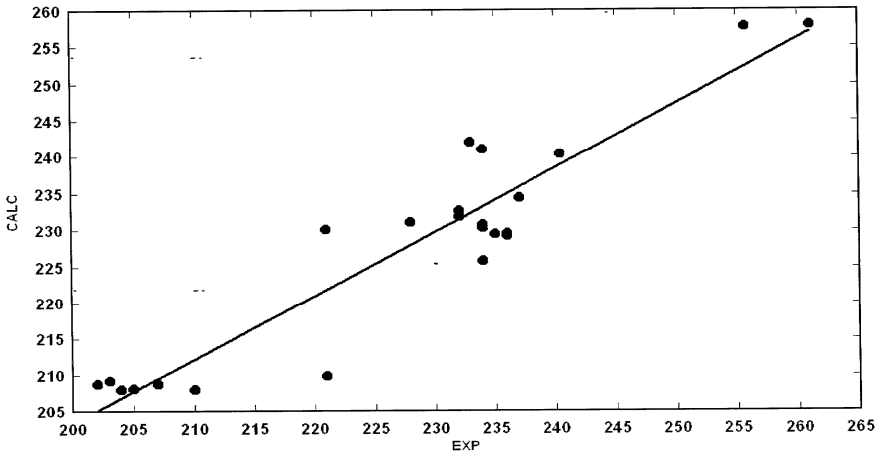

Fig. 3. Plot of experimental T_f. vs. predicted T_f calculated by Eq .3

Four descriptors, the first Eq 4. when depends on four descriptor T.E, H.F, V.W.V and H.E, gave good model with correlation coefficient R^2 values for this model of 0.858, Table 2.

Y=(0.1852 +/-0.8.835X10-2) T.E-(1.1543 +/-0.9175)H.F-(0.29225+/-0.36394)V.W.V-(1.20655+/-3.31078) H.E+
(195.5526+/-31.2161) ……..Eq 4 .

n = 23 R^2=0.858 F=23.390 S=6.704

As well as in the Eq 5. the good correlation coefficient R^2 increase when using the descriptors H.F, Mass ,V.W.V and T.E and become 0.882. .

Y =(0.1964+/- 8.258) H.F+(-0.4151+/-0.1361)V.W. V+(-1.4434+/-0.4594)T.E+(196.4209+/-31.0174)…...…Eq 5.

n = 23 R^2=0.882 F=33.884 S=6.111

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

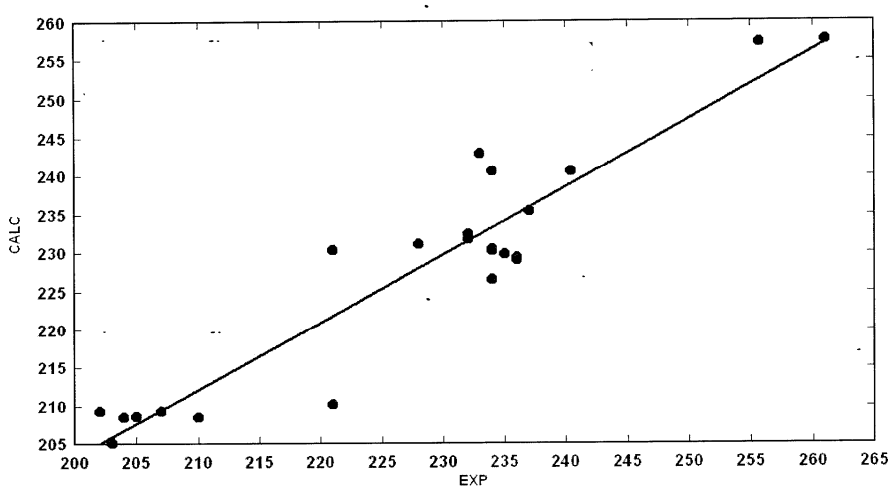

Fig. 4. Plot of experimental T_f. vs. predicted T_f calculated by Eq.5

Eq 6. are best predicated by the depends on the four descriptors H.F, Mass , V.W.V and D.M descriptors gave good model with correlation coefficient R^2 values for this model of 0.888.

Y =(0.1057+/-6.742*10^{-2} H.F)+(0.9608+/-0.2650 MASS)+(-0.7802+/-0.2148 V.W.V)+(-1.0948+/-2.4911 D.M) +(199.4606+/-28.3304)……..Eq 6.

n = 25 R^2= 0.888 F=35.988 S= 5.950

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

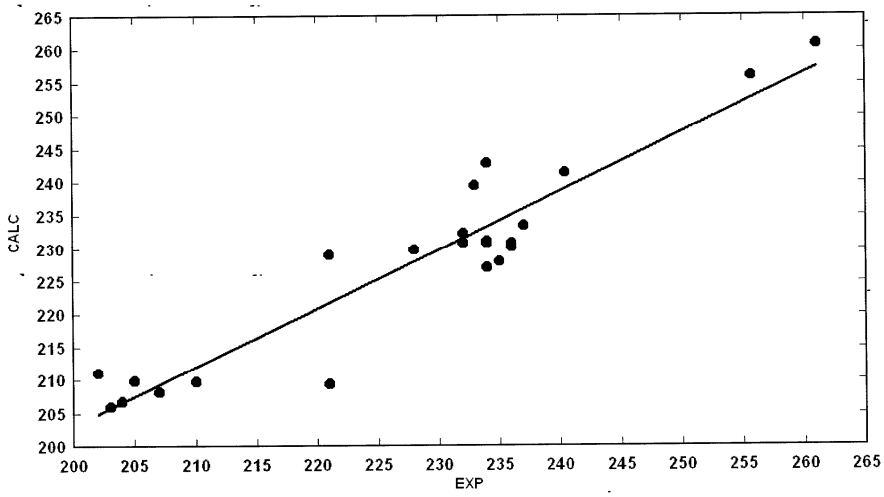

Fig 5. Plot of experimental T_f vs. predicted T_f calculated by Eq 6.

Eq 7. are best predicated by the depends on the four descriptors H.F, Mass , V.W.V and H.E descriptors gave good model with correlation coefficient R^2 values for this model of 0.889.

Y =(9.7952*10^{-2}+/7.0939*10^{-2}) H.F+(1.2706+/-0.7867MASS)+(-1.0886+/-0.7721v.W.V)+(1.9939+/-4.4621H .E)+(196.1214+/-27.3365)……Eq 7.

n = 23 R^2= 0.889 F= 36.099 S=5.942

The Eq 7. Shows the increase in the H.F will increase the T_f, both mass and H.E act in the same direction while the negative value of V.W.V refer to the T_f increase with decreasing V.W.V values. The relationship between the experimental data and predicted plasticization in this model, show in Fig.6.

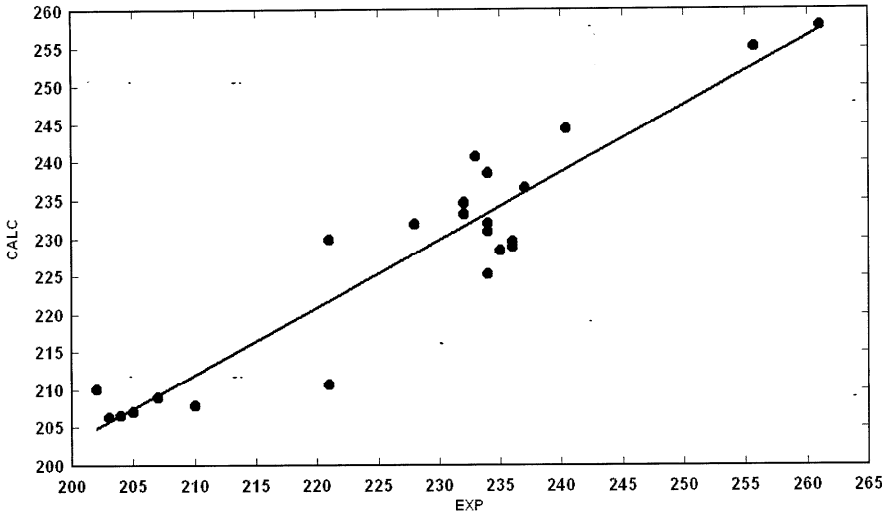

Fig 6. Plot of experimental T_f vs. predicted T_f calculated by Eq 7.

From Table. 3. It is obvious that as the number of descriptors increase the R^2 will increase and shows the effect of increasing the number of descriptors on R^2 values. It can be seen from this figure that increasing the number of parameters has a large influence on improving correlation. On the other hand can be observed tow outlier (compound 3 & 16) was detected in this study.

Table 3. Predicated Experimental data

No.	*Name*	*Exp*	*Calc* R2=0.878 Eq.3	*Calc* R2=0.888 Eq.6	*Calc* R2=0.889 Eq.7
1	Dipropylene glycol dibenzoate	261	257.91	260.65	257.85
2	Diethylene glycol dibenzoate	255.7	257.72	256.01	255.04
3	2,2,4-Trimethyl-1,3-pentanediolisobutyrate benzoate	249.3	*Outlier*		
4	Tris(2-ethylhexyl)trimellitate	240.4	240.43	241.4	244.33
5	Acetyl tris-n-butyl citrate	237	234.47	233.46	236.6
6	Diisodecyl phthalate	236	229.22	230.19	228.84
7	Diisononyl phthalate	236	229.61	230.85	229.58
8	Ditridecyl phthalate	235	229.43	227.97	228.37
9	Tri-n-butyl citrate	234	225.78	227.14	225..2
10	Bis(2-ethylhexyl) phthalate	234	230.32	231.07	230.91
11	Heptyl nonyl trimellitate	234	241.08	242.91	238.48
12	Diisohexyl phthalate	234	230.79	230.93	231.98
13	Bis(2-butoxyethyl)phthalate	233	242.01	239.47	240.59
14	Butyl octyl phthalate	232	231.85	230.89	233.16
15	Dibutyl phthalate	232	232.67	232.25	234.65
16	Bis(2-ethylhexyl) terephthalate	231	*Outlier*		
17	Heptyl nonyl phthalate	228	231.08	229.81	231.82
18	Diundecyl phthalate	221	230.14	228.98	229.81
19	Butyl acetoxystearate	221	209.88	209.37	210.66
20	Diisodecyl adipate	210	207.92	209.71	207.94
21	Bis(2-ethylhexyl) adipate	207	208.72	208.24	208.99
22	Bis(2-ethylhexyl) azelate	205	208.06	209.83	207.06
23	Bis(2-ethylhexyl) sebacate	204	207.94	206.74	206.66
24	Tris(2-ethylhexyl) phosphate	203	209.15	206	206.34
25	Heptyl nonyl adipate	202	208.8	211.08	210.12

CONCLUSION

QSPR model for prediction of the low temperature flex point T_f of plasticized for compounds using MLR based on descriptors calculated from molecular structure have been developed. We have improving the value of R^2, F and S compared QSPR results with previously study, and attempt to rebuilding the best successful QSPR models. The

model depending on the Eq. 3 is the best produced model with a better predictive statistical fit as evident from its R^2 = 0.878, F = 6.043 and S = 45.997 by using three descriptors and n=23, comparable with the previously study R^2 = 0.613, F = 8.24 and S = 10.89, by using three descriptors and n=23. A model was used to improving a predict the data the Plasticization depends on four descriptors with n=23 , shown it a better predictive equations. the values of S and the larger the value of F, the better the QSPR model. Eq. 7 the values of R^2 =0.889 and the values of S =5.942, while the values of F=36.099. The values of R^2, S and F suggest that the best of QSPR models Eq. 7 are predictive and validate. The general feature in the previously discussed models is that the plasticization increases with increasing descriptors [D.M, Mass, Van Der Waals Volum, T.E, H.F and Hydration Energy]. the observed and the predicted values was excellent.

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