Quantitative structure property relationship (QSPR) study of phthalate plasticization for PVC

Sadiq M-H Ismael, Kawkab A. Hussain*Wisam A. Radhi, and Hasanain A S. A Majeed

Department of Chemistry, College of Education Pure Science, University of Basrah

*Department of Chemistry, Polymer Research Center, University of Basrah

دراسة لعلاقة التركيب – الخاصية الكمية لمركبات الفثالات كملدنات للبولي فينيل كلورايد

صادق محمد حسن إسماعيل , كوكب علي حسين,* وسام عبد الحسن راضي , حسنين عبد الصمد عبد المجيد

جامعة البصرة –كلية التربية للعلوم الصرفة- قسم الكيمياء.

*جامعة البصرة –مركز أبحاث البوليمر –قسم الكيمياء

المستخلص

تم حساب المتغيرات التركيبية لعشرة من الفثالات كملدنات لبولي فينيل كلورايد من التراكيب الجزيئية عند الطاقة الدنيا بطريقة (AM1) شبه التجريبية ومن ثم استخدمت تقنية العلاقة التركيبية الخصائصية الكمية QSPR للتنبأ بأوطا نقطة لدرجة حرارة الثني لها (T_f) . انجزت المعادلات التي تربط الصفات التركيبية للملدنات مع أوطئ نقطة لدرجة حرارة الثني(T_f)باستخدام التحليل الخطي المتعدد الارتداد. أظهرت النتائج بأن أفضل موديل QSPR للتنبؤ بنقطة (T_f) يحوي الموصوفات التالية [T.E+POL+LOG P+ SURFACE APPRO+ SURFACE GRID+ Ref+ D.M+N.E وله قيم الوسائط الاحصائية التالية R^2= 0.9490, F= 4.6548, S= 2.1888 ومن هذا الموديل تبين الدراسة التأثير المميز لهذه الموصوفات على أوطأ نقطة لدرجة حرارة الثني لمركبات الفثالات.

Abstract

Ten plasticizers compounds of PVC can be modeled by using quantum chemical calculations. Structural parameters were derived from the structures of minimum energy obtained by molecular mechanics (MM+) and the semiempirical molecular orbital (AM1) calculations. Quantitative Structure – Property Relationship (QSPR) have been computed and established to correlate and predict low temperature flex point (T_f) of plactizater polyvinyl chloride. The influence physic-chemical descriptors on the low temperature flex point (T_f) of phthalate was accomplished by Linear multiple regression analysis (LMR) which were used to generate the equation that relates the structural features to the plasticization properties. Good correlations of the low temperature flex point(T_f) with different structural parameters were obtained. The results show the best model equation 4, with eight descriptors [T.E+POL+LOG

P+ SURFACE APPRO+ SURFACE GRID+ Ref+ D.M and N.E]with R^2= 0.9490, F= 4.6548, S= 2.1888, which indicate that these descriptors play an important role in effect on pasticization properties.

Key words.:Phthalate, Plasticization Properties, (QSPR) Model

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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, 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. Recently marathe and Chandola have been investigated QSPR model for the plasticization efficiency of 25 polyvinylchloride plasticizers with R^2=0.613[14].On the other hand Hussian investigated QSPR model for the plasticization efficiency (low temperature flex point T_f) of 25 polyvinylchloride plasticizers with R^2=0.883[15]. In this paper we have chosen 10 molecular set as described in (14) to build a QSPR model for the low temperature flex point T_f that used as indicator of the plasticization efficiency of polyvinylchloride plasticizers(phthalatecompounds).

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Method geometry optimization

Theoretical calculations were performed by PCGamess, 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 (AM1) semi- empirical method [15-16]**.** The

experimental low temperature flex point (T_f) of 10 compounds under study which use as plasticization of PVC has been taken from reference (14).

Results and Discussion

Four QSPR models were produced in this study. The predictive model of QSPR study has been built up with the help of the descriptors in Table 1.The best model derived from the (MLR) analysis was used to predict the plasticization efficiency of pvc plasticizers of compounds understudy which represented by low temperature flex point(T_f). The resulting parametric models are depicted in Eqs. 1-4, 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,F is the Fisher ratio for the regression and n is the number of compounds used for regression. 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[18-21].]. The statistical parameters of the predictive model of QSPR which based descriptors in tables 2 are summarized.

Table (1): Statistical parameters of the linear regressions models obtained for the 3&4 kinds of descriptors**.**

No molecule	No	Exp T_f	N.E	T.E	D.M	log p	H.E	Ref.	Pol.	Volume	Surface (A)	Surface (G)
6	1	236	1437.751	-202.2719	1.935	7.47	3.92	135.35	52.25	1556.22	1005.32	929.93
7	2	236	1318.8448	-190.818	2.577	6.68	3.19	126.14	48.58	1449.98	933.88	864.22
8	3	235	1781.659	-236.641	2.5805	9.98	6.42	163.06	63.26	1892.71	1230.55	1139.27
10	4	234	1271.988	-179.357	2.931	6.03	2.67	116.79	44.91	1313.8	806.3	770.68
12	5	234	975.639	-156.4585	2.731	4.3	1.11	98.54	37.57	1124.62	722.75	684.51
13	6	233	1077.51	-179.991	4.566	2.52	-2.64	102.33	38.84	1209.03	787.69	747.8
14	7	232	945.083	-156.4669	2.874	4.43	1.25	98.64	37.57	1144.99	732.24	703.47
15	8	232	730.61	-133.5601	2.882	2.84	-0.23	80.24	30.23	928.65	588.4	580.44
16	9	231	3546.1785	-352.9006	7.1352	4.78	-13.28	197.82	74.46	1880.55	915.52	999.16
17	10	228	1175.8712	-179.3747	2.84	6.02	2.78	117.05	44.91	1357.06	874.72	827.23
18	11	221	1534.4668	-213.7352	2.6411	8.39	4.97	144.65	55.92	1682.23	1089.04	1019.96

Definition of descriptors used in this study

T_f = Low Temperature Flex Point,N.E= NUCLEAR ENERGY in hartree, D.M=Dipole moment in depye, T.E=Total energy in hartree, Pol= Polarizabilty, Ref=Refractivity, H.E =Hydration Energy in Kcal/mol, S.G= Surface gride, S.A= Surface Appro, R^2=correlation coefficient, SE= standard error, F= the Fisher ratio.

The seven- and eight- descriptor correlations of the plasticization were given in eq. (1-4) respectively and the resulting parametric models are depicted in figures. 1-4, along with statistical parameters of the regression [22-28]. The first Eq 1. When depends on seven descriptor [N.E+T.E+ D.M+ Log P+S.G+S. A and Ref] gave model with correlation coefficient R^2 values for this model of 0.7602 .

T_f = 0.3501 N.E-9.3741 T.E- 6.9155 D.M+92.0073 Log P+1.1334S. A - 0.8006 S.G-27.4562 Ref+484.3206…..**Eq 1.**

n = 11, R^2 = 0.7602, F = 1.3586, S = 3.8764,

Negative value of S.G, T.E, D.M and REF refer to reversible relation with T_f while positive value of N.E, Log P and S.A refer to a positive relationship with T_f. The relationship between the experimental data and predicted plasticization in this model, Fig.1.

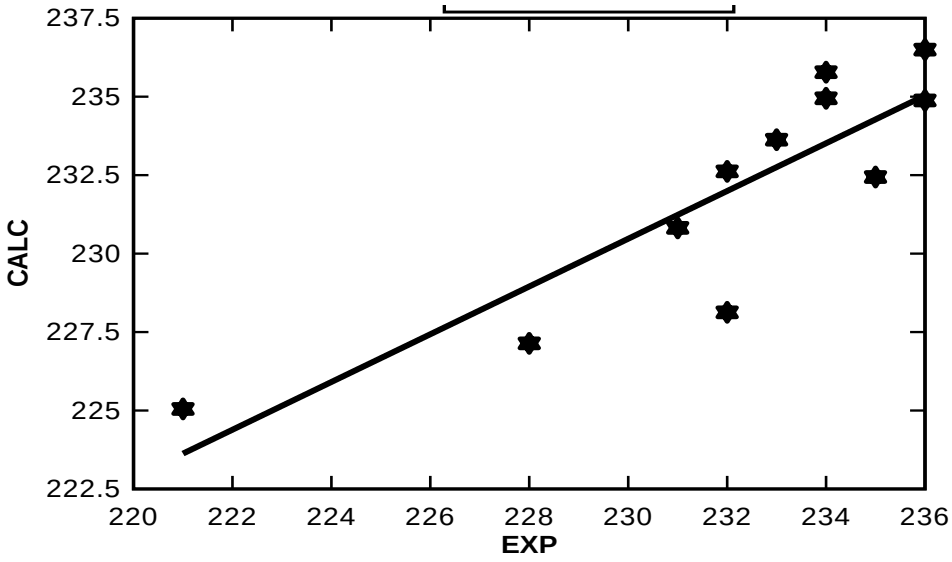

Figure (1): Experimental T_f. vs. predicted T_f calculated by Eq.1

While in the Eq.2 that depends on seven parameters the good correlation coefficient R^2 increase when using the descriptors [N.E+ T.E+POL+ LOG P+S. A+ S. G and VOL].R^2 values for this model of 0.813. .

T_f =0.3922 N.E-7.6961 T.E-77.2650 POL+95.9004 LOG P+1.4049 S.A -1.6151 S.G+0.6869 VOL+ 454.5431……**Eq 2**.

n = 11, R^2 = 0.8135, F = 1.869477, S = 3.41861,

In Eq 2. Negative value of S. G, T.E and POL refer to reversible relation with T_f while increase in $T_f$with increasing N.E, LOG P and VOL S. A**.** Fig. 2, show the relationship between the experimental T_f data and predicted $T._f$by this model.

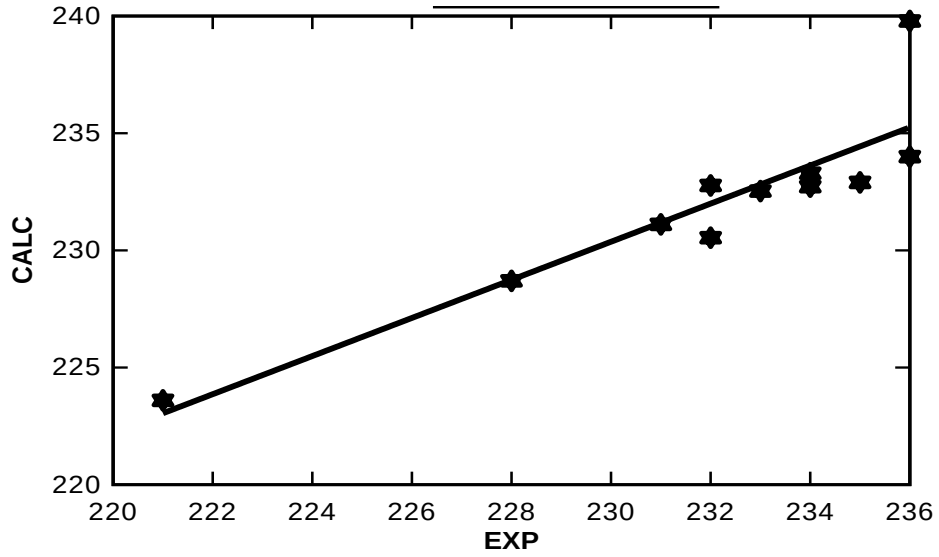

Figure (2): Experimental T_f. vs. predicted T_f calculated by Eq.2

On other hand when replace descriptor Vol in eq 2, by descriptor Ref in eq 3.The seven parameters [N.E+T.E+POL+LOG P+S. A+ S.G+ Ref] are used in the model equation, the correlation coefficient R^2 value raised to 0.8598 . Eq. 3

T_f =0.40208 N.E-15.0665 T.E-60.0189 POL+156.3613 LOG P+1.8979S. A – 1.5882 S. G-17.3673 Ref+495.1673……**Eq 3**.

n = 11, R^2 = 0.8598, F = 2.6297, S = 2.9633,

In Eq 3 Negative value of S. G, T.E, Ref and POL refer to reversible relation with T_f while increase in T_f with increasing LOG P,N.E and S. A**.** Fig. 3 show the relationship between the experimental T_f data and predicted $T._f$by this model .

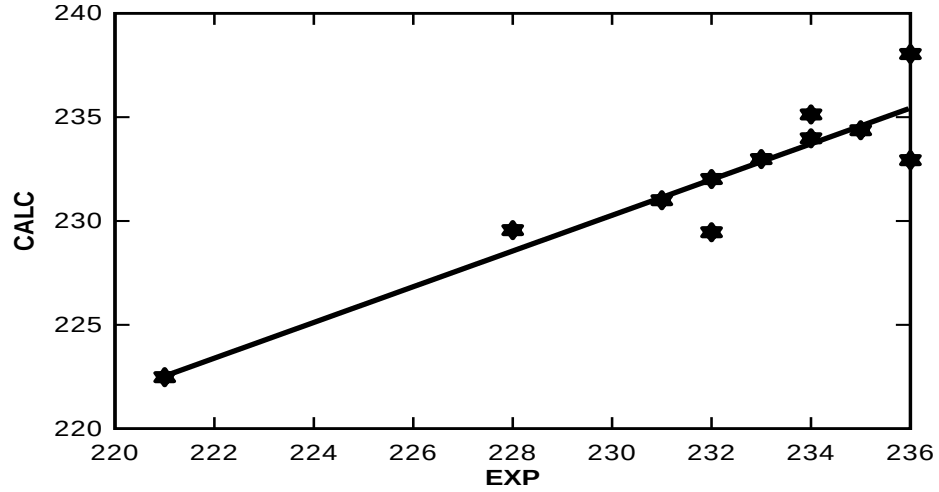

Figure (3): Experimental T_f. vs. predicted T_f calculated by Eq.3

Eq 4 are best predicated by the depends on the eight descriptors [T.E+POL+Log P+ S. A+ S. G+ Ref+ D.M and N.E]this lead to improving of the statistical data of R^2, F and S, and this gave the best model comparable with the equations 1,2 and 3.with correlation coefficient R^2 values for this model of 0.9490.

T_f =0.4496 N.E-22.1339 T.E-67.0672 POL+213.713 Log P+2.1865S. A – 1.8101 S.G-29.6886 Ref-8.8953 D.M+540.8676……**Eq 4**.

n = 11, R^2 = 0.9490, F = 4.6548, S = 2.1888,

The Eq4. Shows the increase in the N.E, S.A and LOG P will increase the T_f, both T.E+POL+D.M+ S.G and Ref act in the same direction. The relationship between the experimental data and predicted plasticization in this model, show in Fig.4.

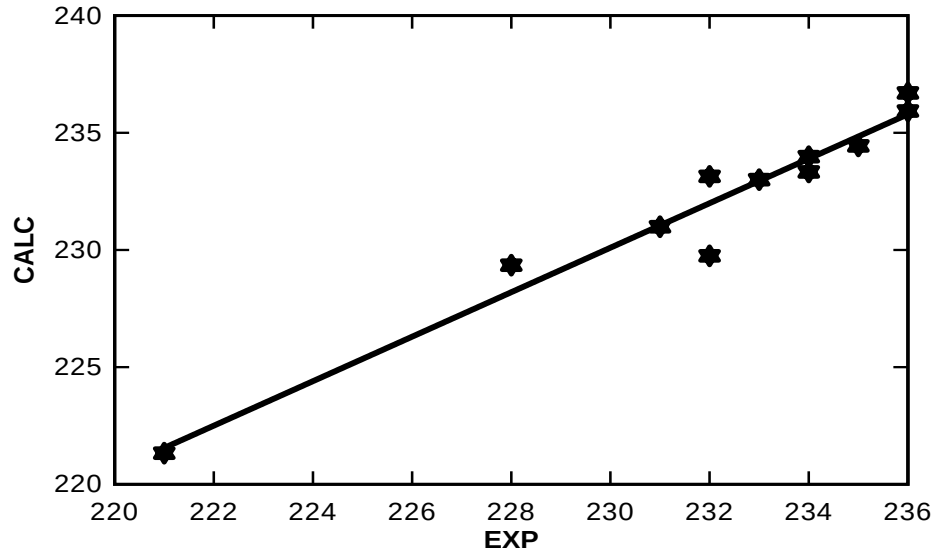

Figure (4): Experimental T_f. vs. predicted T_f calculated by Eq.4

From Table. 2. 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.

Table (2): Experimental data according to Eq. 1-4.

No.	Name	Exp T_f	calc T_f =eq 1	calc T_f =eq 2	calc T_f =eq 3	calc T_f =eq 4
1	Diisodecyl phthalate	236	236.5	234	232.93	235.93
2	Diisononyl phthalate	236	234.88	239.79	238.04	236.7
3	Ditridecyl phthalate	235	232.44	232.9	234.37	234.44
4	Bis(2-ethylhexyl) phthalate	234	235.78	232.72	233.98	233.98
5	Diisohexyl phthalate	234	234.95	233.29	235.13	233.33
6	Bis(2-butoxyethyl) phthalate	233	233.63	232.53	232.98	233
7	Butyl octyl phthalate	232	228.13	230.54	229.46	229.75
8	Dibutyl phthalate	232	232.62	232.77	232.02	233.14
9	Bis(2-ethylhexyl) terephthalate	231	230.82	231.11	231	230.99
10	Heptylnonyl phthalate	228	227.14	228.7	229.56	229.35
11	Diundecyl phthalate	221	225.05	223.6	222.48	221.33

Conclusion

QSPR model for prediction of the low temperature flex point T_f of plasticized for phthalate compounds using MLR based on descriptors is given calculated from molecular structure have been developed. The best successful QSPR models depending (the Eq. 4) the best with a better predictive statistical fit as evident from its R^2= 0.9490, F= 4.6548, S= 2.1888by using eight descriptors[T.E+POL+LOG P+ SURFACE APPRO+ SURFACE GRID+ Ref+ D.M and N.E] and n=10. From all results of the values of R^2, S and F suggest that the best of QSPR models Eq. 4 are predictive and validate. The general feature in the previously discussed models is that the plasticization increases with increasing descriptors T.E+POL+LOG P+ SURFACE APPRO+ SURFACE GRID+ Ref+ D.M and N.E], the observed and the predicted values was excellent.

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