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Prediction of the polarity parameter π for the radical derived from monomer

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Abstract: An artificial neural network (ANN) model was successfully developed for the modelling and prediction of the polarity parameter *π* used in the revised patterns scheme for the prediction of monomers reactivity ratios in radical polymerizations. Four quantum chemical descriptors based on density functional theory (DFT) calculations were used to develop the ANN model. The optimal condition of the neural network was obtained by adjusting various parameters by trial-and-error. Simulated with the final optimum BP neural network 4-4-1, the results show that the predicted parameter *π* values are in good agreement with the experimental ones, with the root mean square (*rms*) errors being 0.053 (*R*=0.960) for the training set and 0.070 (*R*=0.942) for the test set. The ANN model has better statistic quality than the MLR model, which indicates there are nonlinear relationships between these quantum chemical descriptors and the parameter *π*.

Introduction

The *Q*-*e* scheme is an empirical method for establishing quantitative relationships for monomer activity in copolymerization [1, 2]. Although very widely used, the *Q*-*e* scheme is well known to have serious limitations [3 - 5]. Recently, the revised patterns of reactivity scheme have greatly improved both its accessibility and its accuracy [3 - 8]. For the binary copolymerization of monomers 1 and 2, the fundamental equation for the calculation of a reactivity ratio, r_{12} (= k_{11} / k_{12}), is given below [9].

$$\log r_{12} = \log r_{1s} - u_2\pi_1 - v_2 \quad (1)$$

where S denotes the monomer styrene, the logr_{1s} represents the intrinsic reactivity of the polymer radical derived from monomer 1; u_2 and v_2 represent the polarity and the intrinsic reactivity of the monomer M_2, respectively. π_1 represents the polarity of the polymer radical derived from monomer 1. Polarity parameter π_1 is usually almost exactly equal to the Hammett *σ* parameter for the substituent(s) in the α-carbon atom of the radical derived from monomer M_1. Generally, parameter *π* is calculated with following equation.

$$\pi_1 = 0.385 \log[(r_{1A})/0.377(r_{1s})] \quad (2)$$

Here, the symbol A denotes the monomer acrylonitrile.

The development of a reliable quantitative structure-property relationship (QSPR) model for prediction of the basic parameter π is of real interest, particularly for new monomers for which experimental investigation would be expensive. QSPR approach can conserve resources and accelerate the process of development of new molecules [10 - 12].

As much as we know, there are no references published in recent years, on the studies of QSPRs for polarity parameter π for the revised patterns scheme. In principle, quantum chemical theory can provide precise quantitative descriptors of molecular structures and their chemical properties. Furthermore, quantum chemical descriptors have clear physical meanings [10]. The goal of this paper is to produce robust QSPR models that could predict the reactivity parameter π values of vinyl monomers with density functional theory (DFT).

Results and discussion

To find the best QSPR model, the correlation analysis between the polarity parameter π of 55 samples (see Table 1) and the ten descriptors based on density functional theory (DFT) calculation was carried out using stepwise multiple linear regression (MLR) analysis with SPSS for Windows software [13]. Two relatively "best" MLR models were generated and summarized below, along with the statistical parameters.

$$\pi = -1.008 - 4.414\, E_{HOMO} + 0.088\, q^{+}_{sAPT} + 0.049\mu - 0.466\, q^{+}_{hMul} \quad (3)$$

$R = 0.869$, $R^2 = 0.754$, $n = 55$, $SE = 0.097$, $F = 38.374$

$$\pi = -1.153 - 4.211\, E_{HOMO} + 0.072\, q^{+}_{sAPT} + 0.046\mu + 0.133\, R_{MH} \quad (4)$$

$R = 0.868$, $R^2 = 0.753$, $n = 55$, $SE = 0.098$, $F = 38.188$

where R is correlation coefficient, R^2 is squared correlation coefficient, n is the number of samples, SE is the standard error. Model 3 shows that there is negative correlation between the parameter π and q^{+}_{hMul}. But Table 1 indicates the parameter π increases with the increasing q^{+}_{hMul}. This phenomenon indicates Model 3 is not reliable while Model 4 is reliable and regarded as the best MLR model.

Model 4 shows that the best subset of descriptors comprises four descriptors, such as the energy of the highest occupied molecular orbital (E_{HOMO}), the total positive atomic polar tensor (APT) charges with hydrogens summed into heavy atoms (q^{+}_{sAPT}), the total dipole moment (μ), and the ratio between the mean positive Mulliken atomic charge and the most positive Mulliken atomic charge on hydrogen atoms (R_{MH}). These descriptors are shown in Table 1. The characteristics of four descriptors are shown in Table 2.

The four descriptors were then fed to ANN as input vectors. The optimal condition of the neural network was obtained by adjusting various parameters by trial-and-error [14]. The architecture of the final optimum BP neural network is 4-4-1, with the permission error being 0.00001, the momentum being 0.6, and the sigmoid parameter being 0.9. The results from ANN method are listed in Table 1 and depicted in Figure 1, which indicate that the predicted parameter π values are close to the experimental ones. Weights matrixes of neuron links in the networks are shown in Table 3, which indicate that there is only one hidden layer in the final BP neural network.

Tab. 1. Quantum chemical descriptors and π values for 55 Monomers.

Monomer	E_{HOMO}(au)	q^{+}_{sAPT} (au)	μ(D)	R_{MH}	π [a]	π [b]
Training set [c]						
Vinyl acetate	-0.24951	1.811492	1.6810	1.210127	0.315	0.3172
Vinyl bromide	-0.25443	0.322882	1.4905	0.939367	0.179	0.1564
Vinyl chloride	-0.26246	0.388537	1.6128	0.921600	0.128	0.1619
Vinyl chloroacetate	-0.26670	1.991701	3.4374	1.028908	0.345	0.3692
Vinyl ethyl ether	-0.21585	1.117463	1.7253	0.901369	0.192	0.1078
Vinyl ethyl sulfide	-0.21187	0.310587	1.6443	0.888528	-0.038	-0.0558
Vinyl isobutyl ether	-0.21447	1.111332	1.7089	0.879106	0.059	0.1085
Vinyl isothiocyanate	-0.23977	1.700707	2.8484	0.885368	0.277	0.2725
Vinyl phenyl sulfide	-0.21055	0.481243	1.3838	0.859732	-0.090	-0.0602
Vinyl tert-butyl sulfide	-0.20465	0.525030	1.8887	0.934839	-0.029	-0.0487
Vinyl 2-chloroethyl ether	-0.23011	1.465058	1.0868	0.795602	0.105	0.1387
p-Vinylbenzoic acid	-0.24201	1.701390	4.9875	0.491402	0.238	0.2984
Vinyltrimethylsilane	-0.25814	2.245824	0.1263	1.955439	0.277	0.2798
Styrene	-0.22166	0.184223	0.1907	0.948058	0.000	-0.0023
Styrene, α-methyl	-0.22134	0.242174	0.3137	0.857484	-0.077	-0.0572
Styrene, p-chloromethyl-	-0.22898	0.766845	2.4578	0.783234	0.046	0.0686
Styrene, p-methyl-	-0.21480	0.226701	0.6170	0.932210	-0.021	-0.0345
Styrene, p-l-(2-hydroxypropyl)-	-0.21177	0.653592	1.9882	0.397730	0.071	0.0691
Acrylamide, N-methylol	-0.26108	1.799230	3.5004	0.452577	0.432	0.2905
Acrylate, benzyl	-0.24890	1.891312	2.4432	1.049162	0.321	0.3062
Acrylate, 2-chloroethyl	-0.28444	2.094302	3.3281	1.070547	0.492	0.4919
Acrylate, α-chloro-, methyl	-0.26831	1.848114	3.5147	1.271899	0.457	0.4318
Acrylate, methyl	-0.27288	1.700164	1.4984	1.265876	0.421	0.4093
Acrylate, octadecyl	-0.26767	1.857621	2.3856	0.831946	0.417	0.3311
Acrylate, α-phenyl-, methyl	-0.23884	1.683800	4.0697	0.960804	0.438	0.2901
Acrylonitrile	-0.28921	0.308298	3.8831	1.131618	0.701	0.6573
Methacrylate, benzyl	-0.24817	1.822824	2.0021	1.019014	0.281	0.2837
Methacrylate, 2-bromoethyl	-0.27491	1.995715	2.8452	1.044463	0.455	0.4370
Methacrylate, isobutyl	-0.26639	1.700123	1.9092	1.031510	0.315	0.3486
Methacrylate, 2-chloroethyl	-0.27557	2.043189	2.9844	1.026437	0.406	0.4349
Methacrylate, 2-hydroxyethyl	-0.26864	2.004176	3.2751	0.530984	0.238	0.3042
Methacrylate, phenyl	-0.23989	2.135447	3.8061	1.074317	0.146	0.3078
Methacrylonitrile	-0.27713	0.316294	3.8840	1.029098	0.432	0.4341
Methacryloylacetone	-0.24479	1.752657	3.9780	1.031923	0.297	0.2979
Pyridine, 2-vinyl-	-0.23078	0.691800	1.8107	0.875698	-0.014	-0.0068
Pyridine, 4-vinyl-	-0.24747	0.739254	2.4607	0.817169	0.060	0.0677
Phthalimide, N-vinyl-	-0.23730	2.847343	3.1628	1.110572	0.367	0.3247
Propene, 3,3,3-trichloro-	-0.29074	1.321110	2.1973	0.584708	0.277	0.2977
Test set [d]						
Vinyl butyl ether	-0.21547	1.163219	1.7857	0.956204	0.128	0.1182
Vinyl Chloromethyl ketone	-0.26753	1.033306	4.4722	1.077484	0.255	0.2654
Vinyl hendecanoate	-0.24760	1.986098	1.5823	0.909232	0.260	0.2695
Vinylisocyanate	-0.24985	1.779802	2.1562	1.410801	0.277	0.3773
Styrene, 2,5-dichloro-	-0.23976	0.881693	0.3696	0.972949	-0.107	-0.0574
Acrylamide	-0.24847	1.198453	3.5335	0.834248	0.237	0.2436
Acrylate, butyl	-0.26910	1.845408	1.7185	1.076655	0.443	0.3950
Acrylate, ethyl	-0.26999	1.793280	1.6646	1.168328	0.436	0.4123
Acrylate, 2-nitrobutyl	-0.28253	2.883656	2.5804	1.204528	0.610	0.5642
Methacrylamide, N-phenyl-	-0.21777	1.765428	3.4554	0.623463	0.126	0.2872
Methacrylate, butyl	-0.26575	1.711456	1.8956	0.967924	0.267	0.3286
Methacrylate, glycidyl	-0.26847	2.245570	2.1421	1.037693	0.325	0.4315
Methacrylic acid	-0.27325	1.170482	1.5819	0.584672	0.002	0.1459
Pyridine, 2-methyl-5-vinyl-	-0.22652	0.729918	1.7369	0.937548	-0.007	-0.0103

Allyl chloride	-0.27381	0.413728	2.2890	0.843459	0.162	0.1834
Pyridine, 2-vinyl-5-ethyl-	-0.22667	0.618116	2.2222	1.013851	0.006	-0.0117
Vinyl ethyl sulfoxide	-0.22177	0.884377	3.9857	1.248407	0.046	0.1022

[a] π experimental from reference [9]. [b] π calculated from the BP ANN model. [c] Training set consisting of 38 monomers. [d] Test set consisting of 17 monomers.

Root mean square (*rms*) errors obtained from the ANN model are 0.053 (R=0.960) for the training set and 0.070 (R=0.942) for the test set, which are acceptable and accurate. While *rms* errors for the MLR model are 0.083 (R=0.899) for the training set and 0.125 (R=0.795) for the test set. Evidently, the ANN model has better statistic quality than the MLR model. The results confirm the nonlinear relationship between these quantum chemical descriptors and the parameter π. We did not compare the ANN method with non-linear regression methods, although they still can be found as better ones.

Tab. 2. The characteristics of descriptors in Model 4.

Descriptor	Coefficients	Std. Error	*t*	*Sig.*	*VIF*
Constant	-1.153	0.148	-7.793	0.000	/
E_{HOMO}	-4.211	0.636	-6.623	0.000	1.288
q^{+}_{sAPT}	0.072	0.022	3.323	0.002	1.363
μ	0.046	0.013	3.482	0.001	1.232
R_{MH}	0.133	0.058	2.286	0.027	1.181

Tab. 3. Weights matrixes of neuron links in the networks.

The first hidden layer				The output layer
-2.8857	-3.7520	-3.0248	-1.3031	8.1117
-2.2596	-1.2510	-5.2169	0.4832	-10.3987
-13.2458	-1.8220	0.6304	-7.7796	2.1395
6.5663	0.6407	4.6548	2.7025	-5.0837

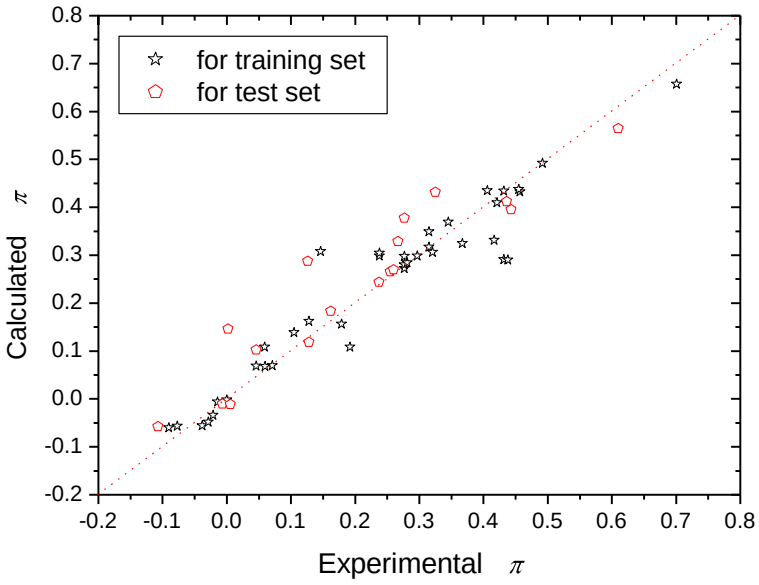

Fig. 1. Plot of experimental π versus calculated π

Table 2 shows all the descriptors are significant. The variance inflation factors (VIF) value greater than 10 is indicative of collinearity. All the *VIF* values in this paper are less than two (see Table 2), which show the descriptors are weakly correlated with each other.

By the *t*-test in Table 2, the most significant descriptor is the energy of the highest occupied molecular orbital, E_{HOMO}, which shows negative correlation with parameter π. According to the frontier molecular orbital (FMO) theory of chemical reactivity [15, 16], the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play major roles in governing many chemical reactions. They are also responsible for the formation of many charge-transfer complexes. The energy of the HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule toward attack by electrophiles. It has been shown the small difference between HOMO and LUMO energies usually means that the molecular is easily polarized. Parameter π represents the polarity of the radical derived from monomer. Thus the descriptor E_{HOMO} is related to π.

The total dipole moment (μ) is a measure of the asymmetry of molecular charge distribution, and is the most obvious and most often used quantity to describe the polarity of a molecule [17, 18]. Therefore, it is easy to understand that the second significant descriptor μ shows positive correlation with the parameter π.

According to *t*-test (see Table 2), the next two significant descriptors are the sum of positive APT atomic charges with hydrogens summed into heavy atoms (q^{+}_{sAPT}), and the ratio between the mean positive Mulliken atomic charge and the most positive Mulliken atomic charge on hydrogen atoms (R_{MH}). Indeed, it has been proven that local electron densities or charges are important in many chemical reactions and physicochemical properties of compounds and can reflect the polarity of a monomer [10]. Thus the two descriptors, q^{+}_{sAPT} and R_{MH}, are correlated with parameter π.

Conclusions

The artificial neural network (ANN) model based on DFT calculation was obtained to predict the parameter π of the radical derived from monomer. Investigated results indicate that the energy of the highest occupied molecular orbital, the total dipole moment, and the atom charges, are the most variables to correlate with parameter π. The proposed ANN model was proved to be accurate and possesses the ability to predict and generalize, with correlation coefficients of 0.960 for the training set and 0.942 for the test set. The ANN model shows better statistic quality than the MLR model.

Experimental part

Data Set

Table 1 shows the data sets for 55 parameter π values of vinyl monomers with structures $C^1H_2=C^2H\cdot X$ (or $C^1H_2=C^2X\cdot Y$), which are taken from reference [9]. The entire set contains a wide range of reactivity parameters values, and is characterized by a high degree of structural variety, for example, the functionalities presented in the side chains include halides, ketones, sulfides, esters, ethers, aromatic rings, and so on. Experimental data for polarity parameter π (see Table 1) were randomly divided into two groups, a training set consisting of 38 monomers and a test set consisting of

17 monomers. The training set was used to build the ANN model which was evaluated with the test set.

Quantum Chemical Descriptors

All monomers were fully optimized and calculated by density functional theory (DFT) using Gaussian 03 [19] program at the B3LYP /6-31G(d) level [20 - 22], in order to obtain some quantum chemical descriptors to fit polarity parameter π. Ten descriptors were calculated, which are the sum of positive APT charges with hydrogens summed into heavy atoms (q^{+}_{sAPT}), the mean positive Mulliken charges in a molecule (q^{+}_{mMul}) and the mean positive APT charges (q^{+}_{mAPT}), the most positive Mulliken atomic charge on hydrogen atoms (q^{+}_{hMul}), the average polarizability of a molecule α, the total dipole moment (μ), the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), and the HOMO and LUMO orbital energy difference (ΔE). In addition, the ratio of the q^{+}_{mMul} (the mean positive Mulliken atomic charge) to q^{+}_{hMul} (the most positive Mulliken atomic charge on hydrogen atoms) is an important variable to fit parameter π. We define the ratio as R_{MH}. To calculate these descriptors, calculations of vibrational frequencies were also carried out with the same basis sets. All of the optimized structures were characterized as true local energy minima on the potential energy surfaces, without imaginary frequencies.

Taking Vinyl acetate as example, among the calculated results of APT charges with hydrogens summed into heavy atoms, there are only two atoms that hold positive APT charges, 1.273957 and 0.537535, thus the q^{+}_{sAPT} (the sum of positive APT charges with hydrogens summed into heavy atoms) value is 1.273957+ 0.537535 = 1.811492. Similarly, in Mulliken atomic charges calculations, there are eight atoms holding positive Mulliken charges, the mean positive Mulliken charges in Vinyl acetate (q^{+}_{mMul}) is then calculated as: q^{+}_{mMul} = (0.606892+ 0.154233+ 0.187477+ 0.186585+ 0.187604+ 0.183301+ 0.155021+0.155084)/8=0.227025. While the most positive Mulliken atomic charge on hydrogen atoms (q^{+}_{Mul}) is 0.187604, thus the R_{MH} of vinyl acetate is 0.227025/0.187604 = 1.210127.

It is important to realize that atomic charges are not observable quantities and that no rigorous definitions of atomic charges exist [23]. Atomic charges such as Mulliken [24] and APT [25, 26] charges can reflect the molecular polarity of molecules. But some charges parameters derived respectively from Mulliken and APT charges may be weakly correlated with each other. For example, the mean positive Mulliken and APT charges ($q^{+}_{\mathrm{mAPT}}, q^{+}_{\mathrm{mMul}}$) for 38 monomers in the training set have a correlation coefficient R of 0.537, which is much less than the maximum collinearity coefficient criterion (R^2=0.90). The results show different schemes of atomic charges calculations may give different results. Thus both APT and Mulliken charges are used in this paper.

Stepwise regression analysis

Stepwise multiple linear regression [13] has proved to be an extremely useful computational technique in data analysis problems. The technique only adds one parameter to a model at a time and always in the order from most significant to least

significant in terms of *F*-test values. Some important statistical parameters were used to assess the model. The goodness of fit can be tested by the regression coefficient (*R*), the *F*-test and the standard error (*SE*) of estimate. High *R* and *F*-test values or low *SE* values indicate that the model is statistically significant. The *t* and *Sig* (*p*) values give a rough indication of the impact of each predictor variable – a big absolute *t* value and small *p* value suggest that a predictor variable is having a large impact on the criterion variable. In general, a descriptor is a significant descriptor and can be acceptable when the *Sig*. value of the descriptor is less than or equal to 0.05 (default level of significance). The variance inflation factors (*VIF*) computed as $VIF = (1-R^2)^{-1}$ (where R^2 is the coefficient of determination) can be used to identify whether excessively high collinearity coefficients exist among the descriptors; *VIF* <10 indicates tolerable collinearity among the descriptors, i.e. squared collinearity coefficients for descriptors do not exceed 0.90.

Artificial neural network

Back Propagation artificial neural network (BP-ANN) [14] was used in this work. The networks consist of an input layer, an output layer, and an intermediate layer known as hidden layer. Each unit in the network is influenced by those units to which it is connected, the degree of influence being dictated by the values of the links or connections. The overall behaviour of the system can be modified by adjusting the values of the connections, or weights, through a repeated application of a learning algorithm.

The best subset of descriptors selected by stepwise multiple linear regression (MLR) analysis was then fed to ANN model, as input vectors. To avoid a local minimum, a simulated annealing technique was used. The single output neuron represents the output value to be compared to the experimental value. The number of neurons in the hidden layer was optimized by trial and validation until no improvement was seen for that model [14, 27 - 29].

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