SUPPORT VECTOR MACHINE REGRESSION FOR REACTIVITY PARAMETERS OF VINYL MONOMERS

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ABSTRACT

Recently, the support vector machine (SVM), as a novel type of learning machine, has been introduced to solve chemical problems. In this study, ε -support vector regression (ε -SVR) and ν -support vector regression (ν -SVR) were, respectively, used to construct quantitative structure-property relationship (QSPR) models of Q and e parameters in the Q - e scheme, which is remarkably useful in the interpretation of the reactivity of a monomer in free-radical copolymerizations. The quantum chemical descriptors used to develop the SVR models were calculated from styrene and radicals with structures $\text{CH}_3\text{CH}_2\text{C}^1\text{H}_2-\text{C}^2\text{HR}^3\bullet$ ($\text{C}^1\text{H}_2=\text{C}^2\text{HR}^3+\text{CH}_3\text{CH}_2\bullet \rightarrow \text{CH}_3\text{CH}_2\text{C}^1\text{H}_2-\text{C}^2\text{HR}^3\bullet$). The optimum ε -SVR model of $\ln Q$ ($C=9$, $\varepsilon=0.05$ and $\gamma=0.2$) and the optimum ν -SVR model of e ($\bar{C}=100$, $\nu=0.5$ and $\gamma=0.4$) produced low root mean square (rms) errors for prediction sets: 0.318 and 0.266, respectively. Thus, applying SVR to predict parameters Q and e is successful.

Keywords: free-radical copolymerizations; Q - e scheme; quantum chemical descriptors; structure-property relations, support vector machine.

INTRODUCTION

Quantitative structure-property relationship (QSPR) studies for prediction of chemical and physical properties of molecules are unquestionably important in modern chemistry,¹ especially for the cases where the reliable experimental data are difficult to obtain from experiments. Usually, a satisfactory QSPR model can serve as a guide to chemists, because it can be used to select molecules (including those not yet synthesized) with the desired properties. Thus, the QSPR approach conserves resources and accelerates the process of development of new molecules for any purpose.¹

The Q - e scheme, as the most widely used general reactivity scheme, is remarkably useful in the interpretation of the reactivity of a monomer in free-radical copolymerizations.^{2,3} In the scheme, the parameter Q measures the general reactivity of a monomer (or a radical) and energetic properties (i.e. thermodynamic properties); the parameter e measures some polar properties of a monomer (or a radical), i.e. the supposed permanent electric charge resulting in mutual attraction or repulsion between the two monomers (or radicals).⁴ Many researchers have predicted the reactivity parameters Q and e with QSPR approaches by using the multiple linear regression (MLR) technique and/or artificial neural network (ANN) approaches.^{2,5-8} In fact, Q and e values are correlated with the reference monomer.^{2,9-11} While these descriptors used in

these QSPR models did not include the information of the reference monomer. In the present work, support vector machine (SVM) models are developed to predict the Q and e values with quantum chemical descriptors obtained from radicals $\text{CH}_3\text{CH}_2\text{C}^1\text{H}_2-\text{C}^2\text{HR}^3\bullet$ ($\text{C}^1\text{H}_2=\text{C}^2\text{HR}^3+\text{CH}_3\text{CH}_2\bullet \rightarrow \text{CH}_3\text{CH}_2\text{C}^1\text{H}_2-\text{C}^2\text{HR}^3\bullet$) and the reference monomer styrene.

MATERIALS AND METHODS

Data collection

Tables 1 and 2 show 60 vinyl monomers with double bonds and their respective experimental $\ln Q$ and e values. These $\ln Q$ and e values were based on the reference monomer styrene ($Q=1.0$ and $e=-0.8$) and taken from the literature.¹² These monomers comprise a variety of substitution groups, such as esters, ethers, sulfides, halides, ketones, acids, amides, aromatic and nonaromatic rings. The data were randomly split into three sets (in the ratio 50%, 25% and 25%): a training set (30 monomers), a validation set (15 monomers) and a test set (15 monomers). The training set was used to train SVM models, the validation set was used to optimize the parameters of SVM models, and the prediction set was used to evaluate its prediction ability.

Table 1: Descriptors and $\ln Q$ values for 60 monomers ^a

No.	Monomer	$E_{\text{pg}}/\text{Hartree}$	$D_{\text{MC}}/\text{electron}$	$q_{\text{dMR}^3}/\text{electron}$	exp. $\ln Q$	$\Delta \ln Q(\text{SVM})$
Training set						
1	Vinyl dichloroacetate	0.22527	0.923259	0.572472	-2.8302	-3.0972
2	p-Vinylbenzylmethylcarbinol	0.17202	0.763987	0.029612	0.5306	0.2694
3	Acrylate, benzyl	0.13439	0.876933	0.433448	-1.1087	-0.9620
4	Acrylate, butyl	0.16322	0.893779	0.438935	-0.9676	-1.0190
5	Acrylate, ethyl	0.16385	0.893180	0.434242	-0.8916	-0.9632
6	Acrylate, methyl	0.15398	0.881077	0.431427	-0.7985	-0.8473
7	Acrolein	0.13006	0.783632	0.027818	-0.2231	-0.1717
8	Acrolein, methyl-	0.13373	0.837829	0.247938	0.6043	0.4398
9	Acrylamide	0.15115	0.913041	0.392726	-1.4697	-0.5788
10	Acrylamide, N-methylol-	0.15173	0.895990	0.422692	-0.6539	-0.8343
11	Acrylonitrile	0.21346	0.859496	0.170140	-0.7340	-0.7826

12	Acryloyl chloride	0.15213	0.828820	0.106172	0.5988	0.5482
13	Allyl acetate	0.22083	1.020450	0.233563	-1.4271	-1.4773
14	Allyl chloride	0.24387	1.031016	0.559691	-3.6497	-3.7004
15	Butadiene	0.21354	0.656558	0.236536	0.5306	0.4802
16	Butadiene-1-carboxylate, ethyl	0.15988	0.618823	0.268439	0.5128	0.4631
17	Butadiene, 2-fluoro-	0.18836	0.662607	0.258051	0.6313	0.6078
18	Imidazole, 1-vinyl-	0.16365	0.863881	0.553052	-2.2073	-2.1570
19	Oxazolidone, N-vinyl-	0.23862	0.869334	0.620975	-2.4418	-2.5362
20	Propylene	0.29195	1.024493	0.646354	-4.7105	-4.6616
21	Pyridine, 2-methyl-5-vinyl-	0.16936	0.761578	0.007327	0.2776	0.2272
22	Pyridine, 2-vinyl-	0.16393	0.777410	0.131296	0.3436	0.3948
23	Pyridine, 2-vinyl-5-ethyl-	0.16408	0.770506	0.132219	0.2546	0.3760
24	Quinoline, 2-vinyl-	0.13819	0.755183	0.146547	0.0392	0.0732
25	Vinyl benzoate	0.19670	0.903608	0.626195	-3.5066	-3.2253
26	Vinyl bromide	0.22064	0.955858	0.273547	-3.2702	-1.7856
27	Vinyl butyl ether	0.27566	0.880772	0.617282	-3.2702	-3.2201
28	Vinyl butyrate	0.23046	0.924082	0.606284	-3.7297	-3.3402
29	Vinyl chloride	0.24777	0.956987	0.195952	-2.8824	-2.8336
30	Vinyl chloroacetate	0.21772	0.933369	0.589633	-3.2442	-3.2597
Validation set						
31	Vinyl formate	0.23388	0.922994	0.550924	-3.1466	-3.1008
32	Vinylisocyanate	0.23332	0.858007	0.565474	-1.9661	-2.0701
33	Vinyltrimethylsilane	0.22412	0.981151	0.518180	-3.6119	-3.1643
34	Styrene	0.17306	0.771092	0.025964	0.0000	0.2821
35	Styrene, m-bromo-	0.15657	0.769569	0.023489	0.2231	0.1515
36	Styrene, p-bromo-	0.16878	0.758891	0.030488	0.2624	0.2418
37	Vinyl hendecanoate	0.23409	0.935626	0.619110	-2.8824	-3.5734
38	Vinyl isobutyl ether	0.27411	0.878907	0.612383	-3.5066	-3.1587
39	Vinyl isobutyl sulfide	0.21112	0.867871	0.022656	-0.7133	-0.5602
40	Styrene, p-methyl-	0.17450	0.764417	0.027010	0.0953	0.2771
41	Styrene, p-1-(2-hydroxybutyl)-	0.17440	0.753247	0.025863	-0.3567	0.2611
42	Styrene, p-2-(2-hydroxypropyl)-	0.17291	0.748369	0.032011	0.1398	0.2518
43	Acrylic acid	0.16414	0.898319	0.386303	-0.1863	-0.4888
44	Vinyl phenyl ketone	0.13210	0.821919	0.194540	0.1484	0.4236
45	Allyl acrylate	0.21037	1.003116	0.260128	-1.1394	-1.2117
Test set						
46	Acrylate, glycidyl	0.16195	0.888131	0.444600	-0.7340	-1.0432
47	Vinyl dodecyl ether	0.27545	0.880658	0.617658	-3.1942	-3.2144
48	Vinyl Ethyl oxalate	0.19077	0.888536	0.579208	-2.8824	-2.5940
49	Vinyl octyl ether	0.27549	0.880666	0.617633	-3.9120	-3.2153
50	Styrene, p-chloro-	0.17469	0.759552	0.028157	0.2852	0.2723
51	Styrene, p-chloromethyl-	0.16888	0.749743	0.028387	0.3293	0.2214
52	Styrene, p-methoxy-	0.16942	0.759190	0.033771	0.4253	0.2503
53	Vinyl isothiocyanate	0.16329	0.753847	0.448005	-0.5276	-0.1506
54	Vinyl methyl sulfide	0.21496	0.875676	0.016800	-0.8675	-0.7290
55	N-Vinylcaprolactam	0.20846	0.853726	0.583579	-1.9661	-2.0242
56	Vinyl pelargonate	0.23192	0.926946	0.619105	-3.0791	-3.4516
57	Acrylate, heptafluorobutyl	0.16489	0.848580	0.442982	-0.0408	-0.7361
58	Vinyl propionate	0.22507	0.938147	0.619306	-3.6119	-3.5441
59	Vinyl acetate	0.23176	0.921440	0.603176	-3.6497	-3.2997
60	Vinyl N,N-diethylcarbamate	0.21120	0.929291	0.653208	-3.5756	-3.6700

^a The unit of E_{pg} : 1 Hartree = 2.6255×10^6 J/mol; the unit of D_{MC^2} and q_{dMR^3} : 1 electron = 1.602188×10^{-19} C;

Table 2. Descriptors and e values for 60 monomers^a

No.	Monomer	$E_{ag} /$ Hartree	$e_g /$ Hartree	exp.ln Q	$\Delta \ln Q$ (SVM)
Training set					
1	Vinyl dichloroacetate	0.14756	0.15183	-1.38	-1.03
2	p-Vinylbenzylmethylcarbinol	0.17070	0.15764	-1.27	-1.12
3	Acrylate, benzyl	0.22966	0.11062	1.13	1.39
4	Acrylate, butyl	0.27810	0.12268	0.85	0.77
5	Acrylate, ethyl	0.27835	0.12138	0.55	0.78
6	Acrylate, methyl	0.28146	0.11256	0.64	0.90
7	Acrolein	0.25861	0.10660	1.31	1.27
8	Acrolein, methyl-	0.25274	0.11601	0.71	1.11
9	Acrylamide	0.27807	0.12988	0.54	0.68
10	Acrylamide, N-methylol-	0.26761	0.11943	1.15	0.91
11	Acrylonitrile	0.25874	0.11439	1.23	1.09
12	Acryloyl chloride	0.26002	0.08420	1.92	1.77
13	Allyl acetate	0.21165	0.17571	-1.07	-0.89
14	Allyl chloride	0.22177	0.17430	-0.6	-0.75
15	Butadiene	0.23326	0.16208	-0.5	-0.15
16	Butadiene-1-carboxylate, ethyl	0.20552	0.12074	1.26	1.11
17	Butadiene, 2-fluoro-	0.25123	0.14804	0.63	0.48
18	Imidazole, 1-vinyl-	0.21430	0.16160	-0.68	-0.42
19	Oxazolidone, N-vinyl-	0.20854	0.18589	-1.7	-1.09
20	Propylene	0.27730	0.19467	-1.69	-1.43
21	Pyridine, 2-methyl-5-vinyl-	0.15595	0.14634	-0.66	-0.81
22	Pyridine, 2-vinyl-	0.16770	0.14072	-0.42	-0.40
23	Pyridine, 2-vinyl-5-ethyl-	0.16354	0.14440	-0.91	-0.65
24	Quinoline, 2-vinyl-	0.14086	0.13472	-0.09	-0.24
25	Vinyl benzoate	0.13120	0.16024	-0.89	-1.04
26	Vinyl bromide	0.21676	0.16365	-0.23	-0.45
27	Vinyl butyl ether	0.24294	0.21005	-1.5	-1.46
28	Vinyl butyrate	0.18616	0.17756	-0.89	-1.16
29	Vinyl chloride	0.24043	0.16753	0.16	-0.32
30	Vinyl chloroacetate	0.16351	0.15853	-1.61	-1.20
Validation set					
31	Vinyl formate	0.18889	0.16830	-1.19	-1.07
32	Vinylisocyanate	0.20546	0.16112	-0.95	-0.58
33	Vinyltrimethylsilane	0.27045	0.16390	0.19	-0.10
34	Styrene	0.17321	0.15264	-0.8	-0.92
35	Styrene, m-bromo-	0.17065	0.14028	-0.27	-0.34
36	Styrene, p-bromo-	0.16577	0.14181	-0.68	-0.49
37	Vinyl hendecanoate	0.18359	0.18347	-0.84	-1.14
38	Vinyl isobutyl ether	0.23721	0.21144	-1.27	-1.39
39	Vinyl isobutyl sulfide	0.20120	0.18655	-0.95	-1.10
40	Styrene, p-methyl-	0.16921	0.15609	-0.63	-1.09
41	Styrene, p-1-(2-hydroxybutyl)-	0.16461	0.14812	-0.97	-0.83
42	Styrene, p-2-(2-hydroxypropyl)-	0.16770	0.15161	-0.49	-0.95
43	Acrylic acid	0.28017	0.11669	0.88	0.83
44	Vinyl phenyl ketone	0.19062	0.11140	1.02	1.32
45	Allyl acrylate	0.15893	0.16424	-0.99	-1.30
Test set					
46	Acrylate, glycidyl	0.27627	0.11621	1.28	0.88
47	Vinyl dodecyl ether	0.23920	0.21037	-1.69	-1.42
48	Vinyl Ethyl oxalate	0.13021	0.14588	-0.65	-0.69
49	Vinyl octyl ether	0.23976	0.21032	-1.57	-1.43
50	Styrene, p-chloro-	0.16572	0.14240	-0.64	-0.52
51	Styrene, p-chloromethyl-	0.16803	0.13749	-0.38	-0.21
52	Styrene, p-methoxy-	0.15622	0.16310	-1.4	-1.29

53	Vinyl isothiocyanate	0.18356	0.13471	0.37	0.19
54	Vinyl methyl sulfide	0.19857	0.18799	-1.66	-1.11
55	N-Vinylcaprolactam	0.17236	0.19400	-1.18	-0.93
56	Vinyl pelargonate	0.18918	0.18037	-1.22	-1.14
57	Acrylate, heptafluorobutyl	0.26690	0.08765	1.34	1.66
58	Vinyl propionate	0.19665	0.17664	-0.68	-1.06
59	Vinyl acetate	0.18766	0.17801	-0.88	-1.15
60	Vinyl N,N-diethylcarbamate	0.22595	0.19458	-1.1	-1.25

^a The unit of E_{ag} and e_g : 1 Hartree = 2.6255×10^6 J/mol.

Molecular descriptors

Previous works have found that atomic charges and frontier molecular orbital energies are related to $\ln Q$ and e .^{2, 6-9} Thus, these descriptors were calculated for radicals $\text{CH}_3\text{CH}_2\text{C}^\bullet\text{H}_2\text{-C}^\bullet\text{HR}^3$ with density functional theory (DFT) in Gaussian 03¹³ program, at the UB3LYP level of theory with 6-31G(d) basis set. Calculations were also performed on styrene using the same methods. Descriptors calculated from radicals include the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of alpha spin states ($E_{\alpha\text{HOMO}}$ and $E_{\alpha\text{LUMO}}$), the energies of HOMO and LUMO of beta spin states ($E_{\beta\text{HOMO}}$ and $E_{\beta\text{LUMO}}$), the energy gap between HOMO and LUMO of alpha spin states (E_{ag}) and the energy gap between HOMO and LUMO of beta spin ($E_{\beta g}$), Mulliken charges of R^3 (q_{MR^3}), and Mulliken atomic spin densities on C^2 (D_{MC^2}). The descriptors for styrene were Mulliken atomic charges of R^3 (q_{SMR^3}) and the HOMO energy (E_{SHOMO}). In addition, we defined two descriptors q_{DMR^3} and e_g . The former was equal to the absolute value of the Mulliken charge difference on R^3 between radicals and styrene, i.e., $q_{\text{DMR}^3} = \text{abs}(q_{\text{MR}^3} - q_{\text{SMR}^3})$. The latter is the absolute value of the energy difference between the LUMO energy of beta spin states ($E_{\beta\text{LUMO}}$) of radicals and the HOMO energy of styrene. it can be expressed as: $e_g = \text{abs}(E_{\beta\text{LUMO}} - E_{\text{SHOMO}})$. A total of 12 descriptors were calculated.

Support vector machine

Support vector machines (SVM)¹⁴⁻²⁵ are a powerful state-of-the-art data mining algorithm for nonlinear input-output knowledge discovery. In SVM, the idea is to map the input data into a high dimensional feature space and subsequently carry out the linear regression in the feature space.^{14, 15} Thus, the input-output pairs of training data of size n

$(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$ $x_i \in R^n, y_i \in R$ ($i=1, 2, \dots, n$) can be expressed as

$$f(x) = \sum_i \phi(x_i) \omega + b \quad (1)$$

where x_i is an input example, Φ is a nonlinear mapping, w is a weight vector and b is the bias of the regression function.^{15, 16} A loss function called ε -insensitive loss had been proposed in the context of the ε -insensitive support vector regression (ε -SVR).^{15, 16}

$$C(y, f(x, \omega)) = \begin{cases} 0 & \text{if } |y - f(x, \omega)| \leq \varepsilon \\ |y - f(x, \omega)| - \varepsilon & \text{otherwise} \end{cases} \quad (2)$$

The standard SVR amounts to (simultaneous) minimization of the norm of the squared weight vector, $\|w\|^2$, and minimization of the sum of permitted errors. To measure the deviation of training samples outside ε -insensitive zone, non-negative slack variables ξ_i and ξ_i^* ($i=1, 2, \dots, n$) are introduced. Thus, ε -SVR can be formulated as minimization of the following functional:

$$\min_{w, b, \xi, \xi^*} J(w, \xi, \xi^*, b) = \frac{1}{2} \|w\|^2 + C \sum_i (\xi_i + \xi_i^*) \quad (3)$$

subject to:

$$\phi^T(x_i)w + b - y_i \leq \varepsilon + \xi_i \quad (4)$$

$$y_i - \phi^T(x_i)w - b \leq \varepsilon + \xi_i^* \quad (5)$$

$$\xi_i, \xi_i^* \geq 0 \quad i=1, 2, \dots, n \quad (6)$$

where ε is a prescribed parameter of the ε -insensitive loss function and C is a penalization parameter. This optimization problem can be transformed into the dual problem and the final solution can be expressed as

$$f(x) = \sum_i^{n_{sv}} (a_i - a_i^*) \phi(x_i) \cdot \phi(x) + b \quad (7)$$

where the coefficients a_i and a_i^* are in the ranges of $0 \leq a_i, a_i^* \leq C$, respectively, and n_{sv} is the number of support vectors. In general, n_{sv} is much smaller than the number of training samples since only a fraction of training samples appear with non-zero coefficients in Eq. 7. These training samples (vectors) are known as the support vectors and hence the name SVM.

According to the SVM training methodology,^{15, 16} one does not need to know explicitly the form of the mapping $\Phi(x)$, but only a kernel function, which maps the samples into a high dimensional space. When a kernel satisfies certain requirements (Mercer's theorem), it can be defined connecting the dot products of the feature vectors to the vectors in the input space

$$K(x, x_i) = \phi(x_i) \cdot \phi(x) \quad (8)$$

The SVM models used in this study implement the Gaussian (or radial basis function, RBF) kernel, given by:

$$K(x_i, x_j) = \exp(-\gamma \|x_i - x_j\|^2) \quad (9)$$

where γ is a parameter to be optimized. γ controls the amplitude of the Gaussian function and, therefore, controls the generalization ability of SVM. The RBF function is one of the most commonly used kernel function in the SVR technique and has been used widely in SVM.^{15, 16}

Besides the parameter γ , the parameters C and ε also need to be adjusted by users when a ε -SVR model is trained. The parameter C , the penalty factor, controls the trade off between errors of the SVM on training data and model complexity. The parameter ε controls the width of the ε -insensitive zone and determines the complexity and the generalization capability of the network.

The tube parameter ε is difficult to select as one does not know beforehand how accurately the function will fit. The ν -SVR was developed to automatically adjust the tube size, ε , by using a parameter ν . In the ν -SVR, the parameter ν replaces the parameter ε of the ε -SVR and used to control the number of support vectors.^{24, 25} Similar to Eq. 3, the primal form is

$$\min_{w, b, \xi, \xi^*, \varepsilon} J(w, \xi, \xi^*, b) = \frac{1}{2} \|w\|^2 + C\nu\varepsilon + \frac{C}{n} \sum_i (\xi_i + \xi_i^*) \quad (10)$$

subject to:

$$\phi^T(x_i)w + b - y_i \leq \varepsilon + \xi_i \quad (11)$$

$$y_i - \phi^T(x_i)w - b \leq \varepsilon + \xi_i^* \quad (12)$$

$$\xi_i, \xi_i^* \geq 0 \quad i=1, 2, \dots, n, \quad \varepsilon \geq 0 \quad (13)$$

The final function, $\hat{f}$, is the same as that of the ε -SVR (see Eq.7). When RBF kernel is still adopted, three parameters C , ν and γ should be tuned in ν -SVR models.

All SVM models from the present paper were obtained with winSVM, which is freely available for download (<http://www.cs.ucl.ac.uk/staff/M.Sewell/winsvm/>). Stepwise multiple linear regression (MLR) was used to select an optimum subset of descriptors and develop a MLR model. Then these descriptors were used to develop SVM models.

RESULTS AND DISCUSSION

By carrying out the correlation between the 12 descriptors and reactivity parameters $\ln Q$ and e in the training sets with stepwise MLR, the optimal MLR models of $\ln Q$ and e were obtained. The optimum subset of descriptors in $\ln Q$ comprises three descriptors: E_{pg} (the energy gap between HOMO and LUMO of beta spin), D_{MC^2} (Mulliken atomic spin densities on C^3), and q_{dMR^3} (the absolute value of the Mulliken charge difference on R^3 between radical and styrene). Statistical parameters corresponding to the MLR model are the following:

$$\ln Q = 7.804 - 13.537E_{\text{pg}} - 6.433D_{\text{MC}^2} - 3.011q_{\text{dMR}^3} \quad (14)$$

$$R = 0.940, R^2 = 0.883, n = 30, se = 0.596, F = 65.682$$

where N is the number of monomers used, R is the correlation coefficient, se is the standard error of estimation, F is the Fischer's ratio. The root mean square (rms) errors for the training, validation and prediction sets are 0.555, 0.578 and 0.496, respectively.

By the view of the frontier molecular orbital (FMO) theory of chemical reactivity, the formation of a transition state is due to the HOMO (electron-rich component) and LUMO (electron-deficient component) interaction. Thus, the FMOs are separated from the other orbitals and become very popular quantum chemical descriptors. In general, the HOMO energy can describe ionization potential; while the LUMO energy can reflect the electron affinity.¹ Moreover, both the HOMO and the LUMO energies are important in radical reactions.²⁶ E_{pg} (the energy gap between HOMO and LUMO) is an important stability index. For example, a large E_{pg} value implies high stability for the molecule in the sense of its lower reactivity in chemical reactions.^{27, 28} The parameter Q measures of the resonance stabilization, i.e. a monomer, that form free radicals easily, possesses a large $\ln Q$ value. Thus, it is easy to understand that a radical with a small E_{pg} value would have high reactivity and a large $\ln Q$ value.

In fact, all chemical interactions are resulted from electrostatic (or orbital), which are based on atomic charges.¹ Atomic charge descriptors can reflect molecular chemical reactivity (or intermolecular interactions). A large D_{MC^2} or q_{dMR^3} implies that the monomer (or the radical) possesses a small resonance stabilization and has a small $\ln Q$ value.

The optimum MLR model of the reactivity parameter e includes two descriptors, E_{pg} and e_{g} . Statistical parameters for e are the following

$$e = 2.339 + 7.314E_{\text{pg}} - 27.988e_{\text{g}} \quad (15)$$

$$R = 0.925, R^2 = 0.856, n = 30, se = 0.417, F = 80.431$$

The rms errors for the training, validation and prediction sets are 0.395, 0.337 and 0.343, respectively. The parameter e is a measure of the polarity of a monomer (or a radical). In Eq. 15, the two descriptors E_{pg} and e_{g} are related

to the FMO energies of radicals. Usually, the FMO energies (or the energy gap E_{pg} between HOMO and LUMO) are correlated with the polarization of a molecule.¹ Thus, E_{pg} and e_{g} are also related to the reactivity parameter e .

The program winSVM⁸ was used to develop SVM models for $\ln Q$ and e . In order to get a satisfactory model, SVM parameters C , ε (or ν) and γ need to be selected properly. Here, take the training of SVM models of $\ln Q$ as an example. Firstly, the training set of $\ln Q$ was selected as the input file and optimized 100 times. Then the output results were inspected. Learning parameters of $C = 10$, $\varepsilon = 0.01$ and $\gamma = 0.2$ produced a low mean squared error. Thus, these SVM parameters were used for the validation set and optimized furtherly. By training the SVM models of $\ln Q$ with different parameters γ of 0.1, 0.15, 0.2, 0.25, 0.3 and 0.4 ($C = 10$, $\varepsilon = 0.01$), the rms errors of the validation set are 0.384, 0.353, 0.332, 0.353, 0.372 and 0.443, respectively. Thus, the optimal γ corresponding to the minimal rms error was set to 0.2. Subsequently, by using $\gamma = 0.2$ and $C = 10$, another parameter ε was optimized with ε being 0.005, 0.01, 0.03, 0.05, 0.07 and 0.08, respectively. The validation set rms errors based on different ε are 0.334, 0.332, 0.323, 0.319, 0.320, 0.330 and 0.327, respectively, which shows that the optimal ε was fixed to 0.05. Similarly, the last parameter C based on ε of 0.05 and γ of 0.2 was optimized. The validation set rms errors are 0.337, 0.320, 0.318, 0.319, 0.322 and 0.326, respectively, when the parameter C was tuned with C of 5, 8, 9, 10, 11 and 12. Thus, the optimal C was 9. Lastly, the optimum ε -SVR model of $\ln Q$ with the RBF kernel ($C = 9$, $\varepsilon = 0.05$ and $\gamma = 0.2$) was tested by the prediction set. The rms errors for the training, validation and prediction sets are 0.343, 0.330 and 0.317, respectively. The $\ln Q$ values calculated with the ε -SVR model are listed in Table 1 and depicted in Figure 1.

The SVM parameters of e were tuned with the same methods. Learning parameters of $C = 100$, $\nu = 0.6$ and $\gamma = 0.6$ were obtained after initial optimization. Then the different parameters γ (0.3, 0.4, 0.5, 0.6, 0.7, and 0.8), ν (0.2, 0.3, 0.4, 0.5, 0.6 and 0.7), and C (10, 50, 90, 100, 110, 130) were tested. In the end, the optimal SVM parameters ($\gamma = 0.4$, $\nu = 0.5$ and $C = 100$) were obtained. The optimal ν -SVR model produced rms errors of 0.257 for the training set, 0.264 for the validation set and 0.266 for the prediction set. The calculated e values from the ν -SVR model are listed in Table 2 and depicted in Figure 2.

Figure 1. Plot of experimental $\ln Q$ versus calculated $\ln Q$ with the ε -SVR model.

The rms errors for prediction sets of the $\ln Q$ and e models based on the ANN approach were 0.313 and 0.271, respectively [8], which are close to the results obtained with the SVM approach. But the ratio (30/30) of fitted samples (15+15 = 30) to training samples (30) in this paper are larger than that (16/40) in previous model [8]. This means that the present SVM models have better statistical quality and generalization capability. For the previous ANN models of vinyl monomers, the training set rms errors were 0.581 for $\ln Q$ and 0.234 for e .⁶ In addition, in the ANN models of acrylate monomers, the training set rms errors were 0.302 for $\ln Q$ and 0.127 for e .⁷ In fact, as long as the correlation coefficient R between the experimental and calculated e values is greater than 0.876, then a good fit has been achieved.² The R values of the ν -SVR model for e in this paper are 0.971 for the training set, 0.943 for the validation set and 0.960 for the prediction set, which are larger than 0.876. This illustrates that our results for the model e are satisfactory and acceptable. In comparison with previous other models, the present SVM model shows satisfying statistical results, although the number of samples used in this article is much greater than that in previous models.^{2, 5-7}

Figure 2. Plot of experimental e versus calculated e with the v-SVR model.

CONCLUSIONS

Two SVR models were developed to predict the reactivity parameters Q and e , respectively, of vinyl monomers in radical copolymerization. Comparison to existing models, the SVM models shows good statistical characteristics. We have the following conclusions:

- 1) To develop the SVR models, calculating quantum chemical descriptors from styrene and radicals with structures $\text{CH}_3\text{CH}_2\text{C}^\bullet\text{H}_2\text{--C}^\bullet\text{HR}^3$ formed from $\text{C}^\bullet\text{H}_2\text{=C}^\bullet\text{HR}^3$ and $\text{CH}_3\text{CH}_2^\bullet$ is feasible.
- 2) The SVR models describing the non-linear correlation between the quantum chemical descriptors and reactivity parameters Q and e is accurate and acceptable.
- 3) Atom charges (D_{MC^2} and q_{dMR^3}) and frontier molecular orbital energies (E_{HOMO} , E_{LUMO} and e_g) are the most important factors in predicting monomer (or radical) reactivity based on the reference monomer styrene ($Q = 1.0$ and $e = -0.8$).

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