DOI:10.19603/j.cnki.1000-1190.2010.03.021

第44卷第3期
2010年9月
华中师范大学学报(自然科学版)
JOURNAL OF HUAZHONG NORMAL UNIVERSITY(Nat. Sci.)
Vol.44 No.3
Sept. 2010

文章编号: 1000-1190(2010)03-0448-07

The retention mechanism of silane derivatives on Apiezon M stationary phase in GC

WANG Ruixia[1], SONG Yuanzhi[2,3,4*], YE Yong[2], RUAN Min[2,3], XIE Jimin[4]

(1. Department of Chemistry, Chizhou College, Chizhou, Anhui 247000;
2. Key Laboratory for Chemistry of Low-Dimensional Materials, Jiangsu Province, Chemistry Department, Huaiyin Teachers' College, Huaian, Jiangsu 223300;
3. Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Ministry of Education, Hubei University, Wuhan 430062;
4. School of Chemistry & Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013)

Abstract: A quantitative structure-retention relationship (QSRR) model has been developed for the chromatographic (GC) Kováts indices of silane derivatives on Apiezon M stationary phase. AM1 method was employed to calculate a set of molecular descriptors of silane derivatives. Using multiple linear regression (MLR), we obtained the empirical functions with high correlation coefficient between Kováts indices and quantum-chemical descriptor. The results indicated that the QSRR models proposed were satisfactory.

Key words: quantitative structure-retention relationship; multiple linear regression; silane derivatives; artificial neural networks

1 Introduction

The study of the quantitative structure-retention relationship (QSRR) of solutes is a useful method for discussing the retention mechanism in gas chromatogram and an important topic in chromatographic thermodynamics.

As a branch of QSAR, the concept of QSRR has been more popular in chromatographic research in recent two decades. As is well-known, the chromatographic retention is based on the interaction between the solute and the stationary phase, which included directional force, induction force, dispersion force, hydrogen bond, and so on. The difference of the retention is the macrocosmic reflection of the molecular structure of the solute and the properties of the stationary phase.

In the last two decades QSRR have often been applied to[1]: (1) predict retention for a new solute; (2) identify the most informative structural descriptors (regarding properties); (3) gain insight into the molecular mechanism of separation operating in a given chromatographic system; (4) evaluate complex physicochemical properties of analytes, other than chromatographic; and (5) predict relative biological activities.

Good correlation was obtained between RI and theoretically calculated data for molecules with different functional groups: alkanes[2], dialkylhydrazones[3], alkenes[4], alkybenzenes and naphthalenes[5], phenol derivatives[6], azo compounds[10], primary, secondary and tertiary amines[7], etc. The interest in studies dealing with the retention behavior of solutes in different sta-

---

收稿日期: 2010-02-16.
基金项目: The project was support by the National Natural Science Foundation of China(20405011), Science Foundation of Jiangsu Province Education Department of China (04KJD150038), Chemical Materials and Engineering Laboratory Center of Anhui Province, The Natural Science Foundation of Anhui Province Education Department (KJ2010A246) and the Natural Science Foundation of Chizhou College (XK0901).
* 通讯联系人. E-mail: Songyuanzhi@126.com.

tionary phases has been increased substantially present years[8].

In the literature several models have been described, from linear ones (MLR) to nonlinear ones (artifical neural network) in order to calculate these values as accurately as possible[9-10]. However, the QSRR of silane derivatives on Apiezon M stationary phases has not been reported.

The goal of our present study is to develop QSRR models for the correlating of chromatographic Kováts indices of a set of silane derivatives on Apiezon M stationary phase with their molecular structures and is to explain on the retention mechanism. The structures of these molecules are represented by quantum chemical descriptors.

2 Theory

2.1 Descriptor generation

To obtain a QSRR model, the compounds must be represented by molecular descriptors and retain as structure information as possible. Here quantum-chemical descriptors were used because they could be easily obtained using quantum chemistry program and also had specific chemical meaning. The calculation of quantum-chemical descriptors was described as follows: all molecules were drawn into MOPAC (ChemOffice, 2004) program and pre-optimized using AM1 method[11]. The Gaussian03[12] with AM1 method was used for optimized structure and calculation of the sum of Mülliken positive charges with hydrogens summed into heavy atoms in molecule (Q), dipole moment (D), the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), entropy (S), nuclear repulsion energy (E_n), Vibrational energies (Evib), and heat capacity at constant volume (C_v).

2.2 Principle of PCA

Application of principal component analysis (PCA) has become a popular method in the last decades. It can provide information: classification, searching similarities, finding relationships, finding physical signifacance to principle components, etc. The principles of PCA can be seen the work by Héberger and Görgényi[13].

2.3 Statistical analysis

In the present work, linear model was used. The linear model was multiple linear regression (MLR), which was a common method used in QSRR study. The QSRR equations were obtained by using stepwise multiple regression techniques following the multilinear forms:

$\mathrm{RI}=b_0+b_1D_1+b_2D_2+\ldots b_n D_n$, where RI was the Kováts indices, D_1, D_2 and D_n were the descriptors, the intercept (b_0) and the regression coefficients of the descriptors (b_1, b_2, ... b_n) were determined by using the least squares method, and n was the number of the descriptors. The statistical evaluation of the data was obtained by the software SPSS. In MLR analysis, the descriptors in the regression equation must be independent. So, in order to reduce the number of the descriptors and minimize the information overlap in the descriptors, the concept of non-redundant descriptors (NRD)[11-15] was used. The linear correlation coefficients value of the two descriptors should less than 0.9.

3 Experiment and Methodology

3.1 Retention indices

In Table 1 Kováts indicess (RI) of silane derivatives on stationary phases (Apiezon M) for model in this paper were taken from the report of I. B. Peetre[16]. The retention data were obtained isothermally at 160℃. In this paper, 63 compounds were random selected from the total compounds, 42 compounds as developing mode set (M group), and 21 compounds as validation set (X group).

3.2 Model developing

The QSRR model developed in MLR was accomplished through the following statistical validation techniques. The RI values of silane derivatives on stationary phases were versus each of the descriptors. The statistics showed that S was the best correlated parameter and was selected for higher-order regression treatments. Then the inter-correlations between S and other descriptors were calculated, on the basis of the concept of non-redundant, some descriptors that closely related to S were deleted. Then, with the rest descriptors, MLR stepwise regression was used to select suitable variables in the model. In the successive step, according to the stepwise multilinear regression method, the noncolinear descriptors were selected and regressed against RI. And the best model was selected based on the correlation coefficient (r), F value (a statistic for assessing the overall significance), the lowest standard error of estimation (S. E) and significance levels of each term (p_1) and of the whole equations (p_2).

4 Result and Discussion

4.1 The molecular descriptors of QSRR models

The Kováts indicess and the molecular descriptors of QSRR models calculated using AM1 method were summarized in Table 1.

Geometry optimization of the compounds presented in Table 1 is the most important step; the calculated frequencies of compounds using AM1 method had no imaginary vibrational frequency, indicating that the optimized geometries were reasonable and reliable.

For minimizing the information overlap in the descriptors, according to the linear correlation coefficients value, the overlap descriptors should be deleted. And the linear correlation coefficients value of the descriptors is summarized in Table 2. Therefore, we selected S, D, Q, HOMO and LUMO as descriptors variable of RI.

Tab. 1 The retention indices on Apiezon M stationary phases and the descriptors of silane derivative

Set	Compound	D	Q	LUMO	C_v	Evib	E_n	S	HOMO	RI
M_1	$MeSi(OMe)_3$	1.4891	1.901	0.04508	40.774	111.763	229.6791216798	118.461	−0.38818	624
M_2	$MeSi(OEt)_3$	1.0110	1.589	0.04544	54.702	168.005	382.2560539425	140.744	−0.38523	772
X_1	$MeSi(OPr)_3$	1.6348	1.914	0.04579	68.741	224.657	552.9924294381	159.731	−0.38267	1015
M_3	$MeSi(OBu)_3$	1.0413	1.921	0.04263	82.868	281.268	726.2630312076	185.33	−0.38649	1271
M_4	$MeSi(OPe)_3$	1.0505	1.921	0.04253	96.998	337.883	911.3589009571	209.687	−0.38638	1538
X_2	$MeSi(OHex)$	1.0561	1.587	0.04253	96.998	337.883	911.3589009571	209.687	−0.38638	1808
M_5	$MeSi(OHept)_3$	1.0596	1.921	0.04245	111.121	394.506	1103.1738296896	233.99	−0.38633	2085
M_6	$MeSi(OMe)(OBu)$	1.1572	1.588	0.04218	68.772	224.828	542.1444270760	161.832	−0.38842	1078
X_3	$MeSi(OMe)_2OHept$	1.3408	1.904	0.04542	68.968	224.864	519.0026189504	165.621	−0.38536	1146
M_7	$MeSi(OEt)_2OPe$	1.0898	1.590	0.04387	68.679	224.671	544.8974824006	159.151	−0.39020	1035
M_8	$MeSi(OEt)(OPe)_2$	1.4545	1.914	0.04592	82.809	281.300	739.1673470733	182.898	−0.38123	1290
X_4	$MeSi(OPr)_2OHex$	1.5721	1.916	0.04538	82.892	281.264	714.2937821354	191.031	−0.38508	1283
M_9	$EtSi(OMe)_3$	1.5355	1.577	0.04470	45.280	130.838	279.1228429224	124.015	−0.38749	723
M_{10}	$EtSi(OEt)_3$	1.5335	1.577	0.04623	59.181	187.075	443.6662625713	142.464	−0.38432	859
X_5	$EtSi(OPr)_3$	1.4421	1.914	0.04581	73.347	243.648	618.5084402536	164.906	−0.38054	1100
M_{11}	$EtSi(OBu)_3$	0.8400	1.921	0.04202	87.520	300.253	792.4993328707	196.097	−0.38357	1353
M_{12}	$EtSi(OPe)_3$	0.8568	1.921	0.04191	101.646	356.874	979.8580701296	220.481	−0.38352	1614
X_6	$EtSi(OHex)_3$	0.8400	1.587	0.04182	115.772	413.495	1172.4312244642	244.955	−0.38348	1882
M_{13}	$EtSi(OEt)_2OPr$	1.5232	1.911	0.04611	63.906	205.934	500.9260049352	150.617	−0.38393	939
M_{14}	$EtSi(OEt)_2OBu$	1.0853	1.919	0.04573	68.689	224.789	550.5756412706	165.094	−0.38131	1028
X_7	$EtSi(OEt)(OPr)_2$	1.5366	1.912	0.04596	68.619	224.795	560.0711658153	158.753	−0.38278	1021
M_{15}	$EtSi(OEt)(OBu)_2$	0.7941	1.588	0.04220	78.241	262.461	667.1645361970	183.052	−0.38247	1191
M_{16}	$PrSi(OMe)_3$	1.3680	1.906	0.04484	49.901	149.763	325.6740755747	133.372	−0.38788	805
X_8	$PrSi(OEt)_3$	1.6229	1.913	0.04609	63.887	205.933	498.4126821888	151.113	−0.38534	933
M_{17}	$BuSi(OMe)_3$	1.5179	1.568	0.04474	54.395	168.729	379.2506761171	136.685	−0.38713	895
M_{18}	$BuSi(OEt)_3$	0.9899	1.923	0.04335	68.770	224.702	553.6903177286	161.056	−0.38450	1013
X_9	$PeSi(OMe)_3$	0.9733	1.584	0.04104	59.350	187.477	423.7139809705	149.876	−0.38867	985
M_{19}	$PeSi(OEt)_3$	1.6032	1.913	0.04663	71.104	243.215	618.4423095567	160.927	−0.38245	1102
M_{20}	$Me_2Si(OMe)_2$	0.6852	1.488	0.04319	38.190	107.175	182.9564983337	110.187	−0.38913	576
X_{10}	$Me_2Si(OEt)_2$	0.6989	1.907	0.04471	47.460	144.677	275.4042519551	123.325	−0.38279	678
M_{21}	$Me_2Si(OPr)_2$	0.7953	1.497	0.04183	56.795	182.482	371.4122768604	141.026	−0.38247	847

Tab. 1 The retention indices on Apiezon M stationary phases and the descriptors of silane derivative

Set	Compound	*D*	*Q*	LUMO	C_v	Evib	E_n	*S*	HOMO	RI
M_{22}	$Me_2Si(OBu)_2$	0.8898	1.908	0.04510	66.204	220.246	464.4102906294	156.95	−0.38195	1024
X_{11}	$Me_3Si(OPe)_2$	0.8750	1.495	0.04501	75.617	257.998	566.5001199016	172.958	−0.38185	1209
M_{23}	$Me_2Si(OHex)_2$	0.6229	1.907	0.04320	83.226	295.019	677.1146536509	185.307	−0.38337	1396
M_{24}	$Me_2Si(Ohept)_2$	0.6160	1.907	0.04316	92.642	332.768	787.1460393022	201.702	−0.38337	1587
X_{12}	$Me_2Si(OMe)OHept$	0.8133	1.492	0.04400	66.278	220.331	459.5785347826	157.077	−0.38534	1098
M_{25}	$Me_2Si(OEt)OHex$	0.8857	1.908	0.04528	66.219	220.246	459.5165721750	157.18	−0.38239	1042
M_{26}	$Me_2Si(OPr)OPe$	2.0180	1.913	0.04461	66.167	220.252	468.5461827643	154.414	−0.38077	1027
X_{13}	$Me_2Si(OPr)OHept$	2.1825	1.505	0.04457	75.584	258.000	569.0734418167	170.855	−0.38077	1218
M_{27}	$Me_2Si(OBu)OHex$	0.6234	1.907	0.04327	73.810	257.273	568.8490790520	168.81	−0.38345	1210
M_{28}	$Et_2Si(OMe)_2$	1.7724	1.492	0.04181	47.319	145.120	279.1467467823	120.098	−0.37696	795
X_{14}	$Et_2Si(OEt)_2$	0.5099	1.900	0.04333	56.589	182.697	386.8437391488	136.826	−0.37979	878
M_{29}	$Et_2Si(OPr)_2$	1.0019	1.492	0.04377	65.956	220.440	498.8910055388	150.87	−0.37560	1047
M_{30}	$Et_2Si(OBu)_2$	1.9673	1.909	0.04308	75.568	258.117	599.7265871598	172.513	−0.37436	1216
X_{15}	$Et_2Si(OPe)_2$	1.9758	1.501	0.04301	84.984	295.865	712.8001606208	188.727	−0.37435	1394
M_{31}	$Et_2Si(OHex)_2$	1.9536	1.918	0.04416	94.363	333.615	821.4699625259	203.867	−0.37086	1580
M_{32}	$Pe_2Si(OMe)_2$	2.1581	1.496	0.04306	75.364	258.478	584.9644456863	171.738	−0.38207	1296
X_{16}	$Pe_2SiO(OEt)_2$	0.6077	1.906	0.04324	84.780	295.922	723.2485596859	184.844	−0.38052	1354
M_{33}	Me_3SiOMe	1.5998	1.850	0.05135	33.664	102.078	139.5457517468	100.616	−0.38282	506
M_{34}	Me_3SiOEt	1.4905	1.384	0.05175	40.405	121.365	178.2070931712	114.884	−0.37820	558
X_{17}	Me_3SiOPr	1.5530	1.861	0.05093	44.979	140.315	220.4298976125	122.145	−0.37779	645
M_{35}	Me_3SiOBu	1.5410	1.861	0.05096	47.705	158.588	263.0874162246	122.799	−0.37819	741
M_{36}	Me_3SiOPe	1.5402	1.861	0.05077	54.390	178.069	306.1391104152	138.245	−0.37777	836
X_{18}	$Me_3SiOHex$	1.5259	1.861	0.05052	57.094	196.363	350.2615649160	139.17	−0.37749	932
M_{37}	$Me_3SiOHept$	1.5362	1.861	0.05070	63.804	215.821	396.3453880183	154.281	−0.37763	1030
M_{38}	Et_3SiOMe	1.5238	1.371	0.04994	49.446	159.523	277.4469107846	120.719	−0.37081	858
X_{19}	$EtSiOEt$	1.4230	1.841	0.05020	54.244	178.213	327.0979435004	129.487	−0.36838	901
M_{39}	Et_3SiOPr	1.3132	1.375	0.04997	58.766	197.226	379.6211840238	138.652	−0.36998	986
M_{40}	Et_3SiOBu	1.5295	1.842	0.04933	63.498	216.034	430.8830505248	146.29	−0.36901	1076
X_{20}	Et_3SiOPe	1.3557	1.848	0.05005	68.277	234.923	476.1752334307	156.86	−0.37035	1169
M_{41}	$Et_3SiOHex$	1.3828	1.375	0.04967	72.923	253.815	531.5322855075	162.408	−0.37012	1262
M_{42}	$Et_3SiOHept$	1.3837	1.843	0.04964	77.631	272.690	582.6402538448	170.534	−0.37012	1358
X_{21}	Bu_3SiOEt	1.4910	1.833	0.04950	81.891	291.728	668.5230793752	175.689	−0.37048	1337

Note: Me-methyl; Et-ethyl; Bu-butyl; Pr-propyl; Pe-pentyl; OMe-methoxy group; OEt-oxethyl; OPr-oxypropyl group; OBu-butoxy; OPe-pentyloxy; OHex-hexanoyl; OHept-heptyl oxygen.

Tab. 2 The correlation matrix for the description used in MLR

	D	*Q*	LUMO	HOMO	*S*	RI
D	1.000					
Q	−0.090	1.000				
LUMO	0.362	−0.182	1.000			
HOMO	0.383	−0.191	0.549	1.000		
S	−0.296	0.470	−0.530	−0.055	1.000	
RI	−0.214	0.395	−0.443	0.084	0.964	1.000

Tab. 3 Result of the principal component analysis

	Factor loading 1	Factor loading 2	Factor loading 3	Factor loading 4	Factor loading 5
D	0.630	0.355	0.435	0.532	0.066
Q	−0.520	0.634	0.450	−0.328	−0.131
LUMO	0.827	0.165	0.044	−0.476	0.248
HOMO	0.653	0.540	−0.486	0.011	−0.214
S	−0.708	0.541	−0.341	0.170	0.248
Explained variance	2.278	1.140	0.746	0.645	0.190
Proportion of the total variance (%)	45.6	22.8	14.9	12.9	3.8

4.2 PCA of descriptors variables

The original matrix was decomposed into loadings and scores matrix by PCA. Table 3 showed the result, which supported that the original variables were not strongly correlated. The first factor explained 45.6%, the second 22.8%, the third 14.9%, the fourth 12.9% and the fifth

3.8%. From Table 3 the significant values were put in bold (the loading were >0.7000[17]). The first factor correlated well with *D*, *Q*, HOMO, LUMO and S.

4.3 Result of the model with MLR

For cross-validation of molecular descriptors, stepwise regression routine was used to develop QSRR models with the descriptors (*D*, *Q*, HOMO, LUMO and *S*) of 42 compounds (M group). The linear model from diverse combination of molecular descriptors of silane derivatives were obtained, and the regression coefficients of the descriptors (included standard estimation errors and correlation coefficients) were listed in Table 4.

From Table 4 it could be seen that the best model has the highest F values, the lowest standard error of estimation (S. E) and significance levels of each term (p_1) at less than 1% level. So, the RI are controlled by HOMO and S.

Tab. 4　The descriptors and regression equations of different stationary phases

	Unstandardized Coefficients	Std. Error	Standardized Coefficients	*t*	Sig. (p_1)	*F*	*R*	*R* Square	Adjusted *R* Square	Std. Error of the Estimate	Sig. (p_2)
(Constant)	2357.255	767.491		3.071	0.004	362.125	0.974	0.949	0.946	75.26182	0.000
HOMO	7634.360	2015.337	0.137	3.788	0.001						
S	10.303	0.384	0.972	26.812	0.000						

4.4 Retention mechanism

Three main types of QSRR have been employed in previous work. The oldest type correlates logarithms of retention factors (log*k*) with the logarithms of *n*-octanol-water partition coefficients (log*P*)[18]. The second type of QSRR is based on the solva-tochromic comparison method and the so-called linear solvation energy relationships (LSERs)[19-21]. The third type of QSRR equation describes the chromatographic retention values in terms of quantum chemical indices and/or other structural descriptors from calculation chemistry[22-23], which is very popular today.

The retention mechanism was discussed as below: From the molecular orbital theory of chemical reactivity, as an electron donator, HOMO represents the ability to donate electrons. It becomes easier to donate electrons with the increasing of energies of HOMO; meanwhile it becomes easier to form hydrogen bond with the stationery phase. From Table 5 the result shows that RI increases with increasing of HOMO energies. The McReynolds constant of Apiezon M is X′: 31; Y′: 22; Z′: 15; U′: 30; S′: 40; the CP value is 3. Apiezon M contains few benzene group, alkenes, carbonyl, etc., which has LUMO orbits to accept electrons from HOMO in silicon derivatives.

The previous works[21-26] have discussed the relationship between RI and ΔS. Retention in GS is described in terms of free energies change, Δ*G*, upon transfer of a solute from a gas mobile to stationary, and expressed as the retention factor *k*:

$$\Delta G=-RT(\ln k-\ln\beta)\ln k=-\Delta H s/RT+\Delta S/Rk^{-1}\ln\beta.$$

Tab. 5　The experimental retention indices of different compounds on stationary phases[16] and calculational values by MLR

Compounds	RI(exp)	RI(cal)	Er	Er%
$MeSi(OPr)_3$	1015	1082	67	6.6
$MeSi(OHex)$	1808	1567	−241	−13.3
$MeSi(OMe)_2OHept$	1146	1122	−24	2.1
$MeSi(OPr)_2OHex$	1283	1386	103	8.0
$EtSi(OPr)_3$	1100	1151	51	4.6
$EtSi(OHex)_3$	1882	1953	71	3.8
$EtSi(OEt)(OPr)_2$	1021	1071	50	4.9
$PrSi(OEt)_3$	933	972	39	4.2
$PeSi(OMe)_3$	985	934	−51	−5.2
$Me_2Si(OEt)_2$	678	706	28	4.1
$Me_3Si(OPe)_2$	1209	1224	15	1.2
$Me_2Si(OMe)OHept$	1098	1034	−64	−5.8
$Me_2Si(OPr)Ohept$	1218	1211	−7	−0.6
$Et_2Si(OEt)_2$	878	868	−10	−1.1
$Et_2Si(OPe)_2$	1394	1444	50	3.6
$Pe_2SiO(OEt)_2$	1351	1357	3	0.2
Me_3SiOPr	645	732	87	13.5
$Me_3SiOHex$	932	909	−23	−2.5
$EtSiOEt$	901	879	−22	−2.4
Et_3SiOPe	1169	1116	−23	−2.0
Bu_3SiOEt	1337	1339	2	0.1
R		0.9724		

where k is the equilibrium constant, T is the absolute temperature, R is the gas constant, β is the phase rate, ΔH is dissolution enthalpy, ΔS is dissolution entropy. ΔH and ΔS are associated with the transfer of a solute from the mobile phase to the stationary phase. So, S is a descriptor associated with RI.

The value of the experimental retention indices used Exp. ; the value of the predictive retention indices used Cal.

4. 5 Predicted RI of silane derivatives (X group)

The predicted RI of silane derivatives and the experimental RI[16] are collected In Table 5 and Fig. 2. The result showed that the relative errors are in range from -13. 3% to 13. 5%, and most of errors are less than 5%. The correlation coefficients between the experimental RI and predicted RI is 0. 9724, indicating that the developing model is satisfactory.

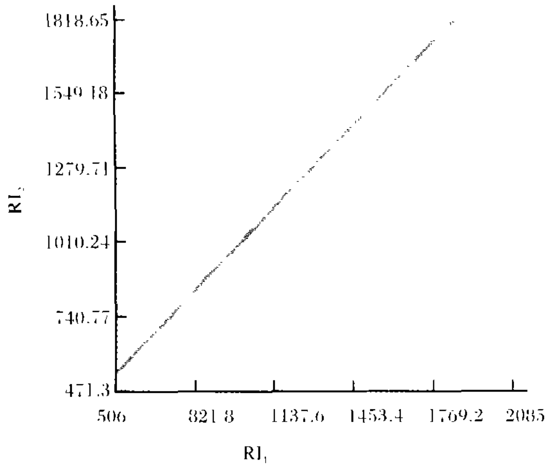

Fig. 1　Plot of the calculated RI_1 vs. experimental RI_2

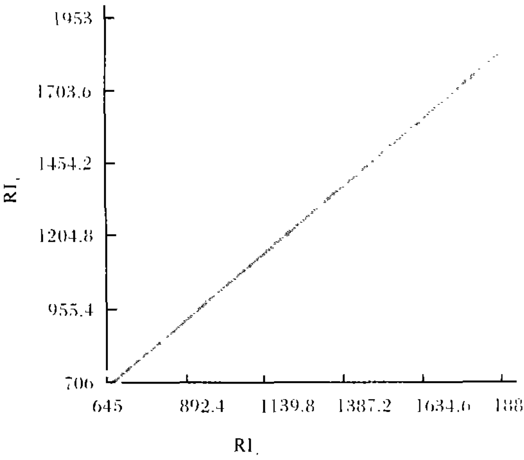

Fig. 2　Plot of predicted RI_4 and experimental RI_3 retention index

5 Conclusion

In the study, based on the quantum chemical descriptors computed by AM1, good model for QSRR of silane derivatives was obtained. The retention mechanism of silane derivatives of separation operating in the gas chromatogram was discussed. The main influence factors of Kováts indices are HOMO and S. The results indicated that the QSRR model proposed was satisfactory.

参考文献:

[1] Kaliszan R, van Straten M A, Markuszewski M, et al. Molecular mechanism of retention in reversed-phase high-performance liquzd chromatography and classification of modern stationary phases by using quantitative structure-retention relationships[J]. J Chromatogr A, 1999, **855**: 455-486.

[2] Gorgényi M, Fekete Z, Seres L. Estimation and prediction of the retention indices of selected bans-diazenes[J]. Chromatographia, 1989, **27**: 581-584.

[3] Kiraly Z, Kortvelyesi T, Seres L. Structure-retention retentionships in the gas chromatography of N, N-dialkylhydrazones[J]. Chromatographia, 1996, **42**: 653-659.

[4] Zhang T Z, Feng Y Q, Fan M, et al. Correlations between molecular structure parameters and retention index of some aromatic pentadienes in gas chromatography[J]. Journal of Central China Normal University(Natural Sciences), 1990, **36**: 49-52.

[5] Dimov N, Osman A, Mekenyan O V, et al. Selection of molecular descriptors used in quantitative structure-gas chromatographic retention relationships Ⅱ. Isoalkanes and alkenes [J]. Anal Chim Acta, 1996, **323**: 15-25.

[6] Kaliszan R, Kaliszan A, Noctor T A G, et al. Mechanism of retention of benzodiazepines in affinity, reversed-phase and adsorption high-performance liquid chromatography in view of quantitative structure-retention relationships[J]. J Chromatogr A, 1992, **609**: 69-81.

[7] Osmialowski K, Halkiewicz J, Radecki A, et al. Quantum chemical parameters in correlation analysis of gas liquid chromatographic retention indices of amines[J]. J Chromatogr A, 1985, **346**: 53-60.

[8] Balcan M, Cserhati T, Forgacs E, et al. Determination of the relative impact of chromatographic conditions and solute structures on the retention behaviour of non-ionic surfactants in RP-HPLC[J]. Biomed Chromatogr, 1999, **13**: 225-228.

[9] Forgacs E, Cserhati T. Use of stepwise regression analysis and cluster analysis for the study of the interaction between nonionic surfactants[J]. Anal, 1998, **18**: 505-511.

[10] Gao Y H, Wang Y W, Yao X J, et al. The prediction for gas chromatographic retention index of disulfides on stationary phases of different polarity[J]. Elsevier Sci, 2003, **59**:

229-237.

[11] Dewar M J S, Zoebisch E G, Healy E F. AM1: a new general purpose quantum mechanical molecular model[J]. J Am Chem Soc, 1985, **107**: 3902-3909.

[12] Frisch M J, Trucks G W, Schlegel H B, et al. Revision C02[M]. Pittsburgh PA: Gaussian, Inc, 2003.

[13] Héberger K, Görgényi M. Principal component analysis of Kováts indices for carbonyl compounds in capillary gas chromatography[J]. J Chromatogr A, 1999, **845**: 21-31.

[14] Katritzky A R, Gordeeva E V. Traditional topoloqical indicesvs electronic, geometrical and combined molecular descriptors in QSAR/QSPR research[J]. J Chem Inf Comput Sci, 1993, **33**: 835-857.

[15] Olivero J, Gracia T, Payares P, et al. Molecular structure and chromatographic retention behavior of the components of ylang-ylang oil[J]. J Pharm Sci, 1997, **86**: 625-630.

[16] Peetre I B, Ellren O, Smith B E F. Gas chromatographic investigation of organometallic compounds and their carbon analogues: VI. Determination, calculation and correlation of Kováts retention indices for alkylalkoxysilanes[J]. J Chromatogr A, 1985, **318**: 41-55.

[17] Körtvelyesi T, Gögenyl M, Héberger K. Correlation between retention indices and quantum-chemical descriptors of ketones and aldehydes on stationary phases of different polarity[J]. Anal Chim Acta, 2001, **428**: 73-82.

[18] Hanna M, Biasi V D, Bond B, et al. Estimation of the partitioning characteristics of drugs: a comparison of a large and diverse drug series utilizing chromatographic and electrophoretic methodology [J]. Anal Chem, 1998, **70**: 2092-2099.

[19] Tan L C, Carr P W, Abraham M H. Study of retention in reversed-phase liquid chromatography using linear solvation energy relationships I. The stationary phase[J]. J Chromatogr A, 1996, **752**: 1-18.

[20] Valko K, Plass M, Bevan C, et al. Relationships between the chromatographic hydrophobicity indices and solute descriptors obtained by using several reversed-phase, diol, nitrile, cyclodextrin and immobilised artificial membrane-bonded high-performance liquid chromatography columns [J]. J Chromatogr A, 1998, **797**: 41-55.

[21] Sándi A, Nagy M, Szepesy L. Characterization of reversed-phase columns using the linear free energy relationship Ⅲ. Effect of the organic modifier and the mobile phase composition[J]. J Chromatogr A, 2000, **893**: 215-234.

[22] Dai J Y, Jin L J, Yao S C, et al. Prediction of partition coefficient and toxicity for benzaldehyde compounds by their capacity factors and various molecular descriptors [J]. Chemosphere, 2001, **42**: 899-907.

[23] Suzuki T, Timofei S, Iuoras B E, et al. Quantitative structure-enantioselective retention relationships for chromatographic separation of arylalkylcarbinols on Pirkle type chiral stationary phases[J]. J Chromatogr A, 2001, **922**: 13-23.

[24] Wu C Y, Cheng J S, Zeng Z R. The Selectivity of crown ether polysiloxane stationary phases[J]. Chromatographia, 1993, **1**: 33-37.

[25] Jung M. Theorelical approach to the gas chromatographic separation of enantiomers on dissolved cyclodextrin derivatives[J]. J Chromatogr A, 1991, **552**: 43-57.

[26] Berthod A, Valleix A, Veronique Tizon, et al. Retention and selectivity of teicoplanin stationary phases after copper complexation and isotopic exchange[J]. Anal Chem, 1992, **64**: 873-879.

阿皮松M负载硅烷类化合物的气相色谱保留机理研究

王瑞侠[1], 宋远志[2,3,4], 叶勇[2], 阮敏[2,3], 谢吉民[4]

(1.池州学院 化学与食品科学系, 安徽 池州 247000;
2.江苏省化学低维材料重点实验室, 淮阴师范学院 化学系, 江苏 淮安 223300;
3.教育部有机功能分子的合成和应用重点实验室, 湖北 武汉 430062;
4.江苏大学 工程学院, 江苏 镇江 212013)

摘　要: 利用AM1法全优化计算了一系列硅烷类化合物, 并将获得的8种量化参数与其在阿皮松M上的气相(GC)Kováts指数进行多元线性回归(MLR), 成功建立了QSRR模型, 该模型的预测值与实验值基本吻合.

关键词: 定量结构-保留关系; 多元线性回归; 硅烷衍生物; 人工神经网络

中图分类号: O641.12　　**文献标识码**: A