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Short Communication

Prediction of gas chromatography retention of BTEX and other substituted benzenes based on quantum chemical parameters

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Quantitative structure-retention relationship (QSRR) models for gas chromatography retention times of BTEX (benzene, toluene, xylenes and ethylbenzene) and other substituted benzenes on DB-624, DB-wax and DB-1 have been developed. The B3LYP hybrid density functional level in the Gaussian 03 program were used to calculate molecular parameters such as dipole moments (μ), molecular volumes (V), molecular radius (r), the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), Mülliken charges (Q) and Mülliken negative charges with hydrogens summed into heavy atoms in molecule (Q_H). Using multiple linear regression method, the correlation between retention time and structural parameters was obtained. Empirical functions with high correlation coefficient are appropriate for the prediction of retention times of BTEX and similar compounds.

Key words: Gas chromatography, retention time, quantitative structure-retention relationship, density functional theory.

INTRODUCTION

Today, the supply of safe drinking water is one of the most crucial problems all over the world. BTEX (benzene, toluene, ethylbenzene and xylenes) and other substituted benzenes are one of the most important pollutants of water (Almeida and Boas, 2004). The World Health Organization (WHO, 1993) has defined the allowable range of these compounds in water as follows: benzene (10 μgl^{-1}), toluene (700 μgl^{-1}), xylenes (500 μgl^{-1}), ethylbenzene (300 μgl^{-1}), styrene (20 μgl^{-1}), monochlo-robenzene (300 μgl^{-1}), o-dichlorobenzene (1000 μgl^{-1}), p-dichlorobenzene (300 μgl^{-1}) and trichlorobenzene (20 μgl^{-1}).

An effective method for identification of these compounds is through the use of gas chromatography technique (Almeida and Boas, 2004). Study of retention mechanism in gas chromatography is very useful for the prediction of retention time (Song et al., 2005). In this way, retention time could be calculated for similar compounds. Quantitative structure-retention relationship (QSRR) is an important and useful method for review of retention mechanism and the prediction of retention time. This method is used for identification of the most important structural parameters affecting retention time, as well as the prediction of retention time for new compounds (Song et al., 2005; Kaliszan et al., 1999; Kortvelyesi et al., 2001; Payares et al., 1997; Woloszyn and Jurs, 1993).

The aim of this work is to develop QSRR method for establishing the relations between retention time of BTEX and other substituted benzenes and structural parameters obtained from quantum mechanics.

So far, the QSRR method has not been developed in connection with BTEX and other substituted benzenes. The equations that are presented in this work could be applied to other similar compounds for which few experimental data are available.

THEORY

Structural parameters have been obtained using quantum

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Table 1. Structural parameters of QSRR models.

Compounds	t_{CPPP} (min)	t_{DMP} (min)	t_{PEG} (min)	V ($cm^3\ mol^{-1}$)	r (A^o)	μ (Debye)	Q	Q_H	HOMO (Hartree)	LUMO (Hartree)
Benzene	8.69	8.00	6.46	87.88	4.09	0.00	-0.90	0.00	-0.257	-0.007
Toluene	11.39	11.33	9.06	80.97	4.00	0.41	-1.94	-0.97	-0.248	-0.016
Chlorobenzene	14.25	13.44	13.00	77.45	3.95	1.86	-1.70	-1.01	-0.257	-0.032
Ethyl benzene	14.42	13.90	11.13	108.01	4.35	0.39	-1.99	-0.80	-0.248	-0.015
p-xylene	14.62	14.11	11.30	99.37	4.25	0.07	-2.78	-1.44	-0.237	-0.015
m-xylene	14.62	14.11	11.44	96.67	4.21	0.38	-2.94	-1.71	-0.241	-0.014
o-xylene	15.28	14.69	12.39	106.71	4.33	0.68	-1.93	-0.67	-0.241	-0.011
1,3-dichlorobenzene	17.96	17.20	16.60	83.36	4.03	1.74	-2.09	-1.47	-0.264	-0.044
1,2-dichlorobenzene	18.69	17.81	17.80	100.27	4.26	2.65	-2.33	-2.59	-0.261	-0.042
1,4-dichlorobenzene	18.79	17.31	17.06	105.89	4.33	0.00	-2.78	-2.15	-0.257	-0.045
1,2,3-tricholorobenzene	22.23	21.28	21.25	108.50	4.36	2.66	-2.39	-1.93	-0.270	-0.049

mechanical calculations. The following parameters have been considered: dipole moments (μ), molecular volumes (V), molecular radius (r), the lowest unoccupied molecular orbital (LUMO), the highest occupied molecular orbital (HOMO), Mülliken charges (Q) and Mülliken nega-tive charges with hydrogens summed into heavy atoms in molecule (Q_H). All calculations were performed with the B3LYP hybrid density functional level using the Gaussian 03 program (Frisch et al., 2003). Geometries of BTEX and other substituted benzenes (Table 1) were optimized at 6-311+G(d,p) basis sets. The calculated frequencies have no imaginary vibrational frequency, indicating that the optimized geometries are reasonable and reliable.

In this work, linear method has been used. The relation between retention time and structural parameters is established by the following multi-linear form:

$$t = a_\circ + a_1 p_1 + a_2 p_2 + ... + a_n p_n \quad (1)$$

Where: t = retention time; p_1, p_1 ... p_1 = structural parameters.

The intercept ($a_\circ$) and the regression coefficients ($a_1, a_2 ... a_n$) were determined using least square method. Sigmaplot software has been used for this purpose. CPPP column (6% cyanopropylphenyl-poly-siloxane, J&W Scientific, Folsom, CA) is suitable for determination of BTEX and other substituted benzenes. Retention times (t) have been reported by J&W Scientific (www.agilent.com/chem).They used 30 m length, 0.53 mm I.D, 3 µm film thickness DB-624.

RESULTS AND DISCUSSION

Firstly, the structures of BTEX and other substituted benzenes were optimized. Frequency calculations have also been done and no imaginary frequency was observed to show the reliability of the structures. Then, structural parameters were calculated. Table 1 presents the quantities of these parameters. Molecular volume and molecular radius control retention time by affecting the rate of mass transfer. Dipole moment is important in the interaction of the molecules with polar and apolar stationary phases. Each increase in polarity of the stationary phase causes a parallel increase in the role of dipole moment. Q and Q_H play an important role in van der Waals interactions between molecules. HOMO as an electron donor and LUMO as an electron acceptor were speci fically effective in chemical reactions.

Using equation 1, the intercept ($a_\circ$) and the regres-sion coefficients ($a_1, a_2 ... a_n$) were obtained. These coefficients are presented in Table 2. Correlation coefficient (R) and square of correlation coefficient (R^2) for this fitting were obtained as 0.9958 and 0.9917, respectively, being very appropriate for prediction of retention times of BTEX and similar compounds.

Subsequently, Polyethylene Glycol (PEG) and Dimethylpolysiloxane (DMP) columns were considered for testing the presented model. Retention times, regression coefficients and square of correlation coefficient related to these columns are shown in Tables 1 and 2, respecttively. Again, it will be observed that a good correlation has been obtained between retention time and structural parameters.

To test the equation 1, two similar BTEX compounds were selected which are not recorded in Table 1 (pentachlorobenzene and 2-Chlorotoluene). Structural parameters were calculated for these two compounds and their retention times were obtained by using equation 1. These data have been presented in Table 3. It was observed that there is a good correspondence between theoretical and experimental values. Consequently, this equation could be used for similar BTEX compounds for which few experimental data are available

Conclusion

In this work, structural parameters have been obtained using quantum mechanical approach. Each parameter is somehow effective in retention time. Using multiple linear regression method, the correlation between retention

Table 2. The intercept ($a_\circ$), the regression coefficients ($a_1, a_2 \ldots a_n$), correlation coefficient (R) and square of correlation coefficient (R^2) of BTEX and other substituted benzenes.

Column	$a_\circ$	$a_1(V)$	$a_2(r)$	$a_3(\mu)$	$a_4(Q)$	$a_5(Q_H)$	a_6 $(HOMO)$	a_7 $(LUMO)$	R	R^2
CPPP	90.423	0.4879	-28.451	1.285	-2.789	1.799	47.750	-186.340	0.9958	0.9917
DMP	110.14	0.5747	-36.016	1.482	-3.202	1.871	36.546	-154.796	0.9940	0.9880
PEG	86.863	0.4638	-27.575	1.387	-1.717	1.135	45.839	-220.78	0.9954	0.9910

Table 3. Structural parameters of QSRR models and retention times for testing equation 1 (CPPP column).

Compounds	t_{theory} (min)	$t_{exp.}$ (min)	V (cm^3 mol^{-1})	r (A^o)	μ (Debye)	Q	Q_H	HOMO (Hartree)	LUMO (Hartree)
pentachlorobenzene	27.72	27.10	156.40	5.07	0.853	-3.22	-3.03	-0.270	-0.066
2 - Chlorotoluene	16.68	16.71	108.08	4.35	1.607	-2.605	-1.68	-0.252	-0.027

time and structural parameters was obtained. The appropriate correlation obtained in connection with different columns showed the efficiency of the applied model for prediction of retention times of BTEX and similar compounds.

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