

# Determination of the Adsorption Energy of Some Volatile Solvents on the Surface of a Mesoporous Carbon Adsorbent by Gas-chromatography

Marian Snauko,<sup>a</sup> Dusan Berek,<sup>a</sup> and Tibor Cserhati<sup>b,\*</sup>

<sup>a</sup>*Polymer Institute of the Slovak Academy of Sciences, Bratislava, Slovak Republic*

<sup>b</sup>*Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, 1525 Budapest, Hungary*

RECEIVED MARCH 8, 2006; REVISED FEBRUARY 15, 2007; ACCEPTED MARCH 14, 2007

*Keywords*  
adsorption energy  
volatile solvents  
gas chromatography

Retention times of 21 volatile solvents were determined on a mesoporous carbon adsorbent stationary phase by gas chromatography at various column temperatures and the energy of adsorption was calculated from the dependence of the retention time on the column temperature. Energies of adsorption showed high variations proving that the carbon stationary phase is suitable for separation of this class of analytes. Quantitative structure-retention computations demonstrated that the strength of adsorption significantly depends on the molecular volume, indicating the dominant role of sterical correspondence in the adsorption.

## INTRODUCTION

Owing to their advantageous adsorption characteristics, various carbon preparations have been frequently used in many fields of chromatographic separation. Thus, the application of glassy carbon electrode<sup>1</sup> and electrode modified by functionalized carbon nanotubes<sup>2</sup> in liquid chromatography has been recently reported. Carbon fibers have been employed for the adsorption of dissolved natural organic matter before size exclusion chromatography<sup>3</sup> and submitted to solid surface mapping by inverse gas chromatography.<sup>4</sup> Porous graphitized carbon (PGC) stationary phase has also been extensively used in high performance liquid chromatography. It has been applied for the separation of isoprostanes in human cerebrospinal fluid,<sup>5</sup> for the analysis of native and permethylated cyclodextrins,<sup>6</sup> carbohydrates,<sup>7</sup> proteoglycans,<sup>8</sup> for the se-

paration of ions in electrochemically modulated liquid chromatography,<sup>9</sup> for the ion chromatographic separation of phosphorous species,<sup>10</sup> for determination of the interaction between PGC stationary phase and various analytes.<sup>11</sup> PGC has been further employed in supercritical fluid chromatography.<sup>12</sup>

A mesoporous carbon adsorbent (CARB SG GR) was developed at the Polymer Institute of the Slovak Academy of Sciences. This sorbent is prepared by pyrolysis of saccharose within the pores of auxiliary silica gel. The matrix of silica gel prevents the agglomeration of particles during pyrolysis and preserves the porous structure. After pyrolysis, silica gel is removed by an alkaline solution. The adsorption characteristics of this carbon preparation depend on the heating process. Heating at low temperature results in a very strong polar adsorbent with

\* Author to whom correspondence should be addressed. (E-mail: tevi@chemres.hu)

undesired irreversible retention of some analytes. The separation parameters of the sorbent heated at high temperatures is similar to those of the commercial octadecylsilica stationary phase. Successful separation of enantiomers of amine isomers<sup>13</sup> and other organic compounds<sup>14,15</sup> on this stationary phase has been performed previously.

Quantitative Structure-Retention Relationship (QSRR) studies have been frequently used in chromatography to elucidate the various aspects of the correlation between chromatographic behaviour and molecular characteristics.<sup>16</sup> Thus, they have been employed for the assessment of the retention indices and physicochemical parameters of polycyclic aromatic hydrocarbons in GC,<sup>17</sup> for the prediction of GC retention indices of saturated O-, N-, and S-heterocyclic compounds,<sup>18</sup> for the determination of enantiomeric excess from overlapping HPLC peaks,<sup>19</sup> for the wavelet analysis of baseline noise in HPLC,<sup>20</sup> *etc.*

Linear and multiple linear regression analyses have been frequently applied for the assessment of the relationship between one dependent and one or more independent variables. Because of their simplicity and good predictive power, they have been successfully applied in various chromatographic techniques as well.<sup>21</sup> These methods have been recently employed for QSRR studies of agonists,<sup>22</sup> phenolic compounds,<sup>23</sup> CNS agents<sup>24</sup> and polarity parameters.<sup>25</sup> Stepwise regression analysis (SRA) is an up-to-date version of multivariate linear regression analysis. In the traditional multivariate regression analysis, the presence of independent variables that exert no significant influence on the dependent variable decreases the significance level of the independent variables that significantly influence the dependent variable. SRA overcomes this difficulty by automatically eliminating insignificant independent variables from the selected equation, thereby enhancing the information power of the computation.

The objectives of the investigation were to measure the energy of adsorption of some volatile solvents on the surface of CARB SG GR sorbent by gas chromatography and to elucidate the relationship between molecular characteristics of solvents and their strength of adsorption. As the retention of analytes on the surface of the stationary phase depends on the energy of adsorption, the results obtained may help a rational design of the optimal separation of this class of solvents. Moreover, they may contribute to a better understanding of the physical and physicochemical processes underlying retention.

## EXPERIMENTAL

The chemical names of volatile solvents are listed in Table I. Solvents of analytical grade were purchased from Sigma-Aldrich GmbH (Steinheim, Germany) and were used as received. 1  $\mu$ L of pure solvents was separately injected. Gas chromatographic measurements were performed on a Carlo

Erba Fractovap 2150 (Milano, Italy) instrument with flame ionization detector connected with a Shimadzu C-R3A integrator (Kyoto, Japan). The carbon sorbent was filled in a glass column, 250 mm  $\times$  2 mm I.D. Detector and injector temperatures were set at 225 °C. Carrier gas was nitrogen. Retention times of analytes were determined at five different temperatures and the mean and relative standard deviations of individual measurements were calculated. Column temperatures were chosen so that the retention values lay in an interval of 3 to 10 min. The intra-day reproducibility was determined by five independent parallel measurements, the inter-day reproducibility was calculated from five replicated measurements performed daily for five days. Standard deviations of inter- and intra-day reproducibilities were compared using the »F« test. Retention times of 3–10 min were obtained by varying column temperatures. Each measurement was carried out in triplicate and the mean retention time and the relative standard deviation (RSD) were calculated for each solvent at each column temperature. To calculate the energy of interaction between the solvents and CARB SG GR adsorbent, the general equation describing the change of the logarithm of retention time ( $\log t_R$ ) with temperature ( $T$ ) was applied:

$$\log t_R = a + b/T \quad (1)$$

where  $t_R$  is the net retention time,  $a$  is the intercept,  $b$  is the slope (a change of the logarithm of retention time with a unit change in temperature),  $T$  is the column temperature (Kelvin scale). Eq. (1) was separately applied for each solvent.

The slope value ( $b$ ) of Eq. (1) was employed to calculate the energy of interaction ( $\Delta H$ ):

$$\Delta H = 2.3 \cdot R \cdot b \quad (2)$$

where  $R$  is the gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>).

A similar GC method was previously employed for the determination of the energy of interaction between some commercial pesticides and a non-ionic surfactant.<sup>26</sup>

The relationship between the strength of adsorption and the physicochemical characteristics of analytes was assessed by SRA. The dependent variable was in each instance the strength of adsorption. Independent variables were the following physicochemical characteristics of analytes:  $\pi$  = Hansch-Fujita's substituent constants characterizing hydrophobicity; H-Ac and H-Do = indicator variables for proton acceptor and proton donor properties, respectively; M-RE = molar refractivity;  $F$  and  $R$  = Swain and Luton's electronic parameters characterizing the inductive and resonance effects;  $\sigma_{Me}$  and  $\sigma_{Pa}$  = Hammett's constants characterizing the electron-withdrawing power of the substituents at *meta* and (*para* + *ortho*) positions;  $E_s$  = Taft's constant characterizing the steric effects of substituents;  $B_1$  and  $B_4$  = Sterimol width parameters determined by the distance of substituents at their maximum point perpendicular to attachment. Physicochemical parameters were calculated according to the additivity rule from the fragmental constants. Fragmental constants

are physicochemical parameters characterizing simple molecular substructures without taking into consideration the possible intramolecular interactions among the substructures in the molecule. SRA was performed twice: in the first SRA, only the linear forms of physicochemical parameters were independent variables; the square of the parameters was also included in the second calculation. Inclusion of the square values was motivated by the fact that the linearity of the relationship between this class of dependent and independent variables has not been previously demonstrated. The number of accepted independent variables was not limited; the acceptance limit was set at the 95 % significance level. Software for SRA was purchased from Compudrug Ltd. (Budapest, Hungary).

## RESULTS AND DISCUSSION

The RSD values of individual measurements were in each instance lower than 1.5 %, the RSD values of intra-day and inter-day reproducibilities varied between 0.68–1.35 % and did not differ significantly. These validation parameters illustrate the good reproducibility and reliability of the chromatographic system. Some parameters of Eq. (1) are compiled in Table I. The coefficients of correlation demonstrate that Eq. (1) fits well to the experimental data. The energy of adsorption showed considerable variations between the individual solvents, indicating that

TABLE I. Parameters of the relationship between the logarithm of the retention time,  $t_R$ , the column temperature,  $T$ , and the energy of adsorption  $\Delta H$  /  $\text{kJ mol}^{-1}$

Solvent	$b \cdot 10^{-4}$	$r$	$\Delta H$
Acetone	2.41	0.996	460
Acetonitrile	2.89	0.992	552
Benzene	2.92	0.998	558
2-Butoxyethanol	5.02	0.985	959
n-Butanol	3.15	0.996	601
tert-Butanol	2.54	0.997	486
Chloroform	2.61	0.992	496
Dioxane	2.79	0.995	533
1,2-Dichloroethane	3.05	0.992	583
Dimethylformamide	2.79	0.981	534
Ethanol	2.96	0.990	515
Ethyl acetate	3.17	0.989	606
2-Ethoxyethanol	2.28	0.965	436
n-Hexane	3.01	0.999	576
2-Methoxyethanol	3.19	0.978	609
Methanol	2.89	0.989	552
2-Propanol	3.03	0.986	579
2-Propoxyethanol	3.54	0.968	677
Tetrahydrofuran	3.50	0.989	668
Toluene	3.56	0.995	681
Trichloroethylene	2.87	0.983	549

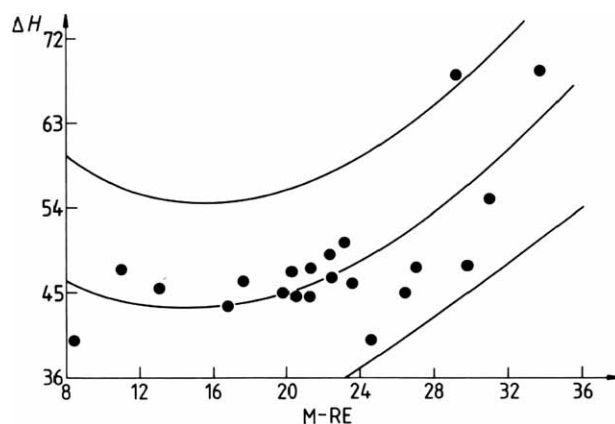


Figure 1. Relationship between the strength of adsorption ( $\Delta H$ ) of solvents on the surface of the carbon stationary phase and their molar refractivity (M-RE). Lower and upper curves represent the confidence interval of 95 %.

the binding of this class of analytes to the carbon adsorbent is markedly different. This finding suggests that CARB SG GR sorbent can be successfully employed in environmental protection for the removal of solvents from groundwater and wastewaters, for the concentration of solvents as a solid phase extraction support and for their chromatographic separation as stationary phase.

The parameters of significant correlations between the strength of adsorption and molecular characteristics are presented in Eqs. (3) to (5).

Linear correlations:

$$\Delta H = 32.41 + 0.7084 \cdot \text{M-RE} \quad (3)$$

$$n = 21; \quad r = 0.6267; \quad r^2 = 0.3927; \quad F_{\text{calc.}} = 12.28$$

Significance level over 99 %

$$\Delta H = 37.47 + 1.71 \cdot B_4 \quad (4)$$

$$n = 21; \quad r = 0.4467; \quad r^2 = 0.1995; \quad F_{\text{calc.}} = 4.73$$

Significance level over 95 %

Quadratic correlation:

$$\Delta H = 45.66 - 0.1697 \cdot \text{M-RE} + 0.0567 \cdot (\text{M-RE})^2 \quad (5)$$

$$n = 21; \quad r = 0.7459; \quad r^2 = 0.5564; \quad F_{\text{calc.}} = 11.29$$

Significance level over 99.9 %

The best correlation with a 95 % confidence interval is depicted in Figure 1. The significance level was over 95 % in each instance demonstrating that the physicochemical parameters included in QSRR calculations exert a

considerable influence on the adsorption strength of the solvent (compare calculated and tabulated  $F$  and  $r$  values). However, the ratio of variance explained was relatively low (see  $r^2$  values). This finding can be tentatively explained by the supposition that other physicochemical characteristics not included in the QSRR computations may also exert a significant influence on the adsorption of this class of analytes. According to the SRA results, the solute-sorbent interaction mainly depends on the sterical parameters of solvents. This finding can be tentatively explained by the supposition that the interaction between the adsorption centers on the carbon surface and the solute molecules is stronger, with solvent molecules exposing a considerable planar surface.

## CONCLUSIONS

The results indicate that SRA can be successfully applied to the assessment of the correlation between the adsorption strength of some volatile solvents on a carbon adsorbent and their physicochemical parameters. Calculations have demonstrated the dominant role of sterical correspondence between the analytes and the stationary phase surface.

## REFERENCES

1. T. Huang, M. E. Garceau, and T. Ramstadt, *J. Pharm. Biomed. Anal.* **38** (2005) 532–536.
2. W. Zhang, F. Wan, W. Zhu, H. Xu, X. Ye, R. Cheng, and L.-T. Jin, *J. Chromatogr. B* **818** (2005) 227–232.
3. W. Cheng, S. A. Dastgheib, and T. Karanfil, *Water Res.* **39** (2005) 2281–2290.
4. M. C. Gutiérrez, S. Osuna, and I. Baráibar, *J. Chromatogr. A* **1087** (2000) 142–149.
5. K. C. Bohnstedt, B. Karlberg, H. Basun, and S. Schmidt, *J. Chromatogr. B* **827** (2005) 39–43.
6. A. Kwarczak and A. Bielejewska, *Anal. Chim. Acta* **537** (2005) 41–46.
7. J. Yuan, N. Hashii, N. Kawasaki, S. Itoh, T. Kawanishi, and T. Hayakawa, *J. Chromatogr. A* **1067** (2005) 145–152.
8. B. Barroso, M. Didraga, and R. Bischoff, *J. Chromatogr. A* **1080** (2005) 43–48.
9. T. Hasan, D. Gazda, M. D. Porter, and R. S. Houk, *Anal. Chim. Acta* **537** (2005) 63–68.
10. V. Ruiz-Calero and M. T. Galceran, *Talanta* **66** (2005) 376–410.
11. C. West, G. Cilpa, K. Gaudin, P. Chaminade, and E. Lesellier, *J. Chromatogr. A* **1087** (2005) 77–85.
12. C. West and E. Lesellier, *J. Chromatogr. A* **1087** (2005) 64–76.
13. D. Berek and I. Novak, *Chromatographia* **30** (1990) 582–590.
14. S. Skrabakova, E. Matisova, E. Benicka, I. Novak, and D. Berek, *J. Chromatogr.* **665** (1994) 27–32.
15. E. Matisova and S. Skrabakova, *J. Chromatogr.* **707** (1995) 145–179.
16. R. Kalisz, *Structure and Retention in Chromatography: A Chemometric Approach*, Harwood Academic Publishers, Australia, 1997.
17. B. Skrbic, N. Djuricic-Mladenovic, and J. Cvejanov, *Chemom. Intell. Lab. Syst.* **72** (2004) 167–171.
18. O. Farkas, K. Héberger, and I. G. Zenkevich, *Chemom. Intell. Lab. Syst.* **72** (2004) 173–184.
19. M. Holik and A. Mannschreck, *Chemom. Intell. Lab. Syst.* **72** (2004) 153–160.
20. A. Felinger and M. Kárá, *Chemom. Intell. Lab. Syst.* **72** (2004) 225–232.
21. H. Mager, *Moderne Regressionsanalyse*. Salle, Sauerlander, Frankfurt am Main, 1982, pp. 135–163.
22. G. Fragkaki, M. A. Koupparis, and C. G. Georgakopoulos, *Anal. Chim. Acta* **512** (2004) 165–171.
23. T. Hanai, *J. Chromatogr. A* **1027** (2004) 279–287.
24. M. R. Hodj Mohammad, P. Ebrahim, and F. Pourmorad, *QSAR & Combinat. Sci.* **23** (2004) 295–302.
25. R. Bosque, J. Sales, E. Bosch, M. Rosés, M. C. Garcia-Alvarez-Coque, and J. R. Toez-Lapasio, *J. Chem. Inf. Comput. Sci.* **43** (2003) 1240–1247.
26. Y. Darwish, T. Cserhádi, and E. Forgács, *Anal. Chim. Acta* **411** (2000) 239–245.

## SAŽETAK

### Određivanje adsorpcijske energije nekih volatilnih otapala na površini mezoporoznog ugljika metodom plinske kromatografije

Marian Snauko, Dusan Berek i Tibor Cserhádi

Retencijska vremena 21 volatilnog otapala na mezoporoznom ugljiku kao stacionarnoj fazi određena su metodom plinske kromatografije pri različitim temperaturama. Adsorpcijska energija izračunata je iz ovisnosti retencijskog vremena o temperaturi kolone. Zapažene su značajne razlike u adsorpcijskim energijama, što dokazuje da je ugljik kao stacionarna faza pogodan za odvajanje ove klase analita. Kvantitativni račun odnosa struktura-retencija pokazali su da adsorpcija značajno ovisi o volumenu, što ukazuje na dominantnu ulogu steričkih faktora prilikom adsorpcije.