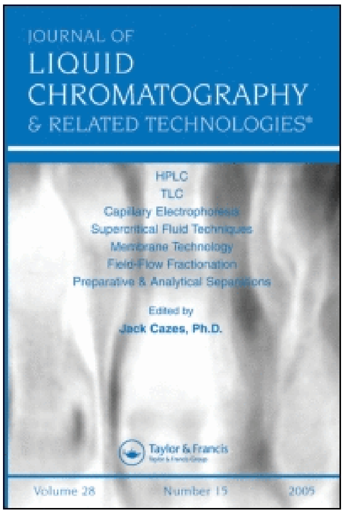

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Effect of Carbon Content Bonded on Silica Surface on Retention Values in Reversed-Phase Liquid Chromatography and Ion-Pair Liquid Chromatography

Hanfa Zou[a]; Yukui Zhang[a]; Minfang Hong[a]; Peichang Lu[a]
[a] National Chromatographic R &A Center Dalian Institute of Chemical Physics Academia Sinica, Dalian, The People's Republic of China

To cite this Article Zou, Hanfa , Zhang, Yukui , Hong, Minfang and Lu, Peichang(1993) 'Effect of Carbon Content Bonded on Silica Surface on Retention Values in Reversed-Phase Liquid Chromatography and Ion-Pair Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 16: 16, 3445 — 3455

To link to this Article: DOI: 10.1080/10826079308019700

URL: http://dx.doi.org/10.1080/10826079308019700

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(16), 3445-3455 (1993)

EFFECT OF CARBON CONTENT BONDED ON SILICA SURFACE ON RETENTION VALUES IN REVERSED-PHASE LIQUID CHROMATOGRAPHY AND ION-PAIR LIQUID CHROMATOGRAPHY

HANFA ZOU*, YUKUI ZHANG, MINFANG HONG, AND PEICHANG LU
National Chromatographic R & A Center
Dalian Institute of Chemical Physics
Academia Sinica
Dalian 116011, The People's Republic of China

ABSTRACT

Effect of the carbon content on the stationary surface (N_S) on retention values in reversed-phase liquid chromatography (RPLC) and ion-pair liquid chromatography (RP-IPC) has been investigated. The k'_{RP} and k'_{ip} values are linearly related with N_S in RPLC and RP-IPC. The linear relationship almost passes through the origin in the former case, but does not pass through origin in the latter case. There is a stronger effect of carbon content on the retention in RP-IPC than that in RPLC. It can be concluded that the retention mechanism of RP-IPC is different from that of RPLC. Effect of the carbon content on the stationary surface on retention in RP-IPC can be explained by the electrostatic model, which also confirms the validity of the electrostatioc model for RP-IPC.

INTRODUCTION

The distribution of solute molecules between the mobile and the stationary phase of a reversed-phase chromatographic system is determined by the molecular structure of the solute, the physico-chemical properties of the stationary phase. There are serveral approaches and descriptors concerning the first two variables[1-7]. The most comprehenssive approach does not treat processes at the stationary phase in detail[1]. The effect of the C_{18} silica surface coverage on the retention in RPLC has been already studied[8-10]. Hennion et al[8] demonstrated the hyperbolic relationship between the logarithm of the retention factor k'_{RP} and the carbon load of the C_{18} silica stationary phase. Solute retention increased up to about 15 percent of carbon content of the bonded phase, subsequently the retention was almost constant. Kaliszan et al[9] proposed a linear relationshop between $\log k'_{RP}$ and C_{18} surface coverage. Petrovic et al[10] and Lu et al [11] proposed a linear relationship between k'_{RP} and C_{18} surface coverage passes through the origin. On the other hand, reversed-phase ion-pair chromatography (RP-IPC) is widely used in separation of ionic organic compounds and inorganic ions. A great number of models of the so-called "mechanism" of ion-pair chromatography have been published and some of these are found in refs [12-19]. But it is likely that uncertainty in the mechanistic interpretion of the retention process is responsible for the fact that quite a number of "retention mechanism" still have been given in the literatures to RP-IPC. With our knowlegde, all of the models proposed have not treated the silica C_{18} coverage affecting the retention in RP-IPC. In this paper, the effect of silica bonded carbon content on the retention in RPLC and RP-IPC has been studied, it has been observed that the retention value in RP-IPC increases with the silica bonded carbon content more rapidly than that does in RPLC, which means that the retention mechanism of RP-IPC is different from that of RPLC.

EXPERIMENTAL

The results of RP-IPC experiment utilized in this work were taken from a paper by C.M. Riley et al[20] which gives an exact description fo analytical conditions. The capacity factors used in RP-IPC were measured in a chromatographic system with Spherisorb-S5 ODS 5 µm (Phase Separation, Queensferry, UK); Partisil 10 ODS and Partisil 10 ODS-2 both 10 µm (Whatman, Maidstone, UK) as well as Hypersil ODS, 5 µm (Shandon Southern Products, Runcorn, UK) as the stationary phases, of which the carbon contents are 5.9, 3.9, 15.0 and 9.9%, corresponding to about 0.271, 0.179, 0.690 and 0.455 mmol/g, respectively; the mobile phase used in RP-IPC is methanol/water (0.5/0.5) containing ion-pair reagent tetradecylbenzyldimethyl-ammonium chloride 0.5 mmol/l, K_2HPO_4 25 mmol/l and pH 7.5 respectively. The results of RPLC experiment used in this work were taken from Kaliszan et al [9], which gives an exact description of analytical conditions. The capacity factors in RPLC were measured in a chromtographic system, in which the stationary phases with different carbon content bonded on the Whatman Partisil 10 support material (Whatman, Clifton, NJ, USA) and mobile phase of methanol/water were used.

RESULTS AND DISCUSSION

The chromatographic retention factor k′ is related to the thermodynamic equilibrium constant K for the reversibile transfer of a solute between the mobile and the stationary phase by

$$k' = \Phi K \qquad (1)$$

where Φ is the phase ratio. One interpretation of the phase ratio can be defined by the expression[10]

$$\Phi = V_c W/V_m \qquad (2)$$

where V_c is the volume of the carbon content bonded phase per unit mass of column packing, W is the mass of column packing and V_m is the volume phase in the column. As V_c is proportional to

Table 1

Capacity factors of 10 solutes obtained in RPLC by varying C_{18} coverage (mmol/g). Mobile phase used is methanol/water with ratio of 0.55/0.45

Solute	k'_{RP}			
	0.154	0.318	0.496	0.66
Phenol	0.54	0.94	1.54	1.86
Acetophenone	1.24	2.19	3.66	4.34
Nitrobenzene	1.51	2.56	4.40	5.57
Methylbenzoate	2.24	4.19	7.66	10.50
4-Methylphenol	1.03	1.88	3.23	3.97
4-Ethylphenol	1.86	3.44	6.66	8.69
4-Propylphenol	4.73	7.31	15.11	20.94
4-sec-Butylphenol	5.86	12.28	26.71	38.80
4-Chloroacetophenone	2.92	5.47	10.03	13.60
3,4-Dichloroacetophenone	6.49	12.81	25.00	36.14

the number of moles of C_{18} bonded phase, N_s, per unit mass of column packing, eqn.(1) can be written in the form

$$k' = A + BN_s \qquad (3)$$

where A and B are the regression coefficients,the former approach zero, and the latter is related to the molecular structure and the mobile phase composition.

The retention data of aromatic compunds in RPLC and ionic benzoic acids in RP-IPC obtained on columns of varying carbon content are presented in Tables 1 and 2. Figures 1 and 2 show

Table 2

Capacity factors of 18 substituted benzoic acids in RP-IPC by varying C_{18} coverage (mmol/g). Mobile phase used is methanol /water (pH 7.5) with ratio of 0.50/0.50 containing ion-pair reagent of tetradecylbenzyldimethyl ammonium chloride 0.5 mmol/l and K_2HPO_4 25 mmol/l.

Substituted Group	k'_{ip}			
	0.179	0.271	0.455	0.690
2-OH	2.1	5.5	8.5	24.0
3-OH	0.65	1.3	1.9	3.1
4-OH	0.89	1.0	1.1	2.1
2-NH_2	1.2	2.8	3.1	8.3
3-NH_2	0.46	0.87	1.0	1.9
4-NH_2	0.35	0.54	0.74	1.3
2-NO_2	1.1	1.7	3.1	6.0
3-NO_2	2.2	4.1	6.3	15.8
4-NO_2	2.0	3.9	5.6	15.8
2-Cl	1.2	2.3	4.5	8.5
3-Cl	4.7	8.1	13.5	36.3
4-Cl	4.7	7.9	12.9	38.0
2-CH_3	1.5	2.7	4.9	11.0
3-CH_3	2.6	4.7	8.1	21.9
4-CH_3	2.6	4.6	7.6	20.4
CH_2~	1.5	2.8	4.0	10.0
CH=CH~~	2.9	5.1	8.5	21.4
H	1.3	2.8	3.8	10.2

~ Phenylacetic acid
~~ Cinnamic acid

k'_{RP} values of nitrobenzene and acetophenone at various methanol concentration as a function of mmoles of the C_{18} bonded phase. Table 3 gives the results of regression analysis according to eqn.(3) for the data shown in Table 1. As predicted by eqn.(1), a linear relationship between k'_{RP} and N_S can be obtained, the intercepts of eqn.(1) are generally small, indicating zero retention of a solute on silica with aqueous mobile phase in RPLC. The value of parameter B is positive, and increases with the

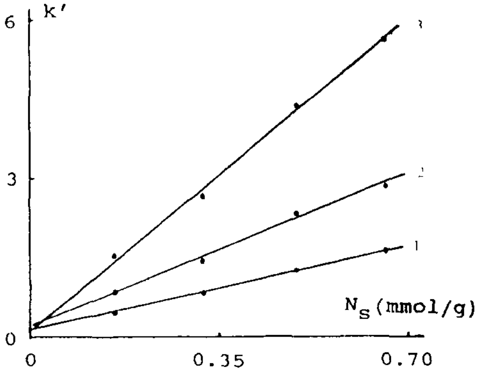

Fig.1 Plots of k'_{RP} in RPLC vs. N_S values according to Eqn.(3) for acetophenone at various methanol concentration.

1. 65% MeOH, $k'_{RP} = 0.146 + 2.13\ N_S$, r=0.9999
2. 55% MeOH, $k'_{RP} = 0.215 + 3.99\ N_S$, r=0.9940
3. 45% MeOH, $k'_{RP} = 0.141 + 8.28\ N_S$, r=0.9960

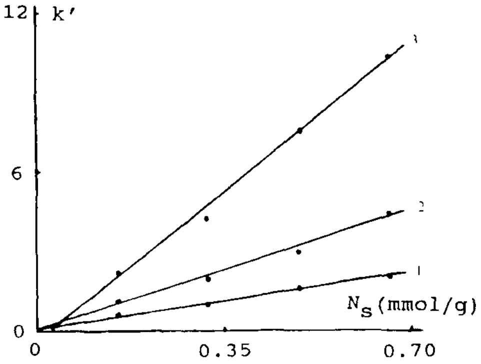

Fig.2 Plots of k'_{RP} in RPLC vs. N_S values according to Eqn.(3) for nitrobenzene at various methanol concentration.

1. 65% MeOH, $k'_{RP} = 0.039 + 3.21\ N_S$, r=0.9993
2. 55% MeOH, $k'_{RP} = 0.013 + 6.87\ N_S$, r=0.9955
3. 45% MeOH, $k'_{RP} = -0.639 + 16.67\ N_S$, r=0.9958

Table 3

Parameters A and B as well as the value of A/k'_{max} in RPLC, r is regression coefficient.

Solute	A	B	r	A/k'_{max}(%)
Phenol	0.124	2.69	0.995	6.7
Acetophenone	0.268	6.36	0.993	6.2
Nitrobenzene	0.141	8.28	0.996	2.5
Methylbenzoate	-0.639	16.67	0.996	6.1
4-Methylphenol	0.083	6.01	0.995	2.1
4-Ethylphenol	-0.537	14.00	0.994	-6.2
4-Propylphenol	-1.529	33.31	0.986	-7.3
4-sec-Butylphenol	-6.317	66.93	0.991	-16.3
4-Chloroacetophenone	-0.788	21.60	0.996	-6.0
3,4-Dichloroacetophenone	-4.182	59.69	0.993	-11.6

hydrophobicity of a solute and the decreasing of organic modifier concentration, which means that the carbon content bonded on the stationary phase and the hydrophobic interaction makes a positive contribution to the retention of a solute.

Table 4 gives the results of regression analysis of retention data shown in Table 2 according to eqns.(3), values of A/k'_{max} in Tables 3 and 4 are the ratio of parameter A in eqn.(3) to maximum value of capacity factor k'_{max} in Tables 1 and 2, which can be used to evaluate the deviation of parameter A from origin at the same scale. With comparison of the data shown in Table 3 and 4, following conclusions can be obtained: (1) Parameter B is positive, which means the retention in RP-IPC increases with

Table 4

Parameters A and B as well as the value of A/k'_{max}(%) in RP-IPC, r is regression coefficient.

Substituted Group	A	B	r	A/k'_{max}(%)
2-OH	-6.471	41.31	0.963	-27.0
3-OH	-0.097	4.583	0.994	-2.9
4-OH	0.356	2.302	0.927	17.0
2-NH_2	-1.306	12.90	0.945	-15.7
3-NH_2	0.018	2.606	0.968	0.9
4-NH_2	0.015	1.803	0.988	1.2
2-NO_2	-0.853	9.578	0.990	-14.2
3-NO_2	-3.233	25.87	0.967	-20.5
4-NO_2	-3.587	26.06	0.954	-22.6
2-Cl	-1.557	14.23	0.996	-23.7
3-Cl	-8.591	60.68	0.962	-21.0
4-Cl	-9.640	63.90	0.962	-23.4
2-CH_3	-2.315	18.37	0.981	-21.0
3-CH_3	-5.491	37.10	0.964	-25.7
4-CH_3	-4.833	34.14	0.962	-23.4
$CH_2\sim$	-1.836	16.05	0.963	-18.4
$CH{=}CH_2\sim\sim$	-4.713	35.51	0.968	-22.0
H	-2.124	16.64	0.956	-20.8

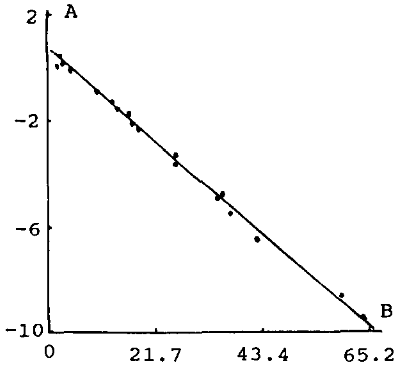

Fig.3 Plot of the parameters A vs. B in eqn.(3) in RP-IPC. $A = 0.579 - 0.157B$, $n=18$, $r=0.9971$, where n is number of data used for correlation.

increasing of carbon content on the stationary surface, and hydrophobic interaction plays an important role in RP-IPC. (2) The value of parameter B in RP-IPC is higher than that in RPLC for the solutes with close retention such as 2-methylbenzoic acid in RP-IPC and nitrobenzene in RPLC, which means that there is a stronger effect of the bonded carbon content on the retention in RP-IPC than that in RPLC. (3) In RPLC, the value of A/k'_{max} varies between 7% and -10.3% with exception of 4-sec-butylphenol -16.3%, which means the parameter A in eqn.(3) approches zero. In RP-IPC, however, the value of A/k'_{max} is lower than -15.0% in most cases and many of them close to -20%, which means the parameter A does not pass through the origin. A linear regression analysis between the parameter A and B in RP-IPC has been carried out and the obtained result is shown in Figure 3. It can be seen that there is a good linear relationship between the parameters A and B, which means the parameter A in RP-IPC has a physico-chemical meaning with parallel to that of the parameter B. (4) From the above results, it can be concluded that the retention mechanism in RP-IPC is different from that in RPLC. According to the electrostatic model of RP-IPC, the capacity factor of ionic solute can be expressed by[17]

$$\ln k'_{ip} = \ln k'_{RP} - ZF\psi_o/RT \qquad (4)$$

where k'_{RP} the capacity factor of a solute in the absence of an ion-pair reagent, F is the Faraday constant, R is the gas constant and T is the absolute temperature, ψ_o is a surface potential between the surface of the stationary phase and the bulk of the mobile phase. We think that the effect of carbon content on the stationary phase in RP-IPC through at least two effects, vis the linearly increased phase ratio done as on RPLC for k'_{RP}, and the increased the electrostatic potential through increasing the adsorbed amount of ion-pair reageat on the stationary surface. As a result, the retention of ionic solutes in RP-IPC varies more rapidly with carbon content on the stationary surface than that of uncharged solutes.

ACKNOWLEDGMENT

The financial support from the Natural Science Foundation of China is gratefully acknowledged.

REFERENCES

1. Cs. Horvath, W. Melander and I. Molnar, J. Chromatogr., 125, 129(1976)
2. D.E. Martire and R.E. Boehm, J. Phys. Chem., 87, 1045(1983)
3. R. Tijssen, H.A.H. Billiet and P.J. Schoenmakers, J. Chromatogr., 122, 185(1976)

4. B.L. Karger, J.R. Gant, H. Hartkopf and P.H. Weiner, J. Chomatogr., 128, 65(1976)

5. L.R. Snyder, J. Chromatogr., 179, 167(1979)

6. P. Jandera, H. Colin and G. Guiochon, Anal. Chem., 54, 435(1982)

7. H.F. Zou, Y.K. Zhang and P.C. Lu, J. Chromatogr., 522, 49(1990)

8. M.C. Hennion, C. Picard and M. Caude, J. Chromatogr., 166, 21(1978)

9. R. Kaliszan, K. Osmialowski, S.A. Tomellini, S.H. Hsu, S.D. Fazio and R.A. Hartwick, J. Chromatogr., 352, 141(1986)

10. S.M. Petrovic and S.M. Lomic, Chromatographia, 27, 378(1989)

11. P.C. Lu, H.F. Zou and Y.K. Zhang, J. Chromatogr., 509, 171(1990)

12. W.R. Melander and Cs. Horvath, in "Ion-Pair Chromatography", (M.T.W. Hearn, ed.), Marcel Dekker, New York, 1986, p.27

13. A. Tilly-Melin, Y. Askemark, K.G. Wahlund and G. Schill, Anal. Chem., 51, 976(1979)

14. B.A. Bidlingmeyer, J. Chromatogr. Sci., 18, 525(1980)

15. J.H. Knox and R.A. Hartwick, J. Chromatogr., 204, 3(1981)

16. J. Stahlberg, Chromatographia, 24, 820(1987)

17. A. Bartha, Gy. Vigh and J. Stahlberg, J. Chromatogr., 506, 85(1990)

18. H.F. Zou, Y.K. Zhang, M.F. Hong and P.C. Lu, J. Chromatographia, 545, 59(1991)

19. H.F. Zou, Y.K. Zhang, M.F. Hong and P.C. Lu, Chromatographia, 32, 328(1991)

Received: January 24, 1993
Accepted: May 23, 1993