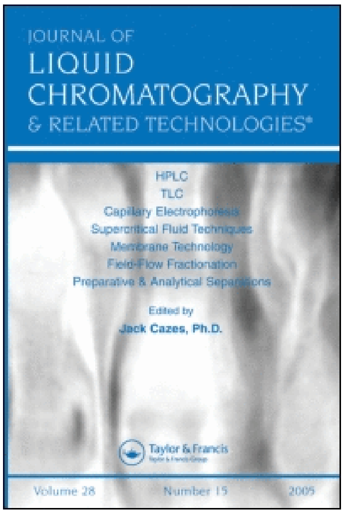

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CORRELATION OF SULPHONIC ACID RETENTION VALUES IN RP-IPC WITH RETENTION VALUES IN RP-HPLC AND ION CHROMATOGRAPHY

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ABSTRACT

The logarithm of capacity factor $\ln k'_{ip}$ in reversed-phase ion-pair liquid chromatography (RP-IPC) linearly deceases with methanol concentration (C_b), and the logarithm of capacity factor $\ln k'_{ic}$ in ion-chromatography (IC) linearly decreases with the logarithm of salt concentration ($\ln C_s$). The intercept ($\ln k^w_{ip}$, A) and slope (c_{ip}, B) values of a linear relationship between $\ln k_{ip}$ vs. C_b in RP-IPC and $\ln k'_{ic}$ vs. $\ln C_s$ in IC were obtained. The logarithm of capacity factor in RP-HPLC and the logarithm of capacity factor in IC, the solute charges and the parameter B in IC have been selected as the descriptors of solute molecular and electrostatic interaction respectively. It has been observed that the logarithm of capacity factors, the parameters $\ln k_{ip}$ and c_{ip} in RP-IPC can be well correlated with the logarithm of capacity factors in RP-HPLC and the logarithm of capacity factors in IC, the solute charges and the parameter B. Both the $\ln k'_{RP}$ in RP-HPLC and the $\ln k_{ic}$ in IC, the solute charges and the parameter B made a positive contribution to the retention and the parameter $\ln k_{ip}$ in RP-PC, but made a negative contribution to the parameter c_{ip} in RP-IPC. It can be concluded that both the molecular and the electrostatic interaction play major role in retention of the ionic solutes in RP-IPC.

INTRODUCTION

Reversed-phase ion-pair liquid chromatography (RP-IPC) is widely used in separations of ionized organic compounds and inorganic ions. The retention can be regulated by the properties and the concentration of the organic modifier and counterion as well as, by a competing ion with the same charge as the analyte. A great number of models of the so called "mechanism" of RP-IPC have been published[1-7], and the excellent reviews for these mechanisms have been appeared[1,8]. A majority of the proposed models, including the ion-pair model[1] and the dynamic ion-exchange model[1,5,6] are stoichiometeric, i.e. they construct a reaction scheme and the correspinding equilibrium constants express the interaction between the oppositely charged ion-pair reagent and analyte ions in the system. By combining these constants with the Langumir-isotherm equations are obtained for the capacity factors as a function of different variables. On the other hand, the non-stoichiometeric models including ion-interaction mechanism [1,3] and electrostatic model in which the Gouy-Chapman theory were applied to the ion-pair liquid chromatography[9-13]. The effects of organic modifier concentration [13], ion-pair reagent[14] and inorganic salt concentration [15], column temperature[16] and solute properties such as solute hydrophobicity and charges on the retention have been investigated. It has been observed that both hydrophobic and electrosatic interaction play important role in the retention of solutes in RP-IPC, and at the most cases the retention order of ionic solutes with the same charges is the same as one in RP-HPLC. But 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. It is believed that gathering of experimental data will accelerate in this field. In this paper, the correlation of sulphonic acid retention values in RP-IPC with their retention values in the ion-chromatography (IC) and the reversed-phase high performance liquid chromatography (RP-HPLC) was studied.

EXPERIMENTAL

1. Materials

The phenylamine and naphthylamine sulphonic acids analysed were obtained from the Dyestuff Lab., Chemical Enginerring Dept., Dalian University of Sciences an Technology. Standard solutions were prepared in water. Doubled-distilled water was used throughout. The methanol, tetrabutylammonium iodide (TBAI), NaH_2PO_4 and KH_2PO_4, NaOH, HCl and KCl used were analytical grade.

2. Apparatus

RP-IPC and IC experiments were done by using stainless-steel columns with demensions 200X4.0 mm I.D. and 250X4.6 mm I.D. contained the reversed-phase and ion-exchange packing materials of Spherisorb-ODS and Spherisorb-SAX with 5 µm particle diameter respectively (Phase Separation Ltd., Deeside, UK). Both columns were packed by the National Chromatographic R & A Center, Dalian, China. The mobile phase in RP-IPC was dilivered by two Waters-510 pumps, and the methanol concentration in the eluent was controlled and regulated by a NEC-APCIV computer with a Waters System Interface Module (Waters Assoc., Milford, MA, USA) by changing the ratio of eluent in pump A to eluent in pump B. The mobile phase in IC was delivered by a Waters-510 pump. The eluates were detected by a Waters-490 programmable multi-wavelength detector set at 254 nm in both RP-IPC and IC. Sample was loaded by a U6K syringe loading sample injector. The flowrate of eluent in RP-IPC and IC is 1.0 ml/min. The eluent pH value was measured by a SA-720 pH measurement meter (Orion Res. Inc., Chicago, IL, USA). All experimental data were processed on a NEC-APCIV personal computer.

RESULTS AND DISCUSSION

The retention times of sulphonic acids in RP-IPC with different methanol concentration and IC with different KCl concentration were measured. The capacity factors of tested solutes calculated from the retention times are given in Tables 1 and 2. It has been observed by many authors that the logarithm of capacity factor in RP-IPC decreases linearly with organic modifier concentration (C_b) and can be expressed[10,17-19]

$$\ln k'_{ip} = \ln k^{w}_{ip} + c_{ip}C_b \qquad (1)$$

where $\ln k^{w}_{ip}$ is the logarithm of extrapolated capacity factor with pure buffer or water as the eluent, c_{ip} is a constant at a given colum system and is mainly determined by the molcular and electrostatic interaction between the solute, the ion-pair reagent and the mobile phase. On the other hand, according to the

Table 1

The capacity factors of 13 phenylamine and naphthylamine sulphonic acids in RP-IPC with different methanol concentration. Other experimental conditions can be found in the text.

Solute	C_b (v/v)			
	0.325	0.281	0.239	0.198
1-Aminobenzene-4-sulphonic acid	0.152	0.301	0.489	1.01
1-Aminobenzene-3-sulphonic acid	0.255	0.53	0.84	1.34
1-Aminobenzene-2-sulphonic acid	0.461	1.00	1.64	3.04
1-Amino-4-methylbenzene-3-sulphonic acid	0.700	1.45	2.35	4.09
1-Amino-4-methoxybenzene-2-sulphonic acid	0.751	1.56	2.46	4.97
1-Amino-4-nitrobenzene-2-sulphonic acid	1.41	3.23	5.38	10.25
2-Aminonaphthalene-5-sulphonic acid	0.779	1.63	2.94	5.75
1-Aminobenzene-2,5-disulphonic acid	0.292	0.676	1.12	2.46
1,3-Diaminobenzene-4,6-disulphonic acid	0.303	0.636	1.25	2.45
2-Aminonaphthalene-4,8-disulphonic acid	0.629	1.63	3.34	9.66
2-Aminonaphthalene-3,6-disulphonic acid	0.760	2.06	4.40	12.04
2-Aminonaphthalene-4,6,8-trisulphonic acid	1.09	3.04	6.98	16.79
2-Aminonaphthalene-3,6,8-trisulphonic acid	1.14	3.25	7.40	17.66

Table 2
The capacity factors of 13 phenylamine and naphthylamine sulphonic acids in IC. The mobole phases contain different concentration of KCl in methanol/buffer (45/55) with KH_2PO_4 10 mmol/l and pH 6.80. Other experimental conditions can be found in the text.

Solute	KCl (mol/l)			
	0.05	0.10	0.20	0.40
1-Aminobenzene-4-sulphonic acid	0.86	0.65	0.31	0.21
1-Aminobenzene-3-sulphonic acid	0.77	0.59	0.30	0.20
1-Aminobenzene-2-sulphonic acid	0.76	0.55	0.29	0.21
1-Amino-4-methylbenzene-3-sulphonic acid	0.80	0.58	0.29	0.21
1-Amino-4-methoxybenzene-2-sulphonic acid	0.70	0.50	0.30	0.18
1-Amino-4-nitrobenzene-2-sulphonic acid	0.61	0.43	0.25	0.14
2-Aminonaphthalene-5-sulphonic acid	0.98	0.71	0.42	0.27
1-Aminobenzene-2,5-disulphonic acid	3.72	2.01	0.72	0.35
1,3-Diaminobenzene-4,6-disulphonic acid	3.25	1.90	0.61	0.27
2-Aminonaphthalene-4,8-disulphonic acid	5.37	2.72	0.90	0.47
2-Aminonaphthalene-3,6-disulphonic acid	4.62	2.50	0.90	0.47
2-Aminonaphthalene-4,6,8-trisulphonic acid	27.31	9.17	1.87	0.62
2-Aminonaphthalene-3,6,8-trisulphonic acid	17.82	6.31	1.41	0.49

ion-exchange equilibirum theory, the effect of salt concentration on the capacity factor in IC can be expressed[20-24]

$$\ln k'_{ic} = A - B \ln C_s \qquad (2)$$

where the parameter A is a constant at the given IC column system and related with the behavior of ion-exchanger and solute, the parameter B is determined by the ratio of the solute charges to the eluent ion charges and is proportional to the solute charges at the given column system. The results of linear regression analysis of the experimental data in Tables 1 and 2 according to eqns.(1) and (2) were given in Table 3. It can be seen that the linear regression coefficient according to eqns.(1) and (2) in most cases is larger than 0.99, which strongly support the validity of eqns.(1) and (2).

It was known that logarithm of capacity factor in RP-IPC was determined by the electrostatic and molecular interaction [15,25]

$$\ln k'_{ip} = \ln \Phi - (\Delta G^{\circ}_{m} + \Delta G^{\circ}_{e})/RT \qquad (3)$$

where Φ is the phase ratio, and ΔG°_{m} and ΔG°_{e} are the molecular and electrostatic free-energy change of retention, R and T are the gas constant and absolute temperature respectively. It is known that the logarithm of the capacity factors in RP-HPLC ($\ln k'_{RP}$) was determined mainly by the molecular free-energy change of retention, and the logarithm of capacity factor in IC ($\ln k'_{ic}$) was mainly determined by the electrostatic interaction which is related with the solute charges (n_e) or the parameter B in IC. Therefore, we could selecte $\ln k'_{RP}$ in RP-HPLC as the descriptor of molecular interaction of solutes and $\ln k'_{ic}$, solute charge n_e or

Table 3

The parameters $\ln k^{w}_{ip}$ and c_{ip} in eqn.(1) for RP-IPC and the parameters A and B in eqn.(2) for IC, r is regression coefficient.

Solute	RP-IPC			IC		
	$\ln k^{w}_{ip}$	c_{ip}	r	A	B	r
1-Aminobenzene-4-sulphonic acid	2.853	-14.57	0.9972	-2.23	0.717	0.986
1-Aminobenzene-3-sulphonic acid	2.887	-12.88	0.9946	-2.30	0.681	0.988
1-Aminobenzene-2-sulphonic acid	3.982	-14.50	0.9967	-2.24	0.671	0.992
1-Amino-4-methylbenzene-3-sulphonic acid	4.135	-13.67	0.9973	-2.22	0.689	0.988
1-Amino-4-methoxybenzene-2-sulphonic acid	4.441	-14.48	0.9967	-2.29	0.662	0.997
1-Amino-4-nitrobenzene-2-sulphonic acid	5.351	-15.25	0.9963	-2.57	0.715	0.994
2-Aminonaphthalene-5-sulphonic acid	5.493	-16.14	0.9984	-1.87	0.634	0.996
1-Aminobenzene-2,5-disulphonic acid	4.412	-16.74	0.9977	-2.13	1.17	0.996
1,3-Diaminobenzene-4,6-disulphonic acid	4.155	-16.46	0.9980	-2.42	1.24	0.992
2-Aminonaphthalene-4,8-disulphonic acid	6.366	-21.06	0.9971	-2.10	1.28	0.996
2-Aminonaphthalene-3,6-disulphonic acid	6.680	-21.38	0.9985	-1.83	1.14	0.995
2-Aminonaphthalene-4,6,8-trisulphonic acid	7.062	-21.37	0.9995	-2.24	1.87	0.997
2-Aminonaphthalene-3,6,8-trisulphonic acid	7.123	-21.39	0.9992	-2.38	1.77	0.997

parameter B in IC as the descriptor of electrostatic interaction of solutes in RP-IPC, and the retention values in RP-IPC eqn.(1) can be correlated with $\ln k'_{RP}$ and $\ln k'_{ic}$, n_e or parameter B by following equation:

$$\ln k'_{ip} = a_1 + b_1 \ln k'_{RP} + c_1 \ln k'_{ic} \qquad (4)$$

$$\ln k'_{ip} = a_2 + b_2 \ln k'_{RP} + c_2 n_e \qquad (5)$$

$$\ln k'_{ip} = a_3 + b_3 \ln k'_{RP} + c_3 B \qquad (6)$$

$$\ln k^{w}_{ip} = a_4 + b_4 \ln k'_{RP} + c_4 \ln k'_{ic} \qquad (7)$$

$$\ln k^{w}_{ip} = a_5 + b_5 \ln k'_{RP} + c_5 n_e \qquad (8)$$

$$\ln k^{w}_{ip} = a_6 + b_6 \ln k'_{RP} + c_6 B \qquad (9)$$

$$c_{ip} = a_7 + b_7 \ln k'_{RP} + c_7 \ln k'_{ic} \qquad (10)$$

$$c_{ip} = a_8 + b_8 \ln k'_{RP} + c_8 n_e \qquad (11)$$

$$c_{ip} = a_9 + b_9 \ln k'_{RP} + c_9 B \qquad (12)$$

where a_i, b_i and c_i (i=1-9) are the constants at the given RP-IPC column system. Table 4 listed the experimentally measured capacity factors of sulphonic acids studied in RP-HPLC with 10 mmol/l phosphate buffer (pH=6.80) as the eluent[26]. The regression results of $\ln k'_{ip}$ in RP-IPC with different methanol concentration versus $\ln k'_{RP}$ in RP-HPLC and $\ln k'_{ic}$ in IC with methanol/phosphate buffer containing KH_2PO_4 10 mmol/l, KCl 0.05 mol/l and pH 6.80 as the eluent, the solute charge n_e and the parameter B were shown as follows:

$C_b = 0.325$

$\ln k'_{ip} = -1.017 + 0.429 \ln k'_{RP} + 0.489 \ln k'_{ic}$, n=13, r=0.8616

$\ln k'_{ip} = -2.900 + 0.550 \ln k'_{RP} + 1.592\, n_e$, n=13, r=0.9087

$\ln k'_{ip} = -3.444 + 0.602 \ln k_{RP} + 3.083\, B$, n=13, r=0.9532

$C_b = 0.281$

$$\ln k'_{ip} = -0.276 + 0.530 \ln k'_{RP} + 0.982 \ln k'_{ic}, \quad n=13, \ r=0.8821$$

$$\ln k'_{ip} = -2.426 + 0.591 \ln k'_{RP} + 1.823 n_e, \quad n=13, \ r=0.9244$$

$$\ln k'_{ip} = -3.057 + 0.649 \ln k'_{RP} + 3.541 B, \quad n=13, \ r=0.9634$$

$C_b = 0.239$

$$\ln k'_{ip} = 0.221 + 0.564 \ln k'_{RP} + 1.137 \ln k'_{ic}, \quad n=13, \ r=0.9092$$

$$\ln k'_{ip} = -2.240 + 0.627 \ln k'_{RP} + 2.090 n_e, \quad n=13, \ r=0.9432$$

$$\ln k'_{ip} = -2.907 + 0.687 \ln k'_{RP} + 3.998 B, \quad n=13, \ r=0.9761$$

$C_b = 0.198$

$$\ln k'_{ip} = 0.802 + 0.622 \ln k'_{RP} + 1.336 \ln k'_{ic}, \quad n=13, \ r=0.9150$$

$$\ln k'_{ip} = -2.143 + 0.712 \ln k'_{RP} + 2.491 n_e, \quad n=13, \ r=0.9603$$

$$\ln k'_{ip} = -2.561 + 0.720 \ln k'_{RP} + 4.404 B, \quad n=13, \ r=0.9754$$

Parameter $\ln k^{w}_{ip}$

$$\ln k^{w}_{ip} = 3.803 + 0.822 \ln k'_{RP} + 2.015 \ln k'_{ic}, \quad n=13, \ r=0.9711$$

$$\ln k^{w}_{ip} = -0.291 + 0.873 \ln k'_{RP} + 3.591 n_e, \quad n=13, \ r=0.9603$$

$$\ln k^{w}_{ip} = -1.196 + 0.932 \ln k'_{RP} + 6.497 B, \quad n=13, \ r=0.9597$$

Parameter c_{ip}

$$c_{ip} = -14.62 - 0.887 \ln k'_{RP} - 3.435 \ln k'_{ic}, \quad n=13, \ r=0.9446$$

$$c_{ip} = -8.110 - 0.873 \ln k'_{RP} - 5.678 n_e, \quad n=13, \ r=0.9092$$

$$c_{ip} = -6.431 - 0.977 \ln k'_{RP} - 10.69 B, \quad n=13, \ r=0.8995$$

It can be seen that the regression coefficient in all cases was from 0.85 to 0.98, which implied that eqns.(4)-(12) could well describe the effect of solute molecular and electeostatic interaction on retention in RP-IPC, and the electrostatic interaction in RP-IPC is diredtly related with the retention in IC, the solute charges or the parameter B in IC. The values of

Table 4

The capacity factors of 13 sulphonic acids in RP-HPLC with 10 mmol/l phosphate buffer (pH=6.80) as eluent and their negative charge n_e.

Compound	n_e	k'_{RP}
1-Aminobenzene-2-sulphonic acid	1	2.31
1-Aminobenzene-3-sulphonic acid	1	1.03
1-Aminobenzene-4-sulphonic acid	1	0.484
1-Amino-4-methylbenzene-3-sulphonic acid	1	8.29
1-Amino-4-methoxybenzene-2-sulphonic acid	1	6.62
1-Amino-4-nitrobenzene-2-sulphonic acid	1	9.51
2-Aminonaphthalene-5-sulphonic acid	1	10.73
1-Aminobenzene-2,4-disulphonic acid	2	0.078
1,3-Diaminobenzene-4,6-disulphonic acid	2	0.093
2-Aminonaphthalene-4,8-disulphonic acid	2	0.179
2-Aminonaphthalene-3,6-disulphonic acid	2	1.07
2-Aminonaphthalene-4,6,8-trisulphonic acid	3	0.027
2-Aminonaphthalene-3,6,8-trisulphonic acid	3	0.032

b_i, c_i (i=1-4) in eqns.(4)-(6) and b_j, c_j (j=4-6) in eqns.(7)-(9) were always positive, which mean that the solute charges and the parameter B in IC always make a positive contribution to the retention and the parameter $\ln k_{ip}$ in RP-IPC. However, the values of b_l and c_l (l=7-9) are always negative, which means that the solute hydrophobicity and the retention value in IC, the solute charges and the parameter B in IC made a negative contribution to the parameter c_{ip} in RP-IPC. The values of a_i, b_i and c_i (i=1-3) increase with decresing the methanol concentration and are much lower than the values of corresponding parameters a_j, b_j and c_j (j=4-6), which means that the retention in RP-IPC increases with drecresing methanol concentration, and the electrostatic and hydrophobic interaction gave rise to greater positive effects with decresing methanol concentration and made a more strongly positive contribution to retention in the absence of organic modifier than in presence of organic modifier. It can be concluded that the retention value of a solute in RP-IPC is determined by the electrostatic interaction and the hydrophobic interaction, the former is related with the retention value in IC, the solute charges and the parameter B in IC; the latter is related with the retention value in RP-HPLC. Otherwise, the retention value of a solute in IC is mainly determined by the electrostatic interaction, and the retention value in RP-HPLC is mainly determined by the hydrophobic interaction. Both natural and ionic componuds can be separated by RP-IPC.

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