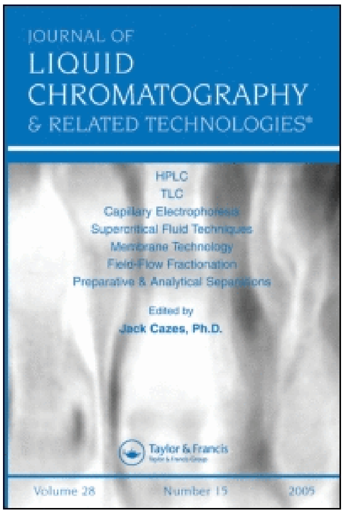

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RETENTION VALUES OF SULPHONIC ACIDS AS A FUNCTION OF THE NATURE AND CONCENTRATION OF INORGANIC SALT IN REVERSED-PHASE ION-PAIR LIQUID CHROMATOGRAPHY

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ABSTRACT

The capacity factors of phenylamine and naphthylamine sulphonic acids in reversed-phase ion-pair liquid chromatography (RP-IPC) with different concentration of inorganic anions were measured. The capacity factors of ionic solutes decreases in the order NaF > NaBr >= $NaNO_3$ > Na_2SO_4, which is the same as their order of anion retention values in anion ion chromatography. The good linear relationship between logarithm of capacity factors at different inorganic salt eluents were observed. The effect of salt concentration (C_s) on retention follows an equation based on the Gouy-Chapman model:

$$\ln k' = A - R(Z_A/Z_I) \ln C_s$$

The absolute value of slopes in RP-IPC is much smaller than the ratio of solute charge to eluent ion charge in ion chromtagraphy, and increases with the ionic solute charges as well as the retention value of the eluent ions in ion chromatography, but decreses with charge of eluent ions. The value of intercepts are also related with physico-chemical behaviors of the ionic solute and eluent ions. The combined effects of salt concentration and salt nature on retention values can be described by

$$\ln k' = a + b/n_e \ln C_s + c \ln t'_s + d\, n_e$$

The salt concentration C_s and adjusted retention value of salt in ion chromatography ($\ln t'_s$) makes the negative, but the negative

charges of sulphonic acids does a positive contribution to retention values in RP-IPC.

INTRODUCTION

Theoretical models which describe the manner in which solute retention varies with changing eluent composition in reversed-phase ion-pair liquid chromatography (RP-IPC) are of fundamental importance to the understanding of solute retention mechanisms. Moreover, valid models provide an essential basis for selection of the best eluent composition to effect a desired separation, whether this selection be performed on a trial-and-error basis, or with the aid of a computer optimization procedure. Since the inception of RP-IPC, a great number of models of RP-IPC have been published[1-7] and the excellent reviews of them have appeared[1, 8].A majority of the proposed models,including the ion-pair model [1] and dynamic ion-exchange model[1,5,6] are stoichiometeric, i.e., they construct a reaction scheme and the corresponding equilibrium constants express the interaction between the oppositely charged ion-pair reagent and the analyte ions in the system. By combining these constants with the Langumir isotherm equations are obtained for capacity factors as a function of different variables. On the other hand, the non-stoichiometeric models include the ion-interaction mechanism[1,3] and electrostatic model in which the Gouy-Chapman theory is applied to ion-pair liquid chromatography[9-13]. However, the study of effect of inorganic salts on retention has been much more limited than that of organic modifiers[13-15] and ion-pair reagents[16]. In this paper, the retention behavior of aromatic sulphonic acids at different inorganic salt eluents in RP-IPC has been studied. A quantitative correlation of solute retention vs. the salt concentration and nature has been observed.

Table 1 Name of Sulphonic Acids and Their Code as Well as Negative Charge (n_e).

Code	Solute Name	n_e
1	1-Aminobenzene-3-sulphonic acid	1
2	1-Amino-4-methoxybenzene-2-sulphonic acid	1
3	1-Amino-4-chlorobenzene-3-sulphonic acid	1
4	1-Amino-4-methylbenzene-3-sulphonic acid	1
5	1-Aminonaphthalene-5-sulphonic acid	1
6	2-Aminonaphthalene-5-sulphonic acid	1
7	1-Aminobenzene-2,4-disulphonic acid	2
8	1,3-Diaminobenzene-4,6-disulphonic acid	2
9	2-Aminonaphthalene-4,8-disulphonic acid	2
10	2-Aminonapthatlene-3,6-disulphonic acid	2
11	2-Aminonaphthalene-4,7-disulphonic acid	2
12	2-Aminonaphthalene-4,6,8-trisulphonic acid	3

EXPERIMENTAL

Materials

The phenylamine and naphthylamine sulphonic acids analysed (listed in Table 1) were from the Dyestuff Lab., Chemical Enginerring Department, Dalian University of Sciences and Technology. Standard solutions were prepared in water. Double-distilled water was used throughout. The methanol, tetrabutylammonium iodide (TBAI), NaH_2PO_4, NaOH, HCl and the eluent inorganics salts NaF, NaBr, $NaNO_3$ and Na_2SO_4 used were analytical grades.

Apparatus

RP-IPC experiments were on a stainless-steel column (150X4.6 mm I.D.) packed with Nucleosil-C_{18}, 7 µm, (Macherey-Nagel, Duren, Germany). The column was packed by the National Chromatographic R & A Center, Dalian, China. The mobile phases were different concentration of inorganic salts in the eluents, keeping constant the ratio of methanol to water at 25/75, the concentration of ion-pair reagent TBAI at 6 mmol/l, the NaH_2PO_4 at 10 mmol/l, pH 7.02 respectively. The eluent delivery was by a Waters-510 pump (Waters Assoc., Milford, MA, USA). Eluates were detected by a BT-3000 UV detector set at 254 nm (Biotronik, Tubingen, Germany). Sample was loaded by a U6K syringe loading sample injector. Eluent pH was measured on a SA-720 pH meter (Orion Res. Inc., Chicago, IL, USA). The flowrate was 1.0 ml/min. All experimental data were processed by a computer.

RESULTS AND DISCUSSION

The retention times of sulphonic acids with different inorganic salt concentration were measured. The capacity factors of test solutes calculated from retention times are in Tables 2 and 3 respectively.It can been observed that the capacity factors in RP-IPC decrease in the order NaF > NaBr >= $NaNO_3$ > Na_2SO_4, which is the same as their order of anion retention values in ion chromatography with XAD-1 as the stationary phase[19], Table 4 gives the adjusted retention time of these four anions in IC. The linear regression analysis of logarithm of the capacity factors at different kinds of inorganic salts with concentration 15 mmol/l has been carried out, and the obtained results are given in Figures 1, 2 and 3 respectively. It can be seen that there is a good linear relationship of the logarithm of capacity factors

Table 2 Capacity Factors of Phenyl and Naphthylamine Sulphonic Acids at Different NaF and NaBr Concentration in RP-IPC. Other Experimental Conditions See Text.

Code	NaF				NaBr			
	0.015	0.025	0.05	0.10	0.015	0.025	0.05	0.01
1	1.12	0.560	0.347	0.380	0.947	0.613	0.433	0.240
2	2.25	1.71	1.39	1.03	1.86	1.31	1.04	0.700
3	3.91	2.98	2.46	1.81	3.14	2.30	1.87	1.28
4	2.17	1.70	1.45	1.01	1.83	1.35	0.993	0.667
5	3.09	2.46	2.07	1.61	2.64	2.02	1.56	1.11
6	7.18	6.21	5.05	4.09	6.17	4.52	3.92	2.82
7	2.09	1.36	0.900	0.467	1.71	0.928	0.560	0.313
8	1.71	1.01	0.647	0.293	1.40	0.751	0.347	0.113
9	4.68	3.48	2.27	1.51	3.95	2.41	1.48	0.727
10	6.55	4.75	3.41	2.26	5.43	3.63	2.18	1.12
11	5.31	3.71	2.64	1.68	4.35	2.48	1.67	0.847
12	11.30	6.57	4.10	1.93	9.05	4.57	2.09	0.747

at different kinds of inorganic salts under the same concentration as the eluent salts, and the values of slope are very close an unity. Therefore, the relative capacity factors are independent on the kinds of eluent inorganic salts in our RP-IPC experimental conditions.

In order to express the effect of eluent inorganic salt concentration on the retention in RP-IPC, the following equation has been derived based on the Gouy-Chapman theory[15]

$$\ln k' = A - R(Z_A/Z_I) \ln C_S \qquad (1)$$

Table 3 Capacity Factors of Phenylamine and Naphthylamine Sulphonic Acids at Different $NaNO_3$ and Na_2SO_4 Concentration in RP-IPC. Other Experimental Conditions See Text.

Code	$NaNO_3$				Na_2SO_4			
	0.015	0.025	0.05	0.50	0.015	0.025	0.05	0.01
1	0.993	0.573	0.420	0.220	0.807	0.633	0.413	0.327
2	1.87	1.30	0.940	0.520	1.67	1.41	1.08	0.907
3	3.16	2.35	1.70	1.13	2.85	2.57	2.19	1.63
4	1.93	1.27	0.953	0.567	1.63	1.39	1.03	0.793
5	2.75	1.95	1.51	1.03	2.39	2.06	1.68	1.33
6	6.48	4.85	3.85	2.90	5.85	5.30	4.17	3.38
7	1.67	0.980	0.433	0.520	1.27	0.873	0.487	0.227
8	1.38	0.787	0.307	0.093	1.03	0.633	0.353	0.140
9	3.67	2.43	1.33	0.620	3.07	2.29	1.57	1.17
10	5.55	3.61	1.96	0.940	4.41	3.43	2.31	1.66
11	4.31	2.63	1.50	0.680	3.24	2.34	1.88	1.17
12	9.02	4.70	1.90	0.487	6.20	3.75	1.97	1.07

Table 4 Adjusted Retention Time of Anions in IC with XAD-1 (0.007 mequiv./g) as the Stationary Phase and 0.1 mmol/l Phthalate Solution (pH 6.25) as the Eluent. Other Experimental Conditions See Ref.19.

Anion	Adjusted Retention Time (min)
F^-	1.40
Br^-	1.88
NO_3^-	1.90
SO_4^{2-}	7.64

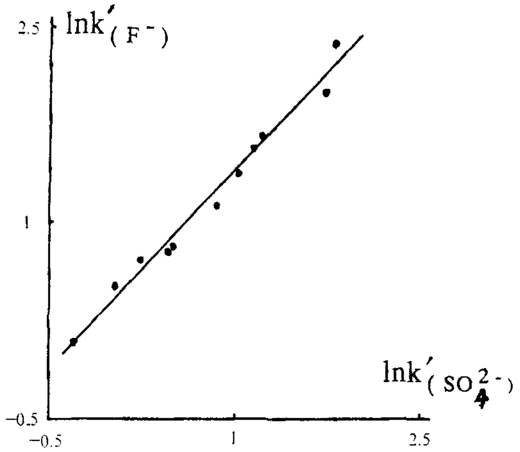

Figure 1 Linear relationship of $\ln k'_{(F^-)}$ with 15 mmol/l NaF as the eluent ion versus $\ln k'_{(Br^-)}$ with 15 mmol/l NaBr as the eluent ion.

$\ln k'_{(F^-)} = 0.180 + 1.006 \ln k'_{(Br^-)}$, $r = 0.9994$, $n = 12$

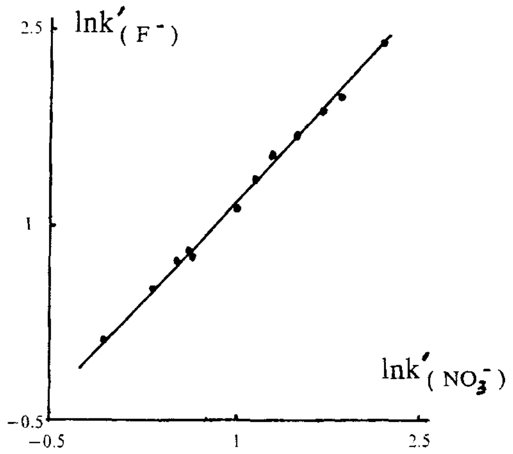

Figure 2 Linear relationship of $\ln k'_{(F^-)}$ with 15 mmol/l NaF as the eluent ion versus $\ln k'_{(NO_3^-)}$ with 15 mmol/l NaNO as the eluent ion.

$\ln k'_{(F^-)} = 0.167 + 1.010 \ln k'_{(NO_3^-)}$, $r = 0.9972$, $n = 12$

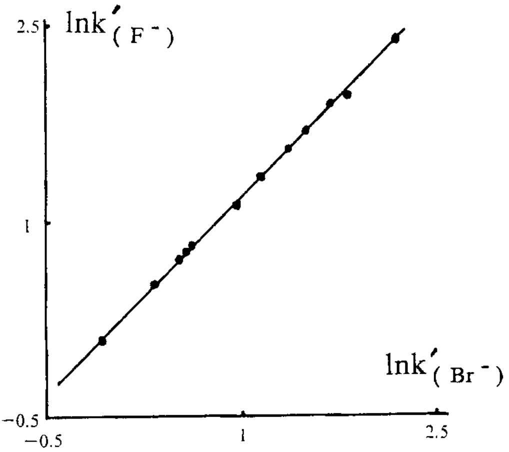

Figure 3 Linear relationship of ln k′$_{(F^-)}$ with 15 mmol/l NaF as the eluent ion versus ln k′$_{(SO_4^{2-})}$ with 15 mmol/l Na_2SO_4 as the eluent ion.

$\ln k'_{(F^-)} = 0.377 + 1.008 \ln k'_{(SO_4^{2-})}$, r = 0.9840, n = 12

where the parameter A is mainly determined by the electrostatic and hydrophobic interactions, Z_A and Z_I are the ionic charges of the analyte and eluent salt respectively, R is a constant related with the physico-chemical behavior of the analyte and eluent ions and smaller than 1.0. Therefore, the value of slope in eqn.(1) in RP-IPC should be much smaller than that in ion chromatography. The results of linear regression analysis of the experimental data in Tables 2 and 3 according to eqn.(1) were given in Tables 5 and 6. It can be seen that the linear regression coefficient from eqn.(1) in most cases is greater than 0.99, which strongly supports the validity of eqn.(1).

Table 5 Intercept A and Slopes of Plots of lnk′ vs. Logarithm of F^- and Br^- Concentration for the Experimental Data Shown in Table 2.

Code	F^-			Br^-		
	A	slope	r	A	slope	r
1	-2.483	-0.564	0.8745	-3.003	-0.698	0.9947
2	-0.879	-0.396	0.9950	-1.481	-0.493	0.9925
3	-0.298	-0.390	0.9938	-0.778	-0.452	0.9923
4	-0.680	-0.341	0.9923	-1.596	-0.522	0.9985
5	-0.282	-0.331	0.9950	-0.917	-0.447	0.9982
6	0.728	-0.297	0.9999	0.156	-0.387	0.9844
7	-2.491	-0.769	0.9960	-3.192	-0.871	0.9952
8	-3.241	-0.898	0.9940	-5.107	-1.307	0.9962
9	-0.968	-0.599	0.9999	-2.282	-0.870	0.9967
10	-0.446	-0.551	0.9988	-1.746	-0.823	0.9981
11	-0.836	-0.593	0.9980	-2.046	-0.827	0.9935
12	-1.383	-0.903	0.9959	-3.229	-1.295	0.9985

Analysing the data shown in Tables 5 and 6, following conclusions can be made: (1) The absolute value of slopes differ markedly between analyte ions, and increases with charge number of a solute, this implies that the charges of solute make an important contribution to the value of slope and the retention in RP-IPC. (2) The absolute value of slopes for the solutes with the same charge, e.g. for the monovalent and divalent solutes, decreases with increasing of the retention value in RP-IPC, which means that the effect of electrostatic interaction on retention

Table 6 Intercept A and Slopes of Plots of lnk′ vs. Logarithm of NO_3^- and SO_4^{2-} Concentration for the Experimental Data Shown in Table 3.

Code	NO_3^-			SO_4^{2-}		
	A	slope	r	A	slope	r
1	-3.218	-0.753	0.9891	-2.285	-0.490	0.9934
2	-2.108	-0.653	0.9932	-0.872	-0.328	0.9964
3	-1.095	-0.534	0.9989	-0.778	-0.452	0.9923
4	-1.968	-0.618	0.9928	-1.121	-0.387	0.9986
5	-1.115	-0.499	0.9948	-0.415	-0.308	0.9993
6	0.109	-0.411	0.9951	0.540	-0.297	0.9959
7	-4.194	-1.124	0.9994	-3.508	-0.905	0.9960
8	-5.506	-1.397	0.9964	-2.111	-0.934	0.9999
9	-2.578	-0.933	0.9974	-1.044	-0.511	0.9978
10	-2.172	-0.933	0.9985	-0.703	-0.521	0.9994
11	-2.543	-0.957	0.9975	-0.974	-0.509	0.9901
12	-4.097	-1.521	0.9939	-3.980	-0.957	0.9815

decreases with increasing of the solute hydrophobicity. (3) The absolute value of slopes increases in the order NaBr >= $NaNO_3$ > NaF for the monovalent eluent ions, which is the same as their order of retention in ion chromatography. But the absolute value of slopes with the divalent anion SO_4^{2-} as the eluent ion is much lower than that with anions Br^- and NO_3^- as the eluent ions, however, the retention of SO_4^{2-} in ion chromatography is much larger than that of Br^- and NO_3^-. This behavior can be

Table 7 Value of Parameters a, b, c And d in Eqn.(2); r Is Regression Coefficient,n Is the Data Number Used For Correlation.

Code	a	b	c	d	r	n
1	-4.505	-0.781	0.164	1.108	0.981	15
2	-3.455	-0.525	-1.101	2.529	0.971	16
3	-2.506	-0.468	-0.990	2.282	0.985	16
4	-3.390	-0.528	-1.077	2.432	0.973	16
5	-2.361	-0.440	-0.880	2.011	0.981	16
6	-1.170	-0.383	-0.860	1.902	0.977	16
7	-5.578	-0.906	-1.256	3.056	0.955	16
8	-8.507	-1.275	-1.837	4.641	0.968	16
9	-4.774	-0.818	-1.542	3.600	0.981	16
10	-4.163	-0.791	-1.451	3.413	0.979	16
11	-4.601	-0.810	-1.562	3.572	0.979	16
12	-6.921	-1.287	-2.034	4.954	0.972	16

attributed to the difference in the charge of eluent anions. (4) The value of parameter A differ markedly between analyte ions, and decreases in the order NaF > NaBr > $NaNO_3$ for the monovalent eluent salts, which qualitatively agree with the order of anion retention values in ion chromatography.But with divalent anion SO_4^{2-} as the eluent ion, such a phenomenon can not be observed, which also showes the important role of the charge of eluent ion. The linear regression analysis of the parameter A at different eluent inorganic salts has been carried out, and the obtained results are follows

$A_{(F^-)} = 0.494 + 0.761\ A_{(Br^-)}$, $r=0.9427$, $n=12$

$A_{(F^-)} = 0.618 + 0.678\ A_{(NO_3^-)}$, $r=0.9308$, $n=12$

$A_{(F^-)} = -0.171 + 0.649\ A_{(SO_4^{2-})}$, $r=0.7520$, $n=12$

It can be seen that there is a linear relationship between the parameter A and the monovalent eluent ions, but no such a linear relationship between the monovalent and divalent eluent ions.

The retention values of ionic solute as a function of the concentration of eluent anions and nature can be expressed by

$$\ln k' = a + b/n_e \ln C_s + c \ln t'_s + d\ n_e \qquad (2)$$

where a, b, c and d are the constants for a given solute, t'_s the adjusted retention time of eluent anions and n_e the negative charge of solutes, respectively. The results of quantitative correlation of experimental data shown in Tables 1, 2, 3 and 4 according to eqn.(2) are given in Table 7. It can be seen that the regression coefficients is higher than 0.97 at the most cases, which supports the validity of eqn.(2). The value of parameter b and c are negative, but the parameter d is positive, which means that the contribution of eluent anion and the adjusted retention time make a negative, but the negative charges of sulphonic acids does a positive contribution to retention value in RP-IPC

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REFERENCES

1. B.A.Bidlingmeyer, J. Chromatogr. Sci., 18, 525(1980)
2. A.Tilly-Melin, Y-Askemark, K.G.Wahlund, G.Schill, Anal. Chem., 51, 976(1979)

3. B.A.Bidlingmeyer, S.N.Deming, W.P.Price Jr., B.Sachok, M.Petrusek, J. Chromatogr., 186, 419(1979)
4. C.T.Huang, R.B.Taylor, J. Chromatogr., 202, 333(1980)
5. P.T.Kissinger, Anal. Chem., 49, 883(1977)
6. J.H.Knox, R.A.Hartwick, J. Chromatogr., 204, 3(1981)
7. S.Afrashtehfer, F.F.Cantwell, Anal. Chem., 54, 2422(1982)
8. Cs.Horvath and W.R.Melander, "Ion-Pair Chromatography-Theory and Biological and Pharmaceutical Application" (edited by M.T.W.Hearn), p.27, Marcel Dekker, New York, 1985
9. J.Stahlberg, J. Chromatogr., 356, 231(1986)
10. A.Bartha, Gy.Vigh, J.Stahlberg, J. Chromatogr., 506, 85(1990)
11. H.Liu, F.F.Cantwell, Anal. Chem., 63, 2032(1990)
12. P.C.Lu, H.F.Zou, Y.K.Zhang, Mikrochimica Acta, III, 35(1990)
13. H.F.Zou, Y.K.Zhang, P.C.Lu, J. Chromatogr., 545, 59(1990)
14. Hong Mingfang, Zou Hanfa, Zhang Yukui, Lu Peichang, Acta Chimica Sinica (in Chinese), 51, 178(1993)
15. Y.K.Zhang, H.F.Zou, M.F.Hong, P.C.Lu, Chromatographia, 32, 538(1991)
16. H.F.Zou, Y.K.Zhang, M.F.Hong, P.C.Lu, Chromatographia, 35, 390(1993)
17. H.F.Zou, Y.K.Zhang, M.F.Hong, P.C.Lu, Chromatographia, 32, 329(1991)
18. H.F.Zou, Y.K.Zhang, M.F.Hong, P.C.Lu, J. Chromatogr., 625, 169(1992)
19. J.S.Fritz, D.T.Gjerde and C.Pohlandt, "Ion Chromatography", A.H.Verlag, Heidelberg, Germany, 1982, p.106.

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