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MODIFIED HYDROXYETHYL METHACRYLATE COPOLYMERS AS SORBENTS FOR ION CHROMATOGRAPHY

II. INFLUENCE OF THE FUNCTIONAL GROUP ON SORBENT SELECTIVITY

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SUMMARY

The selectivity in ion chromatography of sorbents with different functional groups was compared for separation of common inorganic anions using selectivity coefficients. Simplified equations were derived to calculate the selectivity coefficient from the dependence of (a) the capacity factor on the eluent anion concentration, and (b) the separation factor on the capacity factor of one of the ions being separated. Sorbents with the same hydroxyethyl methacrylate matrix and ion-exchange capacity but with different functional groups varying in polarity and basicity were compared. The selectivity coefficients for separation of ions with the same charge generally increased, while those for ions with different charges decreased, with increasing polarity of the functional group. No dependence was found between the sorbent selectivity and its basicity. The application of these results to the preparation of sorbents with desired selectivity is proposed.

INTRODUCTION

Ion chromatography has become a widely used method for the determination of ions, mainly anions, in complex mixtures. High selectivity for the determination of at least several ions in a mixture is expected. So-called "standard conditions"[1] enable many different problems to be solved. However, for some mixtures the resolution achieved is not satisfactory, and accurate determination of the components is not possible. Even if the resolution is sufficient, the separation can be optimized in order to shorten the analysis time.

The selectivity of ion chromatography can be improved in different ways: by improving the chromatographic separation; by using selective detection for the particular component; by separating selectively this (or an interfering) component from

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the mixture before ion chromatography. These possibilities have recently been discussed for inorganic ions[2,3].

The resolution, widely used as a measure of separation quality in chromatography, depends on the separation factor, capacity factor and column performance and can be improved by well known methods[4–6]. Simplified equations, showing how to influence the separation factor and capacity factor in anion chromatography, have been derived[2]. An important factor influencing the separation is the sorbent selectivity.

Clifford and Weber[7] compared the selectivity of 30 commercially available anion exchangers (classic resins with high ion-exchange capacities) for separation of sulphate, nitrate and chloride. The most important factors were found to be the sorbent matrix (type of polymer) and functional group structure. The different basicities of the functional groups are usually supposed to be the cause of different selectivities[8]. No correlation of these two properties, however, was found in the above study[7].

Barron and Fritz[9,10] studied the selectivity of sorbents with different quaternary amine functional groups and found increasing selectivity, *i.e.*, separation factor, for the separation of singly charged anions with increasing hydrophobicity of the functional group.

To compare the influence of functional group polarity or basicity on sorbent selectivity, a series of sorbents with the same hydroxyethyl methacrylate matrix and ion-exchange capacity but with functional groups differing in polarity and basicity was synthesized[11]. The following functional groups have been studied: amino (A), ethylamino (EA), diethylamino (DEA), triethylamino (TEA), dicyclohexylamino (DCHA) and diethanolamino (DEtA). Their polarities and basicities were compared, and their selectivities (selectivity coefficients) were measured and related to the trends in functional group polarity and basicity.

THEORETICAL

The separation of two anions A^{x-} and B^{y-} on a sorbent containing a functional group R^+ and by use of an eluent E^{z-} can be described by the ion-exchange equations:

$$x\overline{(-R^+{}_zE^{z-})} + zA^{x-} \rightleftharpoons z\overline{(-R^+{}_xA^{x-})} + xE^{z-} \qquad (1)$$

$$y\overline{(-R^+{}_zE^{z-})} + zB^{y-} \rightleftharpoons z\overline{(-R^+{}_yB^{y-})} + yE^{z-} \qquad (2)$$

The bars refer to species bound in the sorbent. The reaction can also be described by a simplified equation:

$$x\overline{(-R^+{}_yB^{y-})} + yA^{x-} \rightleftharpoons y\overline{(-R^+{}_xA^{x-})} + xB^{y-} \qquad (3)$$

Only processes described by these equations will be considered and retention caused by other mechanisms, *e.g.*, by adsorption as well as side reactions will be neglected.

With respect to the problems connected with the use of thermodynamic equilibrium constants, selectivity coefficients, K_{nB}^{mA}, will be used for simplicity

$$K_{xE}^{zA} = \eta_A^z[E]^x/[A]^z\eta_E^x \tag{4}$$

$$K_{yE}^{zB} = \eta_B^z[E]^y/[B]^z\eta_E^y \tag{5}$$

or

$$K_{xB}^{yA} = \eta_A^y[B]^x/[A]^y\eta_B^x \tag{6}$$

where η_i is the content (mmol g^{-1}) of component i in the sorbent and $[i]$ is its equilibrium concentration (M) in the mobile phase.

The capacity factors of anions A^{x-} and B^{y-} are

$$k_A = \eta_A m_s/[A]V_m \tag{7}$$

$$k_B = \eta_B m_s/[B]V_m \tag{8}$$

where m_s is the mass of sorbent in the column and V_m is the volume of mobile phase. Using eqn. 4, k_A can be expressed as:

$$k_A = K_{xE}^{zA\,(1/z)}(\eta_E/[E])^{(x/z)}(m_s/V_m) \tag{9}$$

Usually $[A] \ll [E]$ and $\eta_A \ll \eta_E$. Under these conditions and by expressing the specific sorbent ion-exchange capacity, Q_g, by means of the functional group content, η_E can be substituted by Q_g/z. Similarly, by neglecting side reactions, [E] can be substituted by the analytical concentration, c_E. The capacity factor can then be expressed in terms of easily accessible quantities:

$$k_A = K_{xE}^{zA\,(1/z)}(Q_g/z \cdot c_E)^{(x/z)}(m_s/V_m) \tag{10}$$

A similar expression can be derived for k_B.

According to eqn. 10, the capacity factor in ion chromatography can be influenced by the choice of eluent anion, *i.e.*, by the value of the selectivity coefficient, K_{xE}^{zA}, by the sorbent specific ion-exchange capacity, Q_g, and by the eluting anion concentration, c_E.

The separation factor, $\alpha_{A,B}$, is:

$$\alpha_{A,B} = \eta_A[B]/[A]\eta_B \tag{11}$$

The right-hand side of this equation can be transformed to

$$\alpha_{A,B} = \left(\frac{\eta_A^y[B]^x\eta_B^{x-y}}{[A]^y\eta_B^x[B]^{x-y}}\right)^{(1/y)} \tag{12}$$

and by substitution using eqns. 6 and 8, eqn. 13 is derived:

$$\alpha_{\mathrm{A,B}} = {K_{x\mathrm{B}}^{y\mathrm{A}}}^{(1/y)} k_{\mathrm{B}}^{(x-y)/y} (V_{\mathrm{m}}/m_{\mathrm{s}})^{(x-y)/y} \tag{13}$$

Similarly, we obtain:

$$\alpha_{\mathrm{A,B}} = {K_{x\mathrm{B}}^{y\mathrm{A}}}^{(1/x)} k_{\mathrm{A}}^{(x-y)/x} (V_{\mathrm{m}}/m_{\mathrm{s}})^{(x-y)/x} \tag{14}$$

Important conclusions as regards the separation factor in ion chromatography can be drawn from these equations. The separation factor of two ions with the same charge, $x = y$, depends only on the selectivity coefficient, $K_{\mathrm{B}}^{\mathrm{A}}$, and on the charge of the anions, and providing this coefficient is constant, the separation factor does not depend on the eluent anion, its concentration or charge. The separation factor can be changed by changing the sorbent only, *i.e.*, by changing the selectivity coefficient.

The separation factor of two anions with different charges depends on the capacity factor, k, of one of these ions (the capacity factors of the ions are not independent!), and k can be changed according to eqn. 10 by changing the eluent concentration, sorbent capacity, etc.

More representative equations, taking account of the effects of side reactions (protonation of the eluting anion and of the anions being separated, dissociation of functional groups, etc.) and using activities, can be derived. However, they inevitably are very complex and are difficult to handle. They are not necessary for our purposes, when only a qualitative or semiquantitative treatment will be used.

For eluents with more than one eluting anion, the equations derived by Hoover[12] are adequate.

The influence of two factors, functional group polarity and basicity, on sorbent selectivity has been studied in this work. As a measure of the sorbent selectivity for separation of inorganic anions, the selectivity coefficient is better than the separation factor, as follows from eqn. 13, because the former does not depend on the capacity factors of the ions to be separated, even for ions with different charges.

Eqn. 13 in the logarithmic form

$$\log \alpha_{\mathrm{A,B}} = \left(\frac{1}{y}\right) \log K_{x\mathrm{B}}^{y\mathrm{A}} + \frac{x-y}{y} \cdot \log(k_{\mathrm{B}} V_{\mathrm{m}}/m_{\mathrm{s}}) \tag{15}$$

can be written more simply as:

$$\log \alpha_{\mathrm{A,B}} = a + b \cdot \log(k_{\mathrm{B}} V_{\mathrm{m}}/m_{\mathrm{s}}) \tag{16}$$

The selectivity coefficient $K_{x\mathrm{B}}^{y\mathrm{A}}$, can be calculated according to eqns. 15, 16 from the regression coefficient, a, of the dependence of log $\alpha_{\mathrm{A,B}}$ on log k_{B}.

Similarly,

$$\log k_{\mathrm{A}} = \frac{1}{z} \cdot \log K_{x\mathrm{E}}^{z\mathrm{A}} + \frac{x}{z} \cdot \log(Q_{\mathrm{g}}/z) - \log(V_{\mathrm{m}}/m_{\mathrm{s}}) - \frac{x}{z} \cdot \log c_{\mathrm{E}} \tag{17}$$

can be simplified by use of

$$p = \frac{1}{z} \cdot \log K^{zA}_{xE} + \frac{x}{z} \cdot \log(Q_g/z) - \log(V_m/m_s) \qquad (18)$$

and

$$q = -x/z$$

to yield:

$$\log k_A = p + q \cdot \log c_E \qquad (19)$$

The selectivity coefficient, K^{zA}_{xE}, can easily be calculated from the regression coefficient, p, of this equation.

For a more detailed treatment of these and other dependencies see ref. 2.

EXPERIMENTAL

The synthesis and properties of the sorbents, as well as the instrumentation and chemicals, were described in Part I[11]. The basicity of functional groups was estimated as follows: 0.5 g (dry mass) of sorbent (Q_g = 1 mmol g^{-1}) in the hydroxide form were suspended in 50 ml of water and titrated by 0.1 *M* perchloric acid on an automatic titrator Potentiograph E (Metrohm, Herissau, Switzerland) at a rate of 0.3 ml min^{-1}. The column dead volume was calculated from the retention time of a peak due to an excess of methanol present in the sample as compared to the mobile phase composition (50:50, v/v).

The determination of the polarities of the sorbent and precursor gel were based on the solvophobic effect[13], using the capacity factors of non-polar aromatic hydrocarbons [benzene, toluene, xylene; 0.05% solutions in methanol–water (60:40, v/v)]. The column was washed with 100 ml 0.1 *M* ammonia, 200 ml water, 50 ml methanol and with methanol–water (50:50, v/v) until a stable baseline was reached. Retention times were measured by an integrator, three times for hydrocarbons, 9–12 times for the methanol peak. The capacity factors were calculated from the mean retention volumes and mean dead volume.

Capacity factors of anions were measured under the conditions given in Table I. Retention times, recorded by an integrator or calculated from the chromatogram,

TABLE I

CHROMATOGRAPHIC CONDITIONS

Column:	CGC, 150 mm × 3.3 mm, packed with different sorbents
Eluent:	Potassium hydrogenphthalate, c = 0.1–1.0 m*M*, adjusted to pH 6.0.
Flow-rate:	1 ml min^{-1}
Pressure:	1.5–4 MPa
Detection:	Indirect photometry at 254 nm
Sensitivity:	0.01–0.04 a.u.f.s.
Injection:	30 μl, by six-port sampling valve
Sample:	Mixtures of anions, 10–100 mg l^{-1}

TABLE II

CHROMATOGRAPHIC COLUMNS

Sorbent	Q_s *(mmol g⁻¹)*	m_s *(g)*	V_M *(ml)*	d_p *(μm)*
H 1000 A	0.11	0.38	1.01	20
H 1000 EA	0.12	0.35	0.96	20
H 1000 DEA	0.11	0.35	0.95	20
H 1000 DEtA	0.11	0.38	1.02	20
H 1000 DCHA	0.10	0.41	1.04	20
H 1000 TEA	0.09	0.38	1.08	20
H 40 A	0.10	0.40	0.91	25
H 40 DEA	0.13	0.50	1.04	25
H 40 DEtA	0.09	0.40	0.95	25

were measured three times. Each column was equilibrated using at least 400 ml of a new mobile phase. The chromatographic columns used are given in Table II.

RESULTS AND DISCUSSION

Basicity and polarity of functional groups

In order to establish what factor controls the sorbent selectivity, we prepared a series of sorbents, differing only in the functional group structure. These functional groups included primary (A), secondary (EA), tertiary (DEA), quaternary (TEA) amino groups and hydrophilic (DEtA), slightly hydrophobic (DEA) and strongly hydrophobic (DCHA) ones. Their basicities and polarities were compared experimentally.

For an approximate estimate of the functional group basicity, inflection points in titration curves for individual sorbents were compared. The following sequence of increasing basicity was found:

$$\text{A} < \text{DEtA} < \text{DCHA} < \text{EA} < \text{DEA} < \text{TEA} \qquad \text{(A)}$$

The titration curve of sorbent A has no inflection point, *i.e.*, it is a very weak base. A curve was not measured for the sorbent with TEA, a group with strongly basic character, because the sorbent with ion-exchange capacity needed for the titration could not be prepared by our method.

The polarities of the sorbents were compared using the solvophobic effect. The retention of non-polar aromatic hydrocarbons in these systems should be caused by this effect only. Results for unmodified gels are presented in Table III; the polarity of the sorbent matrix decreased in the order:

$$\text{HEMA 300} > \text{HEMA 1000} > \text{H 40} \qquad \text{(B)}$$

Hydrolyzed epoxy groups increase, while additional cross-linking decreases, the sorbent polarity. The polarities of the sorbents tested are compared in Table IV. The values lie between those of unmodified and epoxy-modified (hydrolyzed) gels.

TABLE III

POLARITIES OF UNMODIFIED GELS

Matrix	*k*		
	Benzene	*Toluene*	*Xylene*
HEMA 1000	2.54	3.60	5.07
HEMA 1000 E	2.19	3.12	4.16
S HEMA 1000	2.68	3.90	5.36
HEMA 40	5.60	8.46	11.85
HEMA 40 E	4.53	5.59	8.84
HEMA 300	1.86	2.50	3.26
S HEMA 300	2.41	3.26	4.31

Because of the low functional group content and the precision of the capacity factor measurement (relative standard deviation *ca.* 1%), the differences between the capacity factors with the sorbents compared are statistically insignificant in most cases; only with sorbents having DCHA and TEA groups are the differences greater. However, some increase in capacity factors is observable for non-polar solutes (see Table IV) and thus the functional group polarity is presumed to decrease in the sequence:

$$\text{A} > \text{DEtA} > \text{EA} > \text{DEA} > \text{DCHA} > \text{TEA} \qquad \text{(C)}$$

This can be substantiated by calculating the substituent constant, π, for individual functional groups using values from refs. 14, 15. The following sequence of functional group polarities was then established (calculated values in parentheses):

$$\text{DEtA}\ (-1.54) > \text{A}\ (-1.16) > \text{EA}\ (-0.16) > \text{DEA}\ (0.84) > \text{TEA}\ (1.84) > \text{DCHA}\ (3.84) \qquad \text{(D)}$$

TABLE IV

POLARITIES OF SORBENTS

Sorbent	*k*		
	Benzene	*Toluene*	*Xylene*
H 1000 A	2.28	3.12	4.12
H 1000 EA	2.40	3.25	4.28
H 1000 DEA	2.40	3.20	4.30
H 1000 DEtA	2.39	3.16	4.21
H 1000 DCHA	2.56	3.57	4.72
H 1000 TEA	3.30	4.00	4.91
H 40 A	4.77	7.03	9.98
H 40 DEA	4.94	7.69	10.40
H 40 DEtA	4.93	7.29	10.22

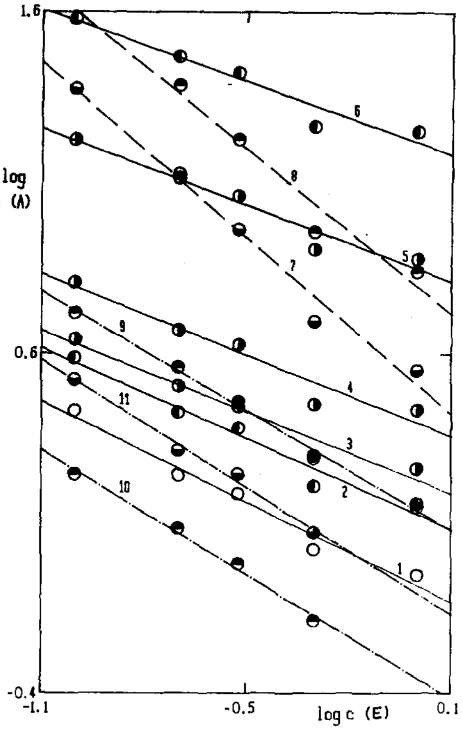
The two sequences C, D differ only in the position of the outlying groups. A sequence of functional group polarities, obtained by combination of C and D, is used in the following discussion:

DEtA > A > EA > DEA > DCHA > TEA (E)

The most important difference between the basicity and polarity sequences A and E is in the position of the highly hydrophobic but only weakly basic DCHA group.

Sorbent selectivity

The anions tested included monovalent (Cl^-, Br^-, I^-, SCN^-, NO_2^-, NO_3^-) and divalent (SO_4^{2-}, $S_2O_3^{2-}$) anions as well as anions of multiprotic acids, existing in two ionic forms at the pH used (HSO_3^-, HCO_3^-, $H_2PO_4^-$). The dependences log k_A *vs.* log c_E for sorbents with DEtA and TEA groups are summarized in Figs. 1, 2. The most pronounced change in the retention with sorbent functionality occurs for some large monovalent anions (curves 4–6; curves 5 and 6 in Fig. 2 are off scale). The selectivity of sorbents was compared according to their selectivity coefficients, K_{xB}^{yA}, calculated from the regression coefficients of eqn. 15. Measured values of V_M



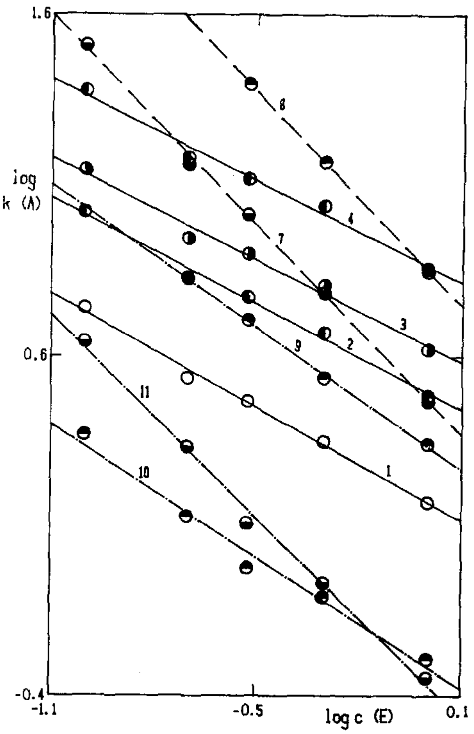


Fig. 1. Plots of log k_A against log c_E (m*M*) for a sorbent with DEtA as functional group. A = Cl^- (1), NO_2^- (2), Br^- (3), NO_3^- (4), I^- (5), SCN^- (6), SO_4^{2-} (7), $S_2O_3^{2-}$ (8), HSO_3^- (9), HCO_3^- (10), $H_2PO_4^-$ (11).

Fig. 2. Plots of log k_A against log c_E (m*M*) for a sorbent with TEA. Details as in Fig. 1.

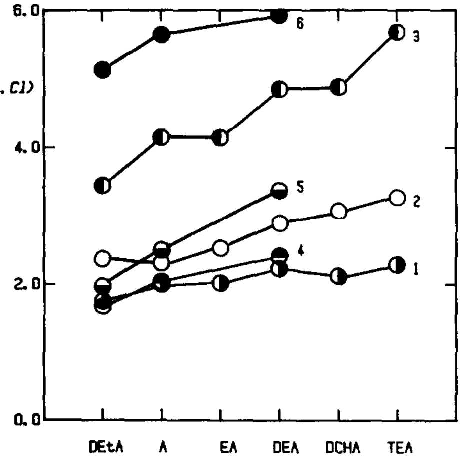


Fig. 3. Plots of the selectivity coefficient, K^{A}_{Cl}, against sorbent polarity. A = NO_2^- (1), Br^- (2), NO_3^- (3) on matrix HEMA 1000; NO_2^- (4), Br^- (5), NO_3^- (6) on matrix HEMA 40.

(= V_m) and m_s, and theoretical charges $y = 1$, $x = 2$ for SO_4^{2-} and $S_2O_3^{2-}$ and $x = 1$ for all other anions, were used for calculation of the selectivity coefficients, K^{A}_{xCl}.

Plots of the selectivity coefficients for univalent anions against functional group polarity are shown in Fig. 3. The selectivity for these anions increases with decreasing functional group polarity. An opposite trend is found for divalent anions (Fig. 4). For HSO_3^-, HCO_3^-, $H_2PO_4^-$ the trend is similar (except for the group DEtA) to that found for divalent anions, although the univalent form of the anions prevails in the mobile phase under the conditions used (Fig. 5). The prevailing form of the anion in the stationary phase can, however, be different from that in the mobile phase.

Comparing the trends in Figs. 3–5 with the sequence A, there is better agree-

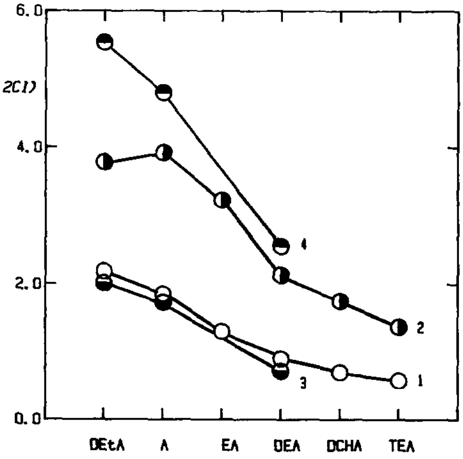


Fig. 4. Plots of the selectivity coefficient, K^{A}_{2Cl}, against sorbent polarity. A = SO_4^{2-} (1), $S_2O_3^{2-}$ (2) on matrix HEMA 1000; SO_4^{2-} (3), $S_2O_3^{2-}$ (4) on matrix HEMA 40.

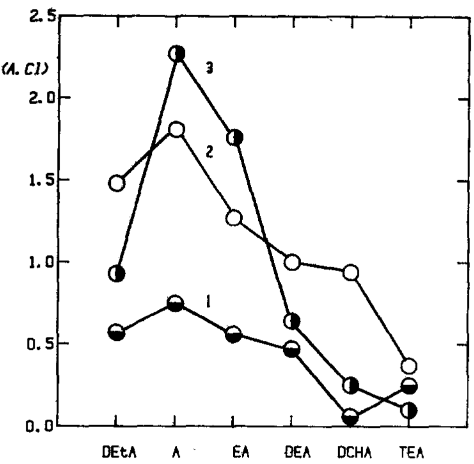


Fig. 5. Plots of the selectivity coefficient, $K_{\mathrm{Cl}}^{\mathrm{A}}$, against sorbent polarity. A = HCO_3^- (1), HSO_3^- (2), $H_2PO_4^-$ (3) on matrix HEMA 1000.

ment of the selectivity order with polarity than with basicity. This supports the hypothesis that functional group polarity is the main factor influencing functional group selectivity.

The trends observed for monovalent anions are in full aggreement with the results of Barron and Fritz[9]. The same authors[10] used relative retention, $t_{R,\mathrm{A}}/t_{R,\mathrm{Cl}}$, to compare the sorbent selectivity for divalent anions. Relative retention, however, depends on the capacity factors of the anions to be separated in a similar way to the separation factor (eqn. 13). Those authors[10] did not, thus, separate the influence of sorbent selectivity from that of other factors. However, our results support their conclusion that the functional group polarity has a considerable influence on the separation of divalent from monovalent anions.

The main factors affecting the selectivity of an ion-exchange resin can be quite different for high- and low-capacity resins. The internal solution composition, *i.e.*, the amount of imbibed water and the degree of cross-linking are the main factors influencing the selectivity of high-capacity exchange resins, *e.g.*, for anion exchangers[16,17], whereas disruption of the water structure[18] may play an important rôle with low-capacity sorbents. The larger and more hydrophobic is the structure of the functional group, the greater is the effect of the "water structure-enforced ion-pairing"[18] in the close proximity of the surface-bound functional group. This is manifested by the dependences of k(A,Cl) on functional group hydrophobicity in Fig. 3. For a given type of functional group with a certain size and hydrophobicity, the water structure-enforced ion pairing should become more important with larger anions[18], as can be seen in the sequence of k(A) for monovalent anions on the sorbent with DEtA as functional group (Fig. 1).

The influence of the sorbent matrix on its selectivity is observable in Figs. 3 and 4. No simple dependence has been found between the sorbent selectivity and its matrix polarity. To study this factor, a series of sorbents differing only in one matrix parameter would be necessary. Such a series was not available and its preparation would be difficult, as the relationships between the matrix parameters are not yet fully known.

As regards sorbent selectivity, the nature of the forces controlling ion exchange is of primary importance. Usually, ion exchange is explained by electrostatic forces causing attraction between a charged functional group and an oppositely charged counter ion. According to the Coulomb law, the attractive force increases with decreasing distance between the charges. The basicity of an ion-exchanger functional group can be considered to be some measure of its charge effect. Therefore, the different selectivities of the sorbents can be explained by the different basicities of their functional groups. However, the results of Clifford and Weber[7] as well as of this work confirm that basicity is not the controlling factor.

The usual sequence of increasing selectivity of an anion exchanger for monovalent anions[19,20].

$$F^- < Cl^- < NO_2^- < Br^- < NO_3^- < I^- < SCN^- < ClO_4^- \qquad (F)$$

cannot be explained by electrostatic forces only, as the anion diameters (even when hydrated) do not correspond to this sequence.

Barron and Fritz[9,10] explain the sorbent selectivity in terms of the formation of ion pairs between a covalently bound, partially movable functional groups and an oppositely charged anion. These ion pairs are forced by the solvophobic effect out of the polar aqueous into the more hydrophobic gel phase in the interphase region. A sequence similar to F was observed when these anions in the form of ion pairs were separated between two phases of different polarity. In addition to the examples discussed by Barron and Fritz[9,10], the extraction of anions with tetraphenylarsonium salts[21] and the separation on sorbents with bonded cyclic ethers (crowns)[22] can be mentioned.

The opposite order of selectivity was observed[23,24] for separation of anions on alumina. Schmidt and Pietrzyk[24] supposed that the retention was caused by ion exchange, as they were able to use indirect photometric detection. Because of the rigid alumina structure, the solvophobic effect can not apply in their case. This is a possible explanation for the different selectivity on alumina.

In the separation of mono- from divalent anions on ion exchangers, the electroselectivity plays an important rôle[10]. Divalent anions are usually more strongly bound to an anion exchanger than monovalent ones. In the mentioned examples[9,10,21,22] of anion separation between two liquid phases, where the electroselectivity cannot be effective, sulphate is extracted less than fluoride or chloride.

Clifford and Weber[7] attributed the different selectivities of anion exchangers studied for separation of mono- and divalent anions to the different distance of two functional groups needed for bonding a divalent anion. In contrast, we have found a greater selectivity for sulphate with the sorbent with DEtA than with A, in spite of the greater steric hindrance from the DEtA group. Thus, the functional group polarity must also play an important rôle.

CONCLUSIONS

It has been shown that sorbent selectivity for the separation of anions by ion chromatography is controlled by a variety of factors (type of eluent, its concentration, type of sorbent, its ion-exchange capacity, etc.). We have derived equations that can serve as a rough guide in choosing experimental conditions for the separation of anions by ion chromatography. The selectivity coefficients are considered as an appropriate measure of sorbent selectivity because they are not influenced by important parameters such as sorbent capacity, capacity factor, eluent concentration.

The polarity of the functional group rather than its basicity has been shown to be the parameter controlling the sorbent selectivity. The selectivity expressed by the appropriate selectivity coefficient increases for the separation of anions having the same charges and decreases for the separation of anions with different charges with decreasing polarity of the functional group. These relationships are of utility for optimization in ion chromatography.

Sorbents with non-polar functional groups enable an increase in the separation factors of anions with the same charge and thus an increase in the resolution of anions which are difficult to separate. On the contrary, sorbents with polar functional groups enable a decrease in the separation ratios and the separation of mixtures of anions having very different capacity factors, using isocratic elution. Finally, by appropriate choice of the functional group polarity, the separation of mono- from divalent anions can be optimized.

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