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Alkanesulfonate homologous series as eluent components in anion chromatography

Novel eluent selection system for monovalent analytes¹

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Abstract

Common inorganic anions can be separated on an anion-exchange column of low capacity using a very dilute solution of alkanesulfonate as eluent components and a conductivity detector. A mathematical relationship has been found between the retention volumes of monovalent analyte using different alkanesulfonates as eluents and quaternary ammonium functionalized styrene–divinylbenzene stationary phase. Retention volumes decrease steadily for the homologous series of alkanesulfonates (methane-, ethane-, propane-, butane- and pentanesulfonates) as the alkyl-chain length increases. This system made it possible to establish the ion-exchange capacity of the separation column and the inter-eluent selectivity coefficients and permitted prediction of retention volume with variation of type and concentration of eluent. The parameters of retention model can be readily derived from elution experiments. The eluent system has been used easily to design separation schemes. Good agreement was obtained between the observed and predicted values for the anions of practical interest (fluoride, chloride, chlorate, nitrite, nitrate, bromide, bromate). Retention of ions can be manipulated by changing either the concentration or carbon number of the alkanesulfonate eluent from homologous series. The response of analyte retention to changing eluent conditions can be illustrated with a retention nomogram.

Keywords: Mobile phase composition; Retention prediction; Alkanesulfonates; Anions

1. Introduction

Ion chromatography (IC) has rapidly evolved into an accepted method for the separation and determination of solute species – ionic and polar substances – in liquid samples. Basically, three parameters can be altered when choosing conditions for an ion chromatographic separation: stationary phase, mobile

phase and detector. The eluent selection provides the greatest flexibility for manipulating the retention of a solute in order to achieve a desired separation. Not only the type of the eluent can be changed, but its pH and concentration can be varied [1]. The choice of eluents for use in anion chromatography is, however, still limited. In the suppressed mode only hydroxide, carbonate and tetraborate have found widespread use [2]. The specifications that apply to a substance to be used as eluent in single column chromatography are strict. Anion determinations have been made with eluents which have high affinity for the low capacity anion exchanger and a

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very low conductance, e.g. phthalate, benzoate and sulfobenzoate salts.

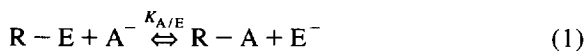
This paper presents an eluent system for the separation of inorganic and organic anions (fluoride, chloride, chlorate, nitrite, nitrate, bromide, bromate, formate, acetate) using single-column ion chromatography. These are the alkanesulfonate homologous series, methane-, ethane-, 1-propane-, 1-butane- and 1-pentanesulfonate eluents. The practical application of this eluent system are twofold. First, these eluents have fully ionized forms, high polarity, moderate conductances, monovalent charge. Its combination of moderate conductance and relatively high polarity, which confers some of practical advantages: it has solubility in water and relatively low adsorption to non-polar portions of the column packing surface. It is important because it allows rapid equilibration and relative freedom from interfering system peaks. Alkanesulfonates are fully ionized forms over the eluent pH range. Eluent pH is therefore not a critical factor in controlling retention. Secondly – as we shall see – the system can also provide a convenient control of retention as a function of eluent changing. This eluent system has been used easily to design separation schemes. The parameters of the retention model can be readily derived from elution experiments [3]. Halogenides and oxoanions were chosen for separation because of their practical importance. The application of a theoretical model as a predictive tool for eluent selection and the calculation of retention behaviour are also presented in this paper.

2. Theory

2.1. Retention changing with variation of eluent concentration

The distribution of solute ions between the stationary and alkanesulfonate mobile phases can be controlled by ion exchange mechanism. This system is supposed to be free from any effects – pH of the eluent, protonization [2], complex formation [4] – and therefore the theoretical considerations of ion-exchange equilibria are of fundamental importance in controlling the retention process. The problem of selection of the eluent composition can be solved on

the basis of a valid model of the retention mechanism. The ion-exchange equilibrium is given by:



where R represents the stationary phase. The eluent system provides the simplest case in ion-exchange chromatography, in which the eluent contains only a single competing eluent ion, E^- , and A^- is the analyte ion. The volumetric distribution coefficient of A^- can be given in terms of $K_{A/E}$, the ion-exchange capacity, Q , of the column (mmol ml^{-1}) and the eluent concentration, $[E^-]$

$$D_A = K_{A/E} Q [E^-]^{-1} \quad (2)$$

The relationship between the volumetric distribution coefficient and retention volume is the following:

$$V_R = V_0 + V_{N,A} = V_0 + D_A X \quad (3)$$

where V_R is the retention volume of the analyte, V_0 is the hold-up volume of the column, $V_{N,A}$ is the net retention volume of the analyte and X is the total inner volume of the column. The net retention volume of an analyte can be calculated by using Eqs. (2,3):

$$(V_{N,A})_{E_1} = K_{A/E_1} Q X [E_1^-]^{-1} \quad (4a)$$

or

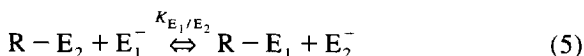
$$(V_{N,A})_{E_2} = K_{A/E_2} Q X [E_2^-]^{-1} \quad (4b)$$

where E_1 , E_2 are different eluent components of alkanesulfonate homologous series. The net retention volume of a solute is determined by the selectivity coefficient, the ion-exchange capacity of the stationary phase and the concentration of the eluent.

2.2. Retention changing with variation of eluent components of homologous series

The practical and theoretical treatment of the inter-eluent selectivity coefficient as a predictive tool for retention behaviour is a new trend in ion-exchange chromatography [5,6]. An important characteristic of our system is the simple predictable manner of retention changes with variation of eluent type and composition. In order to predict retention behaviour, the 'inter-eluent ion-exchange selectivity coeffi-

cients' and column capacity should be known. Using the fact that eluents are components of a homologous series, we can inject the first eluent as a sample into the other one to determine the unknown parameters. If we consider an eluent ion, E_1 , as an analyte and an other eluent ion, E_2 , as a competing ion in an anion exchange system (and vice versa), the following equilibrium applies:



where K_{E_1/E_2} is the inter-eluent chromatographic ion-exchange selectivity constant. Under these circumstances the $K_{A/E_2} \equiv K_{E_1/E_2}$ and $K_{A/E_1} \equiv K_{E_2/E_1}$ and also $K_{E_1/E_2} = (K_{E_2/E_1})^{-1}$. Substitution of these expressions in Eq. (4a) and dividing Eq. (4a) by Eq. (4b) yields the inter-eluent selectivity constant:

$$K_{E_1/E_2} = \sqrt{\frac{(V_{N,E_1})_{E_2} [E_2^-]}{(V_{N,E_2})_{E_1} [E_1^-]}} \quad (6)$$

Multiplying Eq. (4a) by Eq. (4b) leads to the column capacity:

$$QX = \sqrt{(V_{N,E_2})_{E_1} [E_1^-] (V_{N,E_1})_{E_2} [E_2^-]} \quad (7)$$

For a monovalent analyte the following relationship can be obtained also from Eqs. (4a) and Eqs. (4b):

$$(V_{N,A})_{E_2} = K_{E_1/E_2} \frac{[E_1^-]}{[E_2^-]} (V_{N,A})_{E_1} \quad (8)$$

This important linear relationship can be used to predict retention volume of an analyte in another eluent. The retention data of an analyte, $(V_{N,A})_{E_1}$, and the second type of eluent, $(V_{N,E_2})_{E_1}$, are measured in the first eluent (E_1) and the retention data of an analyte in the second eluent, $(V_{N,A})_{E_2}$, can be calculated from Eq. (8). In general Eq. (9) predicts that a linear relationship exists between two net retention volumes:

$$(V_{N,A})_{E_{n+1}} = K_{E_n/E_{n+1}} \frac{[E_n^-]}{[E_{n+1}^-]} (V_{N,A})_{E_n} \quad (9)$$

where n is the number of C atoms in the eluent component of alkanesulfonate homologous series.

From the above derivation it is clear that the type

and concentration of eluent component of the homologous series can play a significant role on retention. Here, the concentration and/or a given eluent component can be readily varied to affect retention data. These theoretical considerations are limited for monovalent analytes.

3. Experimental

3.1. Reagents and solutions

Tripily distilled water was purified by a Milli-Q system (Millipore) containing a 0.45- μ m Millistack filter at the outlet. Eluents were prepared by using analytical grade methane- (MeSA), ethane- (ESA), propane- (PSA), butane- (BSA) and pentane- (PeSA) sulfonic acid sodium salts from Fluka (Buchs, Switzerland) without further purification. Sample solutions of fluoride, chloride, chlorate, nitrite, nitrate, bromide, and bromate were prepared by dissolution of analytical grade sodium salts from Merck (Darmstadt, Germany). The concentration of the anions in the samples varied in the range 1.2–2.2 mM. The samples were analyzed at five eluent concentrations using alkanesulfonate eluents (5, 8, 10, 12, 15 mM).

3.2. Instrumentation

The chromatographic system consisted of a Dionex ion-chromatograph 10 (Dionex, Sunnyvale, CA, USA), a Dionex AS9 anion separator column (250 \times 4 mm), a Thermal Stabilizer Model TS2 and a mechanical solvent delivery pump (LDC, Milton Roy). The injector loop was 25 μ l. The nominal flow-rate was 1.67 ml min⁻¹. The separator column with alkyl quaternary amine functional groups was used and column packing based on a 16- μ m poly-(styrene–divinylbenzene) copolymer (substrate cross-linking 4%) agglomerated with completely aminated anion-exchange latex. The ion-exchange capacity was determined accurately and found to be 21.61 μ mol per column (see Section 4.2). Silica based anion-exchanger with quaternary ammonium functional groups was also used [7]. Retention times were the means of minimum triplicate injections of a single sample.

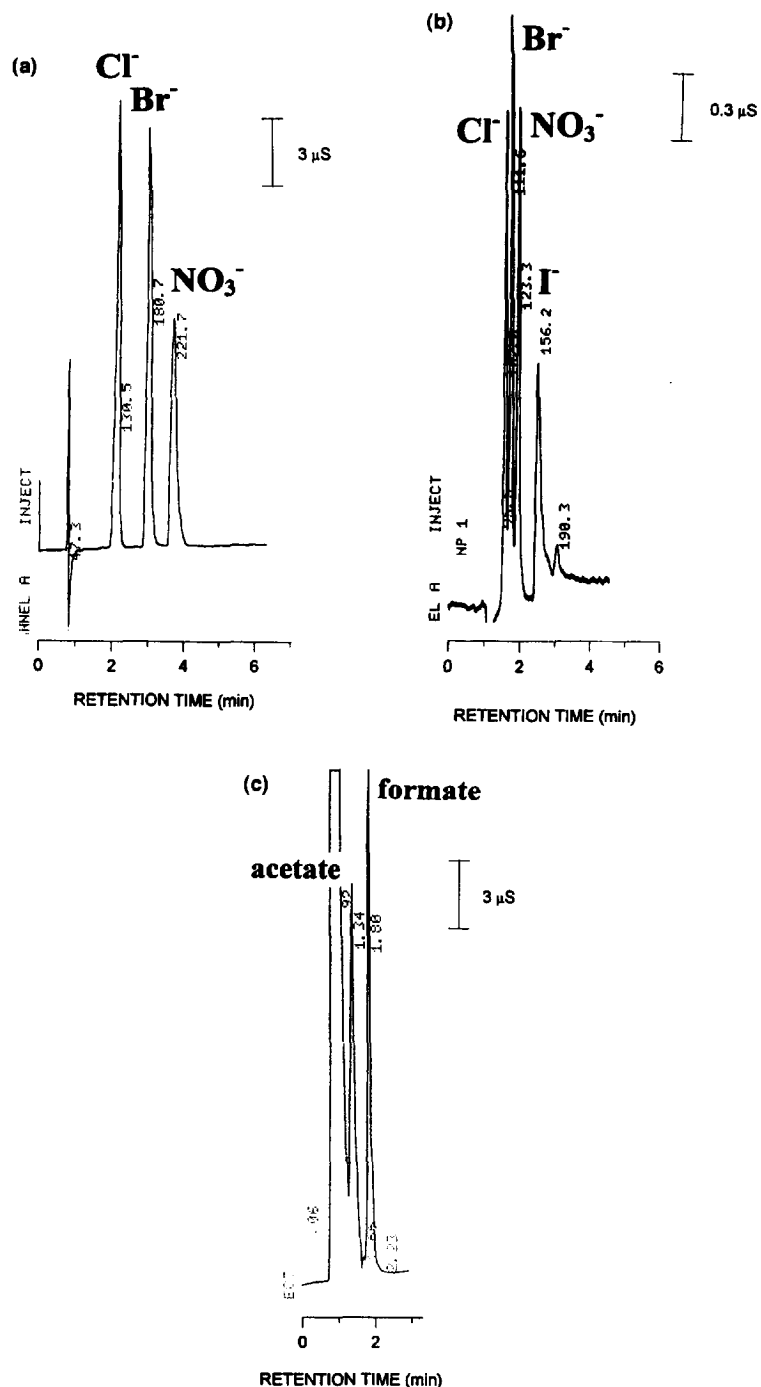


Fig. 1. (a) Separation of monovalent inorganic anions. Eluent: 10 mM propanesulfonate, sodium salt; column, silica based with quaternary ammonium functional groups; $Q=60.8 \mu\text{mol}/\text{column}$; injection volume, 25 μl ; flow-rate, 1.67 ml min^{-1} . (b) Separation of monovalent inorganic anions. Eluent: 6 mM ethanesulfonate + propanesulfonate, sodium salts = 1:4; column, silica based with quaternary ammonium functional groups; $Q=8.1 \mu\text{mol}/\text{column}$; injection volume, 25 μl ; flow-rate, 1.67 ml min^{-1} . (c) Separation of monovalent organic anions. Eluent: 8 mM propanesulfonate, sodium salt; column, Dionex AS9; $Q=21.6 \mu\text{mol}/\text{column}$; injection volume, 50 μl ; flow-rate, 1.67 ml min^{-1} .

4. Results and discussions

4.1. Typical separations

Some typical examples are presented. Fig. 1a–c show, for comparison, the separation of a mixture of common anions under different conditions, using alkanesulfonate eluents and various columns (polymer and silica-based stationary phases) with quaternary ammonium functional groups.

Fig. 1a,b show two examples of separations that can be achieved with silica based stationary phases using alkanesulfonate eluents. In Fig. 1a the ions to be separated comprise an early eluting group – chloride, bromide and nitrate. Baseline resolution was achieved with every peak. Fig. 1b shows a good separation of anions on a column of lower capacity than that used in Fig. 1a. The separation was complete in less than 3 min. Even the iodide, an anion that is normally a later eluting anion, has a retention time of 156 s. Fig. 1c show an example of the separation of monovalent organic anions (acetate, formate) on polymer based stationary phase using propanesulfonate eluent. The total analysis time was ~2 min. Carboxylic acids were sensitively detected as their ionic forms. It can be concluded, that changing the mobile phase composition – type and concentration of eluent anions of alkanesulfonates – and the structure of the stationary phase changed the capacity factors and performance of separations, but did not change peak symmetry. Using methane-, ethane-, propane-, butane- and pentanesulfonates as eluents in non-suppressed ion chromatography is an effective method to separate anions.

The detection of ions using a conductometric detection method is achieved due to the difference in ionic conductances of the sample and eluent ions. The components of homologous series have moderate conductances ($<40 \text{ S cm}^2/\text{mol}$) and when used in dilute solution, provide eluents with low background conductance. Except for methanesulfonate ion the alkanesulfonates have similar conductances to the eluents commonly used in single column systems ($\lambda_{\text{Hphthalate}} = 29.4 \text{ S cm}^2/\text{mol}$, $\lambda_{\text{benzoate}} = 32.4 \text{ S cm}^2/\text{mol}$) [8]. The ionic conductance decreases with the length of aliphatic chain.

For the sensitive detection the concentration domain applied was based on the following:

(1) To obtain symmetrical peaks with good resolution and relatively low retention volumes the total eluent concentration was $[\text{E}^-] \geq 5 \text{ mM}$. The concentration range of the eluent was limited by the operation range of the conductivity detector, $[\text{E}^-] \leq 15 \text{ mM}$.

(2) The injection peak typically located at the start of the chromatogram. The conductance of the injection peak may be greater or less (positive or negative) than that of the alkanesulfonate eluents, depending on the sample and eluent concentration.

Comparison of conductances for the eluents and analytes suggests that direct conductivity detection is possible for all anions studied.

4.2. Determination of the ion-exchange capacity and inter-eluent selectivity coefficients

To be able to calculate retention data a priori, the ion-exchange capacity of the column packing and inter-eluent selectivity coefficients should be known. To determine these parameters, we took advantage of the fact, that eluent components are members of a homologous series and that the separation is based on ion-exchange mechanism (see Section 4.3). The strategy was the following: an eluent component injected as a sample into the other one and vice versa (see the scheme in Fig. 2). The unknown parameters

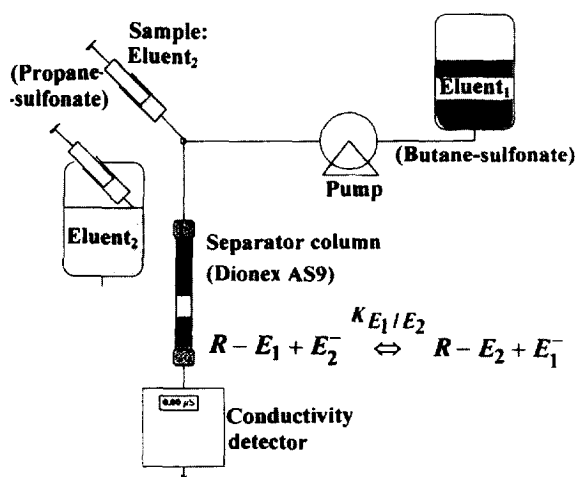


Fig. 2. Schematic representation of the experiments to be made in order to determine the ion-exchange capacity of the separator column and the inter-eluent selectivity coefficients.

Table 1

Column capacities, QX ($\mu\text{mol}/\text{column}$), calculated from the retention volumes of eluent species as sample ions using Eq. (7)

Eluent composition	5 mM PSA	8 mM PSA	10 mM PSA	12 mM PSA	15 mM PSA
5 mM BSA	21.95	21.90	21.36	21.43	21.47
8 mM BSA	22.10	22.05	21.51	21.58	21.62
10 mM BSA	22.15	22.10	21.56	21.63	21.67
12 mM BSA	21.94	21.89	21.35	21.42	21.46
15 mM BSA	21.53	21.49	20.96	21.03	21.07

BSA: butanesulfonate; PSA: propanesulfonate; mean value: $21.61 \mu\text{mol}/\text{column}$; mean of error: 1.5%.

can be calculated based on Eqs. (6,7). In the case of propane- and butanesulfonates, all possible variations in the eluent concentration have been tested. The results of the calculations are summarized in Tables 1 and 2. In Table 1 the capacity values are shown, according to Eq. (7). The actual V_N values were obtained from Figs. 3 and 4. The average of these values is $21.61 \mu\text{mol}$. The data in Table 2 are given by Eq. (6). The mean value of the inter-eluent

selectivity coefficients is 0.87. It can be concluded that no matter which experiment is done, the ion-exchange capacity of the column is $21.61 \mu\text{mol}$ with precision $0.33 \mu\text{mol}$ (1.5%) and the inter-eluent selectivity coefficient ($K_{\text{PSA}/\text{BSA}}$) is 0.87 with precision 0.01 (1.1%). Other inter-eluent selectivity coefficients for all the eluent components determined are as follows: $K_{\text{BSA}/\text{MeSA}} = 1.33$, $K_{\text{BSA}/\text{ESA}} = 1.28$, $K_{\text{BSA}/\text{PSA}} = 1.15$, $K_{\text{BSA}/\text{PeSA}} = 0.73$.

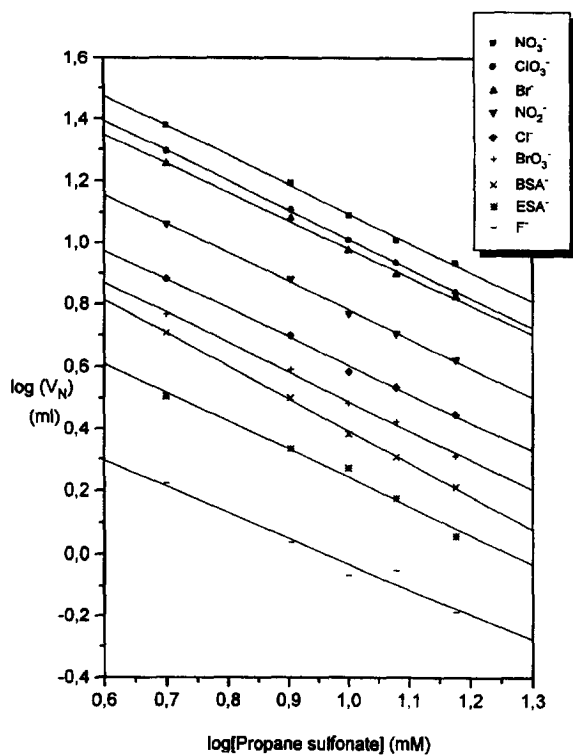


Fig. 3. Logarithmic plot of the retention of analytes as a function of the eluent concentration. Eluent: propanesulfonate (PSA).

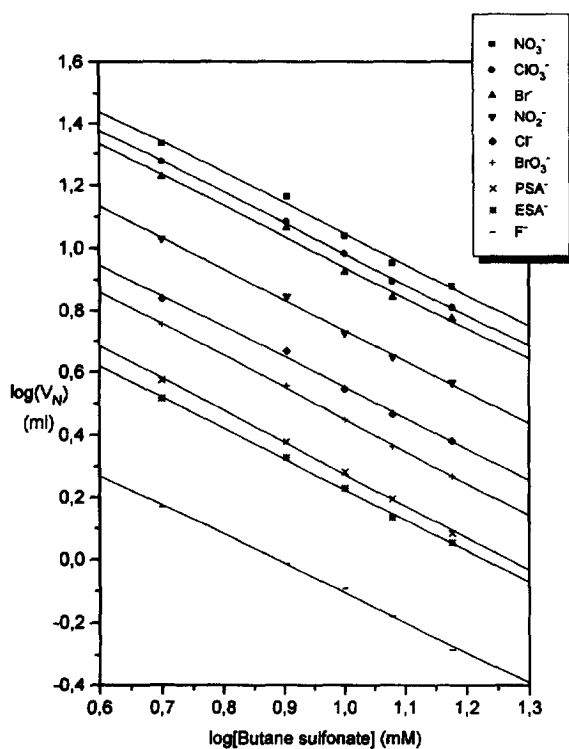


Fig. 4. Logarithmic plot of the retention of analytes as a function of the eluent concentration. Eluent: butanesulfonate (BSA).

Table 2

Inter-eluent selectivity coefficients, $K_{\text{PSA/BSA}}$, calculated from the retention volumes of eluent species as sample ions using Eq. (6)

Eluent composition	5 mM PSA	8 mM PSA	10 mM PSA	12 mM PSA	15 mM PSA
5 mM BSA	0.86	0.86	0.88	0.88	0.88
8 mM BSA	0.87	0.87	0.89	0.89	0.88
10 mM BSA	0.87	0.87	0.89	0.89	0.89
12 mM BSA	0.86	0.86	0.88	0.88	0.88
15 mM BSA	0.84	0.84	0.87	0.86	0.86

BSA: butanesulfonate; PSA: propanesulfonate; mean value: 0.87; mean of error: 1.1%.

4.3. Retention volume of analytes as a function of eluent concentration

Both the concentration (5–15 mM) and the type of the eluent have been varied and retention data were determined for each analyte ion. Since retention times for each analyte were measured at least in triplicate, more than 300 data points were acquired in this study. The logarithmic form of Eq. (2) provides the relationship:

$$\log(V_{\text{N,A}})_E = \log K_{\text{A/E}} + \log(QX) - \log[\text{E}^-] \quad (10)$$

The experimentally determined V_{N} vs. eluent concentration function of various anions eluted by propanesulfonate and butanesulfonate on a pellicular polymer stationary phase are shown on Figs. 3 and 4. Linear regression analysis of $\log(V_{\text{N,A}})_E = \text{constant} + B \log[\text{E}^-]$ for anion elutes with alkanesulfonate anion eluents can be found in Table 3. Linear

function was found with a slope of (–1) at both of eluents and for each solute. It can be seen that retention equation is satisfied and alkanesulfonate concentration does profoundly influence the net retention volumes. That means, the distribution of analyte ions between the stationary and mobile phases, i.e. the retention behaviour is controlled by pure ion exchange mechanism. Varying the eluent concentration, retention volume of a given analyte will change according to the Eq. (10). With the knowledge of $K_{\text{A/E}}$ selectivity coefficient, retention data in a given eluent can be calculated.

The ion-specific selectivity coefficients were also determined for each analyte and eluent ion. The observed values of the selectivity coefficients are summarized in Table 4. Close examination of this table highlights several aspects of the retention characteristics of the analytes used. Selectivity coefficients show increasing tendency with the increas-

Table 3

Linear regression analysis of $\log(V_{\text{N,A}})_E = \text{constant} + B \log[\text{E}^-]$ for anion elutes with alkanesulfonate eluents

Analyte	Propanesulfonate		Butanesulfonate	
	$\text{C}_3\text{H}_7\text{SO}_3^-$ $B \pm \text{S.D.}^a$	r^b	$\text{C}_4\text{H}_9\text{SO}_3^-$ $B \pm \text{S.D.}^a$	r^b
Fluoride	-0.82 ± 0.09	–0.981	-0.94 ± 0.03	–0.998
Bromate	-0.95 ± 0.04	–0.998	-1.03 ± 0.01	–0.999
Chloride	-0.92 ± 0.04	–0.998	-0.99 ± 0.04	–0.998
Nitrite	-0.93 ± 0.03	–0.999	-1.00 ± 0.03	–0.998
Bromide	-0.92 ± 0.03	–0.998	-0.99 ± 0.06	–0.995
Chlorate	-0.96 ± 0.01	–0.999	-0.99 ± 0.02	–0.999
Nitrate	-0.95 ± 0.02	–0.999	-0.98 ± 0.05	–0.997
Ethanesulfonate	-0.92 ± 0.06	–0.993	-0.99 ± 0.03	–0.999
Propanesulfonate	–	–	-1.03 ± 0.03	–0.999
Butanesulfonate	-1.05 ± 0.02	–0.999	–	–

^a Where B is the slope of the $\log V_{\text{N}}$ versus $\log[\text{E}^-]$ (eluent concentration) curves for the monovalent anions.^b r is the correlation coefficient.

Table 4
Ion-specific selectivity coefficients, $K_{A/E}^a$

Analyte	$K_{A/BSA}$	$K_{A/PSA}$
Fluoride	0.36 ± 0.02	0.42 ± 0.05
Bromate	1.31 ± 0.02	1.42 ± 0.05
Chloride	1.65 ± 0.05	1.85 ± 0.08
Nitrite	2.56 ± 0.08	2.80 ± 0.10
Bromide	4.03 ± 0.18	4.41 ± 0.17
Chlorate	4.45 ± 0.07	4.74 ± 0.09
Nitrate	5.16 ± 0.18	5.74 ± 0.16
Ethanesulfonate	0.78 ± 0.02	0.81 ± 0.05
Propanesulfonate	0.87 ± 0.01	–
Butanesulfonate	–	1.15 ± 0.03

^a Average of that determined at different eluent concentrations.

ing retention data and with the decreasing length of the alkane chain of the eluent. There is large difference in binding strength among the halide anions. The selectivity coefficient for bromide is considerably higher than that for chloride as is

expected on the basis of size and polarizability. Bromate is eluted much earlier than chlorate. This phenomenon may be attributed to a shielding effect of the oxygens, resulting in more compact ion with lower charge density and polarizability. An interesting relation was found with singly charged oxyanions (nitrate and nitrite). If the central atom remains the same and the number of oxygen atoms around it increases, so that the ion gets bigger, the affinity to the exchanger increases with the ionic size. Thus, nitrate is bound more strongly than nitrite [9].

4.4. Retention volume of analytes as a function of eluent type of homologous series – eluent selection to be tested

The retention data measured in the first eluent can be calculated for the second eluent using Eq. (9) and the actual inter-eluent ion-exchange selectivity co-

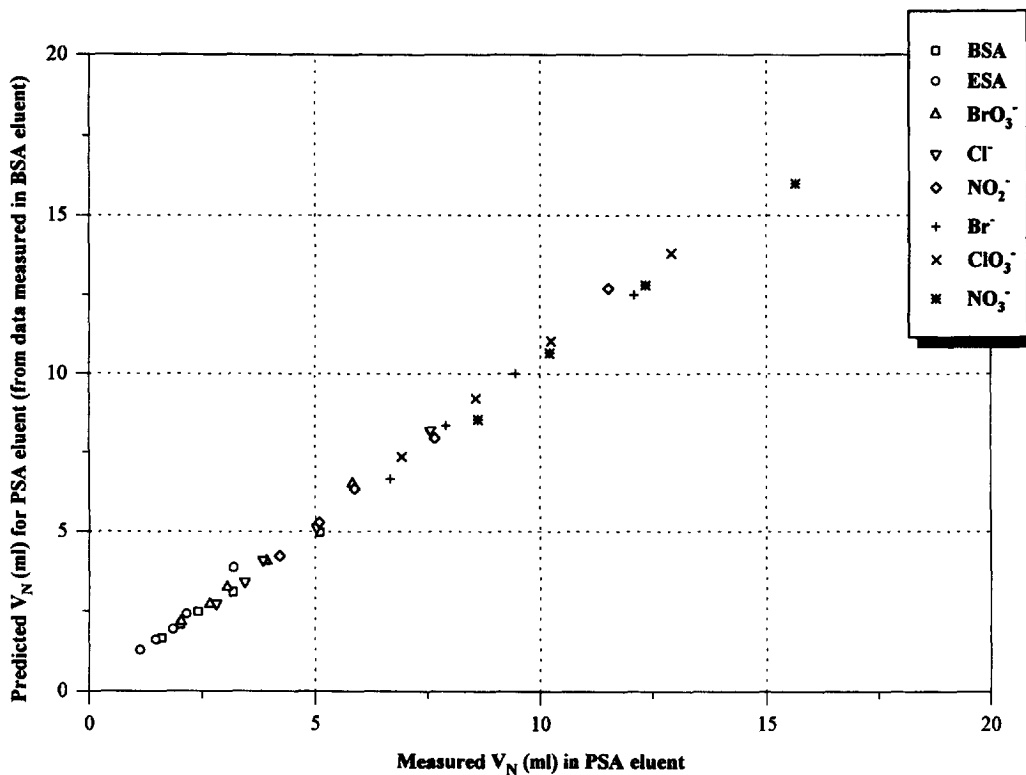


Fig. 5. Relationship between measured and predicted retention volumes. Retention data in different concentration of propanesulfonate eluent were determined from data measured in butanesulfonate eluent.

Table 5

Comparison of the calculated and measured net retention volumes, V_N (ml), using 12 mM alkanesulfonate eluents

Analyte	$[(V_N)_{BSA}]_{\text{meas}}$	$[(V_N)_{PSA}]_{\text{meas}}$	Δ (%)	$[(V_N)_{PSA}]_{\text{meas}}$	$[(V_N)_{ESA}]_{\text{meas}}$	Δ (%)
	$[(V_N)_{PSA}]_{\text{calc}}$			$[(V_N)_{ESA}]_{\text{calc}}$		
Bromate	2.71	2.66	1.9	3.16	3.34	5.4
Chloride	3.41	3.44	0.9	4.11	4.28	4.0
Nitrite	5.30	5.09	4.1	6.22	6.35	2.0
Bromide	8.34	7.90	5.6	9.80	10.21	4.0
Chlorate	9.21	8.56	7.6	10.53	10.90	3.4
Nitrate	10.68	10.21	4.6	12.76	12.63	1.0
Ethanesulfonate	1.61	1.50	7.3	—	—	—
Propanesulfonate	—	—	—	2.22	2.12	4.7
Butanesulfonate	2.07	2.03	2.0	2.56	2.82	9.2
Mean of error (%):			4.3			4.2

efficients. Table 5 shows the individual deviations between the measured (V_{meas}) and predicted (calculated, V_{calc}) retention volumes for all anions as typical examples. The results are summarized for BSA/PSA and PSA/ESA systems, respectively. The errors are given as absolute values of the relative differences, according to the expression $(|V_{\text{calc}} - V_{\text{meas}}|)/V_{\text{meas}}$. These values are given in the last column of the table for each analyte ions. A good agreement could be obtained in the comparison of observed and calculated retention. This conclusion is also supported by the comparative results of Fig. 5: The slope of the function of BSA/PSA system is 1.051. The correlation coefficient calculated for the 37 data pairs is 0.9982. These results confirm the validity of the proposed model and the reliability of the selectivity constants determined. However, it should be mentioned that typically higher errors are experienced in prediction of retention data of fluoride ions. It is due to the fact, that the retention time for fluoride is very short, its peak comes close to the injection peak. Peak disturbance and co-elution occurs at higher eluent concentrations.

The principle of the eluent selection is also illustrated in Fig. 6. Two simultaneous effects are predicted for the propanesulfonate eluent from the measured values of net retention volumes of anions eluted by butanesulfonate eluent. Not only the type of the eluent anion but also its concentration can be changed. The curves show the effect of the eluent concentration on the net retention volume. From Eq.

(4b) $(V_{N,A})_{E_2}$ vs. $[E_2]$ relation gives hyperbolas for each single charged anions determined based on relation: $(V_{N,A})_{E_2}[E_2] = K_{A/E_2}QX$. The significant

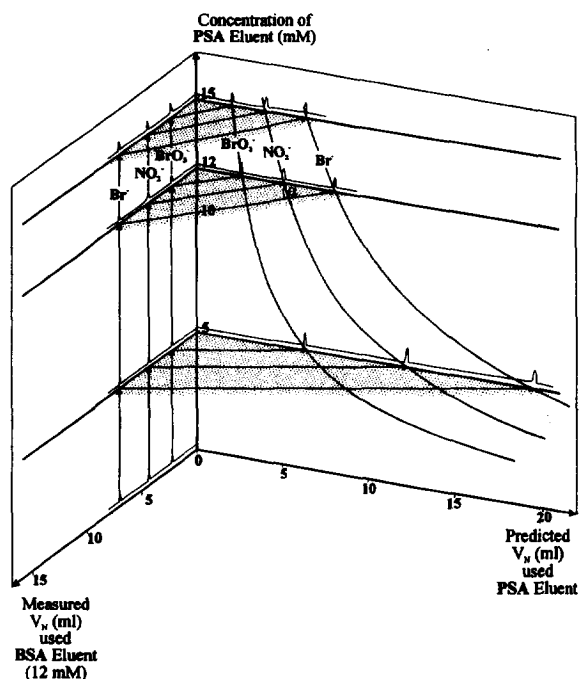


Fig. 6. Method for estimating retention volumes, $[(V_{N,A})_{PSA}]_{\text{calc}}$ in propanesulfonate from measured retention data, $[(V_{N,A})_{BSA}]_{\text{meas}}$ in butanesulfonate eluent at different eluent concentration (5, 12, 15 mM). The position of V_N values using propanesulfonate eluent are determined by the α according to Eq. (8), from which we have $\text{tg } \alpha = K_{PSA/BSA}[PSA]/[BSA]$.

shift of retention expected by the hyperbolic behaviour for analytes. The 'plateau' regions represent the various concentration of the second eluent. Plots can be drawn at each eluent concentration to determine the unknown retention volumes for an anion in a new type of eluent.

Another way of representing the retention process graphically is shown in Fig. 7 where a 'retention nomogram' is drawn for five eluent components of homologous series. The figure is based on the model discussed above. Horizontal dashed lines represent the baseline of chromatograms on which peaks are at given retention volumes corresponding to the level of actual inter-eluent coefficient. The values of $K_{BSA/E}$ are obtained from the preliminary experiments. On the diagrams appear the slope of β lines representing

analytes as a function of its retention volumes. The intersection of these lines with horizontal dashed lines give the position of the actual V_N . Retention volumes of analytes decrease steadily as the alkyl-chain length of homologous series of alkanesulfonates increases. These effects can be attributed to the stronger eluent power of the next eluent than that of the first one.

4.5. Practical aspects of eluent selection system

The retention nomogram will help one to obtain an overall picture of a separation system using homologous series of eluent components when a priori qualitative information is required. The use of homologous series of alkanesulfonates with different

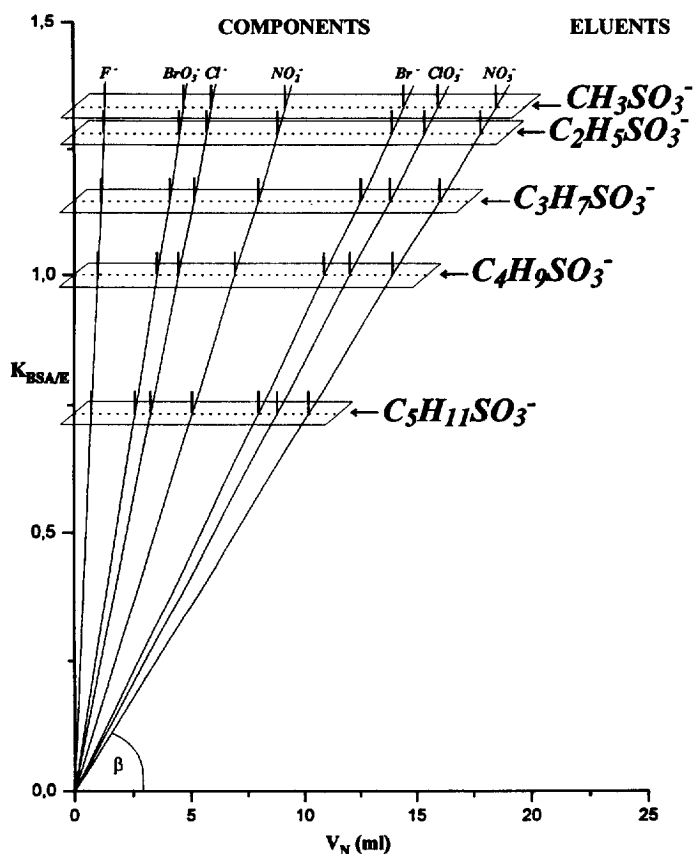


Fig. 7. Retention nomogram for comparative retention data of anions using a variety of alkanesulfonate eluents at 8 mM eluent concentration. The position of V_N values are determined by the β according to Eqs. (4a) and Eqs. (4b), from which we have $\text{tg } \beta = [E^-] / K_{A/BSA} QX$.

alkyl-chain substituents offers a useful parameter for improving the separation of anions. Retention nomogram illustrates a number of general patterns in retention behaviour that can be considered when one is optimizing eluent system.

Because an eluent such as methanesulfonate spreads the ions out, it would be useful for qualitative information of unknown sample composition. There would be more 'windows' available where ions could appear, because differences in retention are maximized. Of course, the separation time can be reduced by increasing the eluent concentration. However, there are limits to use a conductometric detector. As a consequence, in practical work eluent concentration is only allowed to range within certain limits. In general, the eluent components with short alkyl-chain (methane-, ethanesulfonate) have the advantage of providing a complete profile of all anions in a sample, which contains species in the concentration of different order of magnitude. Compared to methane-, ethane-, propane-, butane and pentanesulfonate eluents, which can be operated at wide concentration range, the resolution for more components is limited. As an other consideration, the conductance of the eluent can be minimized by alkyl-chain length, in the interests of maximizing signal-to-noise ratio. We can conclude that the retention can be selectively controlled by the type and concentration of homologous series of alkanesulfonates. This ability can have significance in many chromatographic problems.

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References

- [1] P.R. Haddad and P.E. Jackson, *Ion Chromatography—Principles and Applications*, Journal of Chromatography Library, Vol. 46, Elsevier, Amsterdam, 1990.
- [2] P. Hajós, O. Horváth and V. Denke, *Anal. Chem.*, 67 (1995) 434.
- [3] Gy. Fóti, P. Hajós and E.sz. Kováts, *Talanta*, 41 (1994) 7.
- [4] P. Hajós, G. Révész, C. Sarzanini and G. Sacchero, *J. Chromatogr.*, 640 (1993) 15.
- [5] P. Hajós, G. Révész, O. Horváth, J. Ppear and C. Sarzanini, *J. Chromatogr. Sci.*, 34 (1996) 291.
- [6] J. Madden, P.R. Haddad and P. Hajós, *Trends Anal. Chem.*, 15 (1996) 531.
- [7] Gy. Fóti, G. Révész, P. Hajós, G. Pellaton and E.sz. Kováts, *Anal. Chem.*, 68 (1996) 2580.
- [8] Landolt-Börnstein: *Zahlenwerte und Funktionen aus Physik-Chemie-Astronomie-Geophysik und Technik; Eigenschaften der Materie in Ihren Aggregatzuständen*, 7. Teil, Elektrische Eigenschaften II; Springer, Berlin, Göttingen, Heidelberg, 1960.
- [9] B. Chu, D.C. Whitney and R.M. Diamond, *J. Inorg. Nucl. Chem.*, 24 (1962) 1405.