Journal of Chromatography, 360 (1986) 1–12
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 511

INDUCED PEAKS AND THE RETENTION MECHANISM IN ION-INTERACTION REVERSED-PHASE LIQUID CHROMATOGRAPHY OF INORGANIC ANIONS

W. E. HAMMERS*, C. N. M. AUSSEMS and M. JANSSEN
Laboratory for Analytical Chemistry, State University, Croesestraat 77A, 3522 AD Utrecht (The Netherlands)

(First received October 31st, 1985; revised manuscript received January 13th, 1986)

SUMMARY

The mechanism of ion chromatography with a non-polar stationary phase and an hydrophobic ion-interaction reagent in the eluent, to augment the retention of inorganic anions, has been investigated. Ion pairing, ion exchange and double-layer ionic adsorption were examined as possible processes that may control the retention of the anions. The phenomenon of induced (system) peaks is qualitatively explained and related to the retention mechanism. The merits of benzyltributylammonium acetate as an ion-interaction reagent for the analysis of inorganic anions are briefly evaluated and compared with those of some other reagents used for anion analysis.

INTRODUCTION

Ion chromatography has been rapidly developed into a versatile high-performance liquid chromatographic (HPLC) technique with many applications, in particular in environmental and pharmaceutical analysis. Various modes can be distinguished with respect to the column configuration, type of resin and detection method[1]. This paper deals with the separation of inorganic anions on a reversed-phase adsorbent with an eluent containing a hydrophobic, UV-absorbing cationic reagent dissolved in an aqueous buffer. The reagent is physically adsorbed to the adsorbent surface and retains the solute anions in the column. Due to UV absorption by the eluent, the emergence of a solute is revealed either by a positive or a negative detector response, depending on the eluent composition. This technique is attractive because it is cheap, simple and flexible to operate and to optimize, and usually more sensitive than single-column ion chromatography with conductivity detection[2]. However, a drawback is the occurrence of one or more induced (system) peaks that may interfere with solute peaks, or cause an increase in the total analysis time.

In the ion chromatographic analysis of hydrophobic organic ions the phenomenon of induced peaks has been discussed by Bidlingmeyer and co-workers[1,3], Strahanan and Deming[4], Denkert *et al.*[5] and Hackzell and Schill[6]. The occurrence of induced peaks due to injection of inorganic anions has not yet been described in

0021-9673/86/$03.50

relation to the retention mechanism. In this paper, ion pairing[7,8], ion exchange[7,9] and double-layer ionic adsorption[1,3,10] will be examined as possible mechanisms.

Though this paper mainly deals with mechanistic questions, some attention will be paid to practical aspects.

THEORETICAL

In the following, the ion-interaction reagent (B^+A^-) is denoted by BA, the buffer salt (Na^+A^-) by NaA, the buffer acid by HA and the solutes by NaZ. The reagent is benzyltributylammonium acetate, the buffer is an aqueous solution of sodium acetate and acetic acid and the analytes (Z) are univalent inorganic anions. The concentrations, c, of the various components of the system are expressed in mol per g of adsorbent or eluent. It is tentatively assumed that only the hydrophobic ions B are adsorbed to the adsorbent surface, either as $\overline{BA}$ or as $\overline{BZ}$ (the bar denotes the adsorbed state), where the anions A and Z are adsorbed in the diffuse part of the double layer. In terms of the Stern–Gouy–Chapman theory, we assume that the ions B are located in the inner Helmholtz plane (IHP) and that the positions of closest approach between the ions B and A or Z are in the outer Helmholtz plane (OHP), *i.e.*, one hydrated anion plus cation radius remote from the IHP. Although adsorption in a (diffuse) double layer ought to be described in terms of surface excess concentrations, we prefer simply to use concentrations in this work because this will not have any impact on the conclusions and is more convenient. According to Lundgren and Schilt[11] the adsorption of salts, such as BA, on an hydrophobic adsorbent can be described with a Langmuir isotherm

$$c_{\overline{BA}} \equiv K_{\overline{BA}} c_B c_A c_R = K_{\overline{BA}} c_B c_A c_{R0}/(1 + K_{\overline{BA}} c_B c_A) \quad (1)$$

where c_R and c_{R0} represent the actual and the maximum unoccupied adsorbent surface area, expressed in mol of $\overline{BA}$ per gram of adsorbent, respectively, and $K_{\overline{BA}}$ is the adsorption coefficient of BA. The capacity ratio, k, of BZ is given by

$$k \equiv \beta c_{\overline{BZ}}/(c_Z + c_{(BZ)}) = \beta c_{\overline{BZ}}/c_Z(1 + K_{(BZ)} c_B) \quad (2)$$

where β is the ratio of the weights of the adsorbent, W_a, and the eluent, W_m, in the column, and $K_{(BZ)}$ is the ion-pair formation constant of BZ in the eluent (the brackets denote an ion pair and BZ without brackets a pair of ions). Combination of eqns. 1 and 2 gives:

$$k = \beta K_{\overline{BZ}} c_B c_{R0}/(1 + K_{\overline{BA}} c_B c_A)(1 + K_{(BZ)} c_B) \quad (3)$$

Suppose that the retention of Z is governed by the adsorption of ion pairs (BZ) present in the eluent, then it holds that $K_{(BZ)} c_B \equiv c_{(BZ)}/c_Z \gg 1$. In that instance eqn. 3 becomes:

$$k(\text{ip}) = \beta K_{\overline{BZ}} c_{R0}/K_{(BZ)}(1 + K_{\overline{BA}} c_B c_A) \quad (4)$$

However, when ion association in the eluent is not significant, $K_{(BZ)} \approx 0$, and k may be described in terms of an ion-exchange model. It follows from eqn. 3 that:

$$k(\text{ie}) = \beta K_{\overline{BZ}} c_B c_{R0}/(1 + K_{\overline{BA}} c_B c_A) \quad (5)$$

The double-layer ionic adsorption model, outlined by Cantwell[10] and based on the Stern–Gouy–Chapman theory, gives essentially the same equation for k as the ion-exchange model (eqn. 5), but expressed in surface excess concentration of BA. Therefore, it suffices to deal with the case wherein the anions Z are supposed to be adsorbed in the IHP. In that case, k is given by[10]:

$$\log k \approx a_Z + b\sqrt{c_A} \quad (6)$$

Unfortunately, this equation cannot readily be verified under practical chromatographic conditions, because the parameters a_Z and b will be constant only at very large ionic strengths of the eluent. However, specific adsorption of small inorganic anions in the IHP is not plausible as it would imply an extensive dehydration of these anions, which is energetically unfavourable. For that reason, Cantwell[10] assumed that the retention of small hydrophilic ions in chromatographic systems of the type examined in this work is governed by an ion-exchange mechanism.

Next, some methods will be mentioned to distinguish between ion pairing and ion exchange. Ion pairing will contribute significantly to the retention of Z only when $K_{(BZ)}$ is sufficiently large. In that case the degree of ion association, $1 - \alpha$, can readily be estimated from Ostwald's law. For a diluted solution of BZ in water:

$$K_{(BZ)} = (1 - \alpha)/\alpha^2 c_{BZ} \quad (7)$$

Provided c_{BZ} is sufficiently small, the molar conductivity, Λ, of this solution is proportional to that at infinite dilution, Λ_0:

$$\Lambda = \alpha\Lambda_0 \quad (8)$$

Elimination of α in eqns. 7 and 8 gives:

$$\Lambda c_{BZ} = \Lambda_0^2/\Lambda K_{(BZ)} - \Lambda_0/K_{(BZ)} \quad (9)$$

Values for Λ_0 and $K_{(BZ)}$ can be estimated from a plot of Λc_{BZ} *versus* Λ^{-1} for a series of BZ solutions. Subsequently, α can be calculated from eqn. 7. This method gives reliable results for weak electrolytes, such as acetic acid, in water provided the concentrations are $\leqslant$ 10 mmol/l[12].

In diluted solutions of (moderately) strong electrolytes the above mentioned Arrhenius theory is not applicable due to long-range electrostatic interactions. These interactions are taken into account by the Debye–Hückel–Onsager theory. According to Onsager

$$\Lambda = \alpha[\Lambda_0 - (a'\Lambda_0 + b')\sqrt{\alpha c_{BZ}}] \quad (10)$$

wherein the magnitude of the constants a' and b' depends on the temperature and the charge number of the ions[12]. For univalent ions, eqn. 10 holds for aqueous solutions wherein $\alpha c_{BZ} \lesssim 2$ mmol/l. Methods to estimate Λ_0, α and $K_{(BZ)}$ based on this equation have been outlined in detail by Davies[12].

An ion-exchange mechanism is based on the equilibrium:

$$Z + \overline{BA} \rightleftharpoons A + \overline{BZ} \qquad \text{(E1)}$$

It is evident that, when ion exchange is the only mechanism operating, no peaks will emerge for non-UV-absorbing ions, using UV detection at a suitable wavelength.

Although the above mentioned diagnostic tests seem to be straightforward, it will be shown below that a systematic examination of the induced peak phenomenon is required in order properly to describe the various processes in the column.

EXPERIMENTAL

Chemicals, eluent preparation and adsorbent characterization

The solutes were of analytical grade. Water was distilled and degassed before use by saturation with nitrogen, followed by sonication. Sample solutions of acetic acid, sodium acetate, chloride, nitrite, bromide and nitrate (50 μg anion per ml) were prepared in the eluents. The salt mixture was prepared in water. Benzyltributylammonium chloride (Fluka, Buchs, Switzerland) was quantitatively converted into the hydroxide on an Amberlite IRA 400 strong anion-exchange column. The eluate was titrated with 1 *M* acetic acid to the desired pH. Subsequently, a known amount of sodium acetate–acetic acid buffer of the same pH was added, and this solution was diluted to the desired molarity of the ion-interaction reagent in the eluent. The various eluent compositions are given in Table I. LiChrosorb 10 RP-18 (E. Merck, Darmstadt, F.R.G.) was used as reversed-phase adsorbent. It has an ODS surface concentration equal to 4.4 μmol/m^2 and a BET specific surface area of about 171 m^2/g[14].

Apparatus and procedures

The liquid chromatograph consisted of a Kipp Analytica 9208 HPLC pump, a six-port Valco sample valve equipped with a 50-μl loop and an Altex M 153 UV detector. Measurements were carried out at 254 nm. The background absorbance by the eluent was subtracted with a simple d.c.-offset circuit. The column (precision-bore stainless steel, 15 cm × 4.6 mm I.D.) was surrounded by a water-jacket and thermostatted to 25.0 ± 0.1°C. The column was packed by a viscous-slurry technique. The slurry [10% (w/w) LiChrosorb RP-18 in 10 ml of toluene–dioxane (1:1) and 20 ml of cyclohexanol] was degassed and homogenized by sonication, and forced into the column with 300 ml of hexane at 500 bar from a home-made slurry reservoir using a Haskel MCP 110 pump. In order to stabilize the packed bed, 100 ml of acetonitrile and 200 ml of methanol were consecutively flushed through the column. Thereafter, the column was disconnected and the pump was flushed with water to achieve an abrupt eluent switch from methanol to water in the column. The aim of this procedure will be explained below.

The void volume, V_m, of the column was estimated from the onset of retention of the "water" peak. Capacity ratio data were calculated from the net retention volume, $k = V_N/V_m$. Samples of 2.5 μg of the above mentioned anions, the benzyltributylammonium cation and of acetic acid were injected. Chromatograms of the mixture of the sodium salts in water were also recorded. The reproducibility of the obtained peak patterns was tested to verify that true equilibrium was attained in the column after an eluent switch.

RESULTS AND DISCUSSION

Retention mechanism and induced peaks

Capacity ratio data for the examined anions obtained with the various eluents are presented in Table I. Data for fluoride, iodide and sulphate are not given. The fluoride peak coincides with the BA peak. Iodide could be eluted within reasonable time only at the highest acetate concentrations used, whereas the sulphate peak emerges only at such large sample sizes that the column was evidently overloaded.

The possibility of an ion-pairing mechanism will be considered first. Fuoss and Kraus obtained accurate ion-pair formation constants for tetrabutylammonium bromide ($K = 0.62$ l/mol)[15], tetrabutylammonium iodide ($K = 2.70$ l/mol)[15] and for tetraisoamylammonium nitrate ($K = 1.20$ l/mol)[16]. From these data it can be calculated that the α values at a salt concentration of 1 mM in water are 0.999, 0.997 and 0.999, respectively. Such large α values are obtained for strong electrolytes, such as potassium nitrate. For benzyltributylammonium chloride we obtained a straight line plot of Λ *versus* $\sqrt{c}$, indicating that also for this salt $\alpha \approx 1$ (see eqn. 10). From these results it can be concluded that ion pairing in the eluent cannot contribute significantly to the retention of the inorganic anions examined. Water structure-enforced ion association of organic ions, as discussed by Diamond[17], can be expected for the above mentioned salts only at much higher concentrations than currently applied in chromatographic practice.

TABLE I

COMPOSITION AND pH DATA FOR THE EXAMINED ELUENTS, CAPACITY RATIOS, k, AND HYDRATED RADII, r_h, FOR SOME UNIVALENT ANIONS

Eluent	*Concentrations (mmol/l)*			*pH*	*k*				
	B	*A*	*HA*		*A*	*Cl*	NO_2	*Br*	NO_3
1	3.0	3.0	3.1	4.70	5.6	7.4	10.5	11.9	16.1
2	3.0	11.0	9.4	4.80	3.8	4.0	4.7	5.3	7.3
3	3.0	3.0	0.5	5.60	4.4	6.3	8.6	9.8	13.1
4	3.0	3.0	0.1	6.25	3.9	5.1	7.1	8.2	10.9
5	4.0	5.0	5.0	4.75	6.3	23.0	33.0	43.0	
6	4.0	15.0	15.0	4.75	5.0	12.0	17.4	23.3	31.7
7	4.0	25.0	25.0	4.75	4.1	8.0	11.4	15.6	22.1
8	4.0	35.0	35.0	4.75	3.5	6.2	9.2	12.6	18.5
r_h (Å)[13]					4.0	3.9	3.7	3.6	3.1

Before discussing the possibility of an ion-exchange mechanism, some attention will be paid to the adsorption of the ion-interaction reagent BA to the RP-18 layer. The $\overline{BA}$ adsorbed from eluent 7 (see Table I) was collected by flushing the column with water. The amount of BA in the eluate was determined from a calibration plot and appeared to be equal to 1.1 mmol per g of adsorbent, or 6.4 μmol/m^2. This high surface concentration indicates that the ions B are adsorbed as a dense monolayer because only 26 Å^2 per ion is available on the RP-18 layer. The amount of adsorbed organic salt depends on the hydrophobicity and the charge number of the adsorbed ion, but also on the type and charge number of the counter ion in the eluent[3]. In the present chromatographic system it is expected that an increase of the concentration of the non-adsorbable counter ions A in the eluent will cause a compression of the diffuse part of the double layer. This is due to the fact that the attraction of the counter ions is increased, whereas the thermal diffusion of these ions is not strongly affected by an increase in c_A. As a result of the increased concentration of counter ions in or close to the OHP, the (electrical) potential decay, on going from the OHP to the bulk eluent, is steeper due to the increased screening effect on the counter ions further from the OHP. The increase in the number of ions A in the double layer is compensated by an increase in the amount of ions B in the IHP. The adsorption of B is facilitated by a reduction in the electrostatic repulsion forces between the ions B in the IHP due to the enhanced charge density of the counter ions in the OHP. Obviously, only steric restrictions seem to control the maximum amount of $\overline{BA}$ in the present system.

The possibility of ion exchange in the diffuse part of the double layer as the sole retention mechanism can be ruled out because peaks emerge. On the other hand, the k data can be described very well with eqn. 5 as is shown in Fig. 1 where straight line plots of k^{-1} *versus* c_A are presented. It seems logical to examine the phenomenon of induced peaks in order to explain this apparent contradiction of results.

A schematic summary of the various chromatograms is given in Fig. 2. In order to give a comprehensive description of the rather capricious behaviour of the induced peaks, only the most relevant quantitative aspects of these chromatograms are shown. Thus, the various peak sizes are divided into three categories and the peak size variations will be discussed only incidentally.

(1) Injection of BA, dissolved in the eluent. In all cases a very small negative void-volume peak and a relatively large positive BA peak is observed. This pattern is expected because the injected BA is dissolved in the eluent. The retention of BA decreases with increasing c_A, as expected for BA adsorption according to a convex adsorption isotherm (see eqn. 1).

(2) Injection of NaA, dissolved in the eluent. In all cases a large negative void-volume peak is obtained, and a large positive peak with the same retention as the BA peak. This result is predicted by the double-layer ionic adsorption model. As a net result of the injection of A the equilibrium

$$A + B \rightleftharpoons \overline{BA} \qquad \text{(E2)}$$

will shift to the right-hand side at the top of the column. Consequently, c_B locally becomes smaller than in the eluent. This deficiency of B is eluted and recorded as a (negative) vacancy peak with a similar retention to that of the void-volume peak.

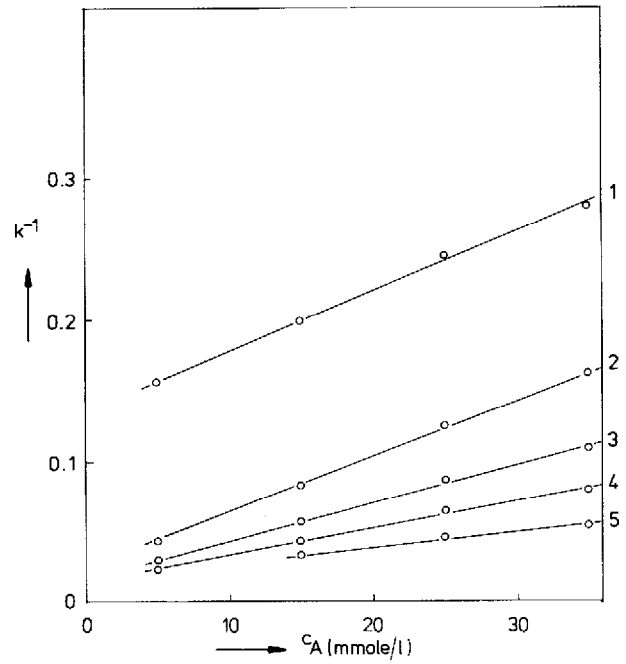

Fig. 1. Plots of experimental k^{-1} values *versus* c_A for the analyte anions acetate (1), chloride (2), nitrite (3), bromide (4) and nitrate (5). The k data were obtained with eluents 5–8 (see Table I).

The local excess of adsorbed BA at the top of the column is similarly eluted as an injected amount of BA.

(3) Injection of NaZ, dissolved in the eluent. In all cases a negative void-volume peak, a negative BA peak and a positive solute peak is obtained. This pattern can be explained when the equilibrium

$$Z + B \rightleftharpoons \overline{BZ} \qquad \text{(E3)}$$

is established at the top of the column. Analogously to a shift of E2 to the right-hand side, this will give rise to a negative void-volume peak and a positive BZ peak. This process is underestimated by double-layer ionic adsorption theory, but appears to be of crucial importance in this mode of ion chromatography. The occurrence of a negative BA peak can be explained as follows. As a result of the adsorption of BZ, c_B at the top of the column will decrease and therefore E2 will shift to the left-hand side. The resulting deficiency in B in the IHP is eluted and recorded as a vacancy BA peak with similar retention to that of a positive BA peak. If on adsorption of BZ an equimolar amount of BA were to be desorbed, the net result would be similar to that of an ion-exchange process according to E1 and no peaks would be observed. This is clearly not the case, even at the highest concentrations of A and B applied in the eluent. Fig. 3 shows that the size of the BA peak increases with increasing solute retention. This result is compatible with the above proposed shifts of the equilibria E2 and E3, for k_Z is proportional to the ratio $c_{\overline{BZ}}/c_Z$. The larger this ratio, the more

BA has to be desorbed to re-establish the equilibrium E2 at the top of the column, and the larger the vacancy BA peak will be.

From Table I it follows that the k values increase with decreasing radius of the hydrated solute anions. Cantwell and Puon[18] reported a similar influence of the counter-ion type on the k value of the benzylammonium cation on XAD-2, using chloride, bromide and perchlorate as counter ions in the eluent. These authors gave four possible explanations for this phenomenon. A smaller radius of the hydrated counter ions will result in a decrease in the distance between the (positive) charge surface and the OHP. As a result the capacitance of the double layer will increase and cause an increase in the charge density in the IHP at a constant surface potential. This effect may be amplified by the polarization of the anions which appears to increase as the crystal radii of the anions increase. Another explanation may be that water structure effects play a rôle. It is well known that water adjacent to a hydrophobic surface is more structured than bulk water. This structure will be destroyed to an extent depending on the "water structure breaking" ability (chaotropic character) of the anion. Therefore, the transfer of BZ from the eluent to the double layer is accompanied by a positive entropy change, and thus a negative change in the free energy of adsorption. In the remaining explanations, (partial) dehydration of the

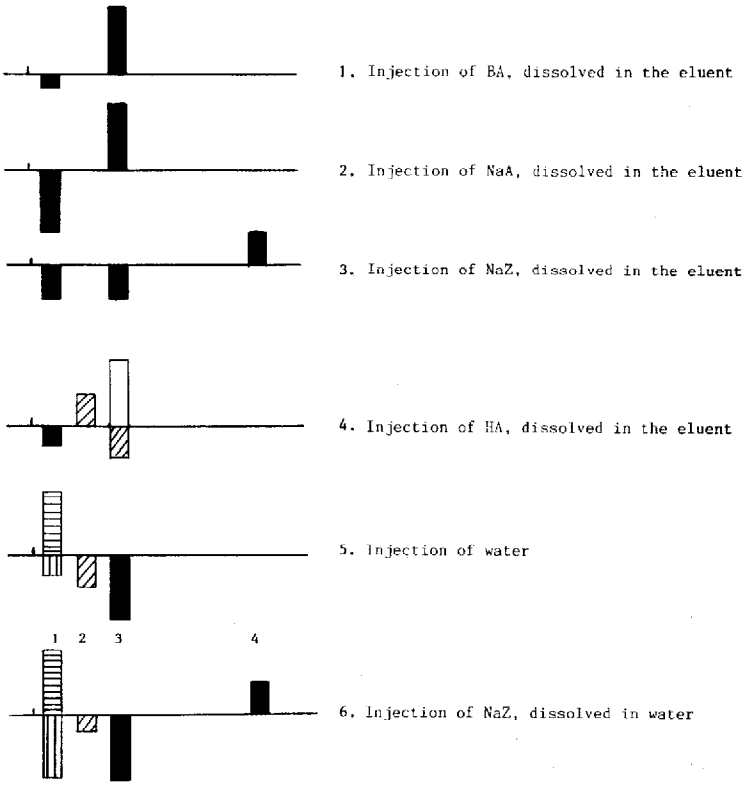

Fig. 2. A schematic presentation of the various peak patterns. Void-volume peak (1), HA peak (2), BA peak (3) and BZ peak (4), observed under the following experimental conditions: ■, in all eluents; ▨, if pH $\lesssim$ pK_a(HA); □, if pH > pK_a(HA); ▥, if $c_A + c_{HA} \lesssim 7.1$ mmol/l; ▤, if $c_A + c_{HA} \gtrsim 8.6$ mmol/l.

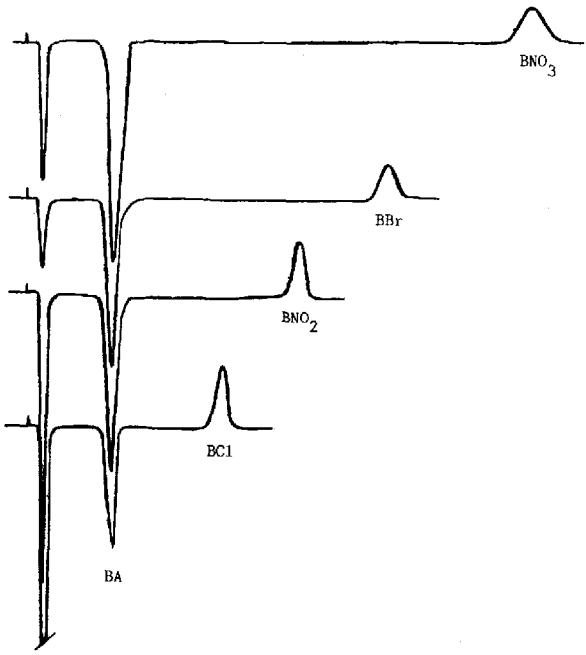

Fig. 3. Chromatograms of the various anions obtained with eluent 6 (see Table I).

counter ions has to be presupposed, which seems less plausible. It is noted that ion exchange on conventional polystyrene–divinylbenzene resins can be described very well in terms of a Donnan equilibrium provided hydrated ion radii are applied[19,20].

Returning to Fig. 3, there are a few other quantitative aspects to be considered. The first is that the size of the BZ peak areas do not increase with increasing capacity ratio. This fact seems to be inconsistent with the above explanation of the relationship between the size of the BA peak and k. The second is that the sum of the negative peak areas is not equal to the peak area of the positive BZ peak, but considerably larger. This is not expected for a sample of NaZ dissolved in the eluent. The only plausible explanation seems to be that the occurrence of peaks is mainly due to the disturbance of the eluent–adsorbent system at the top of the column where c_Z is relatively large. However, as BZ is eluted and c_{BZ} decreases due to peak broadening, the mechanism based on the above mentioned shifts of E2 and E3 becomes less important and ion exchange in the diffuse part of the double layer obviously becomes a more favourable process. In this manner a large portion of BZ (and to a less extent of BA) is not detected as a peak, but merely gives rise to a slight increase in the background signal. Although this explanation is somewhat speculative from a theoretical point of view, it is compatible with the fact that the k values can be described with eqn. 5. Therefore we conclude that the retention of the anions is mainly controlled by an ion-exchange mechanism, but that the Stern–Gouy–Chapman theory is required to explain the occurrence of peaks.

Finally, it is noted that c_A is in equilibrium with c_{HA} and that the amount of BA can increase with increasing c_{HA}, due to a shift of E2 to the right-hand side in

combination with a dissociation of HA. This may explain why the k values obtained with eluent 1 are larger than those obtained with eluents 3 and 4 (see Table I).

(4) Injection of HA, dissolved in the eluent. In the chromatograms discussed so far an HA peak did not emerge because the injected samples had the same pH as the eluent. When HA is dissolved in an eluent with a pH > pK_a(HA), it will dissociate in the sample solution. As a result, a chromatogram will be obtained that is similar to that due to the injection of NaA dissolved in the eluent (see section 2). When the eluent pH $\leqslant$ pK_a(HA), a positive HA peak and a vacancy BA peak is obtained. Obviously, HA is able to desorb BA to some extent if c_{HA} is sufficiently large:

$$HA + \overline{BA} \rightleftharpoons \overline{HA} + BA \qquad (E4)$$

Desorption will be strongest at the top of the column but will continue during the elution of HA. Consequently, two (tailed) peaks of opposite signs are observed.

(5) Injection of water. In all cases a large vacancy BA peak is obtained as a result of the decrease in c_A and c_B at the top of the column and the accompanying desorption of $\overline{BA}$ according to E2. Empty sites due to desorption of $\overline{HA}$ will largely be reoccupied by the more hydrophobic cations B. Consequently, c_B within an HA band will be smaller than in the surrounding eluent, and a negative HA peak is expected. Such a peak is indeed observed, provided the eluent pH $\leqslant$ pK_a(HA). The void-volume peak is large and positive or small and negative when the total acetate concentration (including HA, see section 4) is $\geqslant$ 8.6 or $\leqslant$ 7.1 mmol/l, respectively.

This result is explained as follows. On injection of water, $\overline{BA}$ will be desorbed and $c_A \approx c_B$ in the water band at the top of the column. During the elution of water, c_A and c_B within the water band will gradually increase till equilibrium E2 is re-established. Since at high total acetate concentrations more BA is adsorbed than at low acetate concentrations, c_B within the water band can become larger than in the surrounding eluent. This explains the occurrence of a positive "water" peak at high total acetate concentrations. At smaller acetate concentrations it is expected that c_B within the water band increases less rapidly on elution because of the convex shape of the adsorption isotherm. A negative void-volume peak will be observed when c_B cannot grow to the level in the surrounding eluent before the water band leaves the column.

(6) Injection of NaZ, dissolved in water. From the foregoing it is expected that the injected water will cause either a positive or a negative void-volume peak (depending on the total acetate concentration), a negative HA peak when the eluent pH $\lesssim$pK_a(HA) and a negative BA peak. Upon this pattern, will be superposed the peaks that emerge on injection of NaZ dissolved in the eluent to give the final chromatogram. It is worth noting that the BZ peaks are roughly a factor of 1.5 larger than those obtained for salt samples dissolved in the eluent.

It is concluded that a mixed retention mechanism is operating, notwithstanding the fact that the k values can be described satisfactorily with a single mechanism, *i.e.*, ion exchange. The other mechanism is most important at the top of the column and gives rise to the emergence of peaks that are the result of shifts in equilibria controlled by the electrochemical conditions in the column. The mechanism as a whole is rather inefficient with respect to UV-detection sensitivity.

Practical aspects

The results presented above were obtained on a "rough" (R) RP-18 layer. Such a layer can be obtained when a swollen RP-18 layer in contact with methanol collapses due to an abrupt eluent switch from methanol to water. The instant collapse of the layer gives rise to a rough surface. A "smooth" (S) layer of regularly associated ODS chains can be obtained by heating at 80°C the layer in contact with water, followed by slow cooling to ambient temperature[21]. For benzene, nitrobenzene and phenol the ratio k_R/k_S of the k values on the two layers is equal to 1.11, 1.19 and 1.29, respectively[21]. For the solutes examined in this work, $k_R/k_S = 1.67$. The larger retention on the R layer is ascribed to the better solute–adsorbent contact, but is expected only on reversed-phase adsorbents with a sufficiently large surface concentration of bound alkyl chains[21]. Ion-interaction chromatography on a R layer is recommended in view of the larger selectivity.

The ion-interaction reagent used in this work is of moderate hydrophobicity which allows rapid analysis of univalent anions, provided a rather hydrophilic counter ion, such as acetate, is applied. Addition of counter ions of a higher hydrophobicity is required to elute divalent anions within reasonable time. However, in our case this is not practical because the use of a stronger eluent decreases the resolution of the univalent anions. This problem can be solved in two ways. Barber and Carr[22] used α-naphthylmethyltributylammonium acetate as the ion-interaction reagent, in combination with hexanesulphonate as counter ion, in a sodium acetate–acetic acid buffer. They obtained a good separation of the univalent anions and sulphate within 6 min. A similar result was reported by Molnár *et al.*[8], who used tetrabutylammonium hydroxide dissolved in a phosphate buffer (pH = 6.7) as the eluent. In this system the divalent counter ions in the eluent strongly reduce the retention of sulphate ions to about that of nitrite ions. The reagent is commercially available. Promising results (at the ng level) have been obtained by us with this eluent. They will be published soon.

The detection limits achieved with the present system are about equal to 25 nmol when eluent 7 is applied. This result is rather poor, but can be improved when short columns packed with 5-μm RP-18 particles are used. Barber and Carr[22] achieved a detection limit of about 1 nmol. This result can (at least partly) be ascribed to the large molar extinction coefficient of the naphthyl group. Similar low detection levels can be attained when a non-UV-absorbing ion-interaction reagent is used in combination with UV-absorbing counter ions, as will be shown in a future publication.

CONCLUSIONS

Ion chromatography on a "rough" LiChrosorb RP-18 adsorbent with an aqueous 7.5 mM acetate–acetic acid buffer (pH = pK_a), containing 4 mM of benzyltributylammonium cation, as the eluent, and UV detection at 254 nm is a suitable technique for analysis of univalent anion samples at the nmol level.

A systematic study of the induced peak patterns can reveal interesting details of column processes in ion chromatography. The retention of inorganic anions in the present system can be described with the double-layer ionic adsorption model, and is due to a mixed mechanism. The occurrence of solute peaks is a result of a local

disturbance of the adsorption equilibrium of the reagent cations in the IHP, induced by the analyte anions and controlled by the electrochemical conditions of the double layer. The capacity ratio data of the anions can be described in terms of an ion-exchange process in the diffuse part of the double layer (including the OHP).

REFERENCES

1 B. A. Bidlingmeyer, S. N. Deming, W. P. Price, Jr., B. Sachok and M. Petrusek, *J. Chromatogr.*, 186 (1979) 419.
2 R. A. Cochrane and D. E. Hillman, *J. Chromatogr.*, 241 (1982) 392.
3 B. A. Bidlingmeyer and F. V. Warren, Jr., *Anal. Chem.*, 54 (1982) 2351.
4 J. J. Strahanan and S. N. Deming, *Anal. Chem.*, 54 (1982) 1540.
5 H. Denkert, L. Hackzell, G. Schill and E. Sjögren, *J. Chromatogr.*, 218 (1981) 31.
6 L. Hackzell and G. Schill, *Chromatographia*, 15 (1982) 437.
7 W. E. Melander and C. Horváth, *J. Chromatogr.*, 201 (1980) 211.
8 S. Molnár, H. Knauer and D. Wilk, *J. Chromatogr.*, 201 (1980) 225.
9 J. L. M. van de Venne, J. L. H. M. Hendrikx and R. S. Deelder, *J. Chromatogr.*, 167 (1978) 1.
10 F. F. Cantwell, in J. A. Marinsky and Y. Marcus (Editors), *Ion Exchange and Solvent Extraction*, Marcel Dekker, New York, 1985, p. 339.
11 J. L. Lundgren and A. A. Schilt, *Anal. Chem.*, 49 (1977) 974.
12 C. W. Davies, *Ion Association*, Butterworths, London, 1962, p. 78.
13 H. L. Haller and F. B. LaForge, *J. Am. Chem. Soc.*, 59 (1937) 1675.
14 W. E. Hammers, G. J. Meurs and C. L. de Ligny, *J. Chromatogr.*, 246 (1982) 169.
15 R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, 79 (1957) 3304.
16 R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, 55 (1933) 1019.
17 R. M. Diamond, *J. Phys. Chem.*, 67 (1963) 2513.
18 F. F. Cantwell and S. Puon, *Anal. Chem.*, 51 (1979) 623.
19 G. E. Boyd and B. A. Soldano, *Z. Electrochem.*, 57 (1953) 162.
20 H. P. Gregor, *J. Am. Chem. Soc.*, 73 (1951) 3537.
21 W. E. Hammers and P. B. A. Verschoor, *J. Chromatogr.*, 282 (1983) 41.
22 W. E. Barber and P. W. Carr, *J. Chromatogr.*, 260 (1983) 89.