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Studies on the separation of hydronium ion using surfactant-modified reversed-phase stationary phases and eluents containing an acidified electrolyte

Pavel N. Nesterenko[a], Paul R. Haddad[b,*], Wenzhi Hu[c]

[a]*Department of Chemistry, Moscow State University, Vorob'evy Gory GSP-3, Moscow 119899, Russia*
[b]*School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart 7001, Australia*
[c]*Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

Abstract

A further investigation of a chromatographic system allowing determination of hydrogen ions is reported. For this purpose an octadecylsilica column dynamically modified with sodium dodecylsulfate (SDS) or lithium dodecylsulfate (LDS) was used as stationary phase and a slightly acidified electrolyte (usually KCl)–SDS solution was used as the eluent. The concentration of SDS, KCl and the acidity of the eluent affected the structure of aggregates formed by the molecules of dodecylsulfate at the surface of the stationary phase. These aggregates of dodecylsulfate were found to be responsible for the appearance of a chromatographic peak attributed to the presence of H_3O^+ ions in a sample. Other cations in the sample could be separated in the same manner, permitting the simultaneous separation of monovalent cations from H_3O^+. The detection limit for H_3O^+ ions was $2.25 \cdot 10^{-6}$ M using an eluent comprising 0.3 mM LDS, 50.0 mM KCl and 0.10 mM H_2SO_4. The proposed method is shown to be applicable for the determination of free H_3O^+ ions in aqueous solutions of strong acids.
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1. Introduction

A very important task in analytical chemistry is the determination of the concentration of free hydrogen ions (H_3O^+). Potentiometric measurement using H_3O^+-selective electrodes [1,2] is the mostly widely used method although some other approaches (e.g.

NMR and spectrophotometric methods) are also applicable [3–7]. In the pH range from 2 to 12, the accuracy of potentiometric measurement of H_3O^+ is usually about 95% [1,8]. This arises from the difficulty in calculating the absolute value of pH of the buffers used to calibrate the electrodes, with accuracy being not higher than 0.01 pH units, and the difficulty in minimizing the residual liquid-junction potential. This level of accuracy is reasonable for normal H_3O^+ measurements, but errors become more significant in the measurement of small changes in the concentration of H_3O^+ ions.

*Corresponding author. Tel.: +61-3-6226-2179; fax: +61-3-6226-2858.

E-mail addresses: paul.haddad@utas.edu.au (P.R. Haddad), hu@ees.hokudai.ac.jp (W. Hu).

As a possible alternative to potentiometric measurements, separation of H_3O^+ by ion chromatography (IC) followed by conductivity detection offers several potential advantages for the determination of H_3O^+ ions. First, H_3O^+ ions have an extremely high equivalent ionic conductance ($\lambda_+ = 350$ S cm^2 equiv.$^{-1}$) in comparison to other cations, which can provide very sensitive conductivity detection. Second, H_3O^+ can potentially be separated from anions present in the samples, so that possible buffering effects caused by these anions (especially anions of weak acids) are avoided and matrix effects which influence the junction potential of pH electrodes can be minimised. Third, the IC stationary phase is continuously cleaned by the flowing eluent, which excludes possible contamination effects from a previous sample. Finally, additional information on the concentration of other cations in the sample can be also obtained as their complete separation from each other as well as from H_3O^+ is possible.

De Borba et al. [9] have demonstrated the separation of H_3O^+ from other cations using a conventional sulfonated cation-exchanger and an aqueous solution of sodium ethanesulfonate as the eluent. Some problems were observed due to the presence of residual carboxylate groups arising from the reactions used to introduce sulfonate groups onto the polystyrene–divinylbenzene (PS–DVB) matrix in the stationary phase. These effects could be overcome by addition of H_3O^+ to the eluent to protonate the carboxylate groups. However, this step increased the detection limit for H_3O^+ and limited the practical application of the method to samples containing higher levels of H_3O^+ than that present in the eluent. Hu et al. [10] proposed a reversed-phase octadecylsilyl (ODS) column dynamically modified with lithium dodecylsulfate (LDS) as an alternative separation medium for the determination of H_3O^+. It is interesting that separation selectivity for this dynamically modified column was different from that observed on the sulfonated PS–DVB column. Thus, Hu et al. obtained a retention order of $Na^+ < NH_4^+ < K^+ < H_3O^+$ [10], whilst De Borba et al. observed a retention order of $Li^+ < H_3O^+ < Na^+ < NH_4^+ < K^+$ [9]. This difference in the retention order of monovalent cations could be due in the latter case to the effect of residual carboxylate functionalities or due in the former case to the special selectivity attributed

to the formation of aggregates of dodecylsulfate molecules at the surface of the ODS phase.

The present study is devoted to the characterization of the separation system consisting of an ODS column dynamically modified with SDS and acidified KCl–SDS eluent in order to understand the origin of the chromatographic peak of H_3O^+ and the validity of the proposed method for the determination of sample acidity. The possible separation mechanism involved in this IC system is also considered.

2. Experimental

2.1. Apparatus

A DX-600 IC system (Dionex, Sunnyvale, CA, USA) consisting of a GS50 gradient pump, AS50 autosampler, U120 universal interface and CD25 conductivity detector was used for this study. An additional model 730 conductivity detector (Waters, Milford, MA, USA) suited for detection at high conductivity levels of the eluent and a model 210 pH meter (Activon, Sydney, Australia) equipped with a microelectrode and a custom-made flow cell were also used to monitor the conductivity and pH of the column effluent. The injection valve and chromatographic column were maintained at 30 °C. Dionex PEAKNET 6 software was used for collection and treatment of data.

2.2. Reagents

The sulfonated surfactants used to create the stationary phase had a high degree of purity (>99.99%). LDS was obtained from Wako (Osaka, Japan) and SDS from Fluka (Buchs, Switzerland). Other chemicals of analytical-reagent grade used to prepare solutions of the model analytes were also obtained from Wako. Water used throughout this study was prepared using a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Column preparation

Two ODS columns 150×4.6 mm I.D. and 250× 4.6 mm I.D. (L-column, 5 μm particle size, 120 Å

pore size, 340 m^2 g^{-1}, 17 mass% of carbon) were obtained from the Chemical Evaluation and Research Institute (Tokyo, Japan). The method used for column preparation was as described in a previous paper [10]. The chromatographic column was initially modified by pumping a 30 mM aqueous solution of SDS or LDS through the column at a flow-rate of 1.0 ml/min for about 30 min. Before use with a new eluent the chromatographic column was equilibrated until stable baseline was obtained for both conductivity and pH detectors. The amount of adsorbed LDS in the column at 40 °C after equilibration with an eluent containing 0.3 mM LDS was found to be 0.48 mmol/150×4.6 mm I.D. column (which is about 80% of the amount adsorbed at 25 °C). The amount of the adsorbed surfactant in the ODS-packed column was determined using the method described previously [11].

3. Results and discussion

3.1. Dynamic modification of ODS with dodecylsulfate

3.1.1. Aggregation of the surfactant

The main feature of the proposed method is the use of a relatively simple chromatographic system comprising an ODS column modified with dodecylsulfate molecules. The addition of strong electrolytes such as alkali metal chlorides or nitrates to the eluent at concentrations up to 50 mM, together with 0.3 mM SDS or LDS and a small amount of a mineral acid were shown in previous paper to be necessary for the appearance of a chromatographic peak which was attributed to H$_3$O$^+$ [10].

The dynamic modification of an ODS column with dodecylsulfate has also been used by Ito et al. [12,13] for IC separation and determination of ammonium, alkali- and alkaline-earth metals with an eluent comprising dilute nitric acid solutions containing 0.1–0.4 mM SDS and conductivity detection. Those authors observed two system peaks at higher concentrations of SDS [12] or after addition of 0.2–0.4 mM cerium trichloride used for indirect photometric detection [13]. Although the authors did not discuss the nature of these system peaks their appearance could be associated with dodecylsulfate

and H$_3$O$^+$. The other important observation is that these system peaks appeared only after addition of strong electrolytes to the eluent or with an increase of the concentration of SDS in the eluent. Both of these factors contribute to the stabilization of aggregates of SDS at the surface of the ODS phase.

The critical micelle concentration (CMC) of SDS in aqueous solution is 8.3 mM at 25 °C [14]. The CMC of SDS depends strongly on the concentration of electrolytes and for example, reduces to about 2.2 mM in 50 mM NaCl [14]. There is some evidence in the literature that the silica hydrocarbon interface might be important in stabilizing a densely organized structure below the CMC [15] and that the process of surfactant aggregation at the hydrophobic surfaces takes place at a critical aggregation concentration (CAC) which is much lower than the bulk-phase CMC. Moreover, an interesting phenomenon was described by Montgomery and Wirth [16] who found that a greater amount of SDS was adsorbed to a hydrophobic ODS surface for a SDS concentration just below the CMC than above the CMC. It is therefore probable that the presence of 0.2–0.4 mM SDS in an eluent containing 50 mM KCl is sufficient for the formation of aggregates at the surface ODS. These aggregates could play a role in the appearance of the hydronium peak and the observed selectivity (Li$^+$<Na$^+$<NH$_4^+$<K$^+$< H$_3$O$^+$) which is different from the conventional selectivity (Li$^+$<H$_3$O$^+$<Na$^+$<NH$_4^+$<K$^+$) known for sulfonated cation-exchangers. To evaluate the role of surface aggregates of SDS in determining selectivity, the effects of the concentration of strong electrolytes and acidity of the eluent were studied.

3.1.2. Effect of added electrolyte

The separation of lithium, sodium, ammonium and potassium using 0.3 mM SDS–10 mM H$_2$SO$_4$ as eluent was obtained in 120 min and was used as a starting point for the present investigation. In this separation, the expected negative peaks (resulting from indirect conductivity detection) for each of the analyte cations was observed, but there was no additional chromatographic peak attributable to hydronium. It is clear that the presence of 0.3 mM SDS in the eluent led to efficient dynamic modification of ODS producing a cation-exchange stationary phase of reasonably high ion-exchange capacity. The addi-

tion of strong electrolyte to the eluent at millimolar concentration levels decreased the retention times of cations and caused the appearance of an additional chromatographic peak just before the potassium peak. This was attributed to hydronium ion on the basis of a measurable pH change on a micro pH-electrode placed in a specially designed flow-cell.

It has been shown previously [10] that the nature of the strong electrolyte added to the eluent had little effect on the separation of alkali metal cations and hydronium. The choice of KCl as the added electrolyte was based on the relatively strong elution power of K^+, which resulted in a faster elution of H_3O^+. In addition the lower solubility of potassium dodecylsulfate compared with SDS can serve to stabilize the aggregates of dodecylsulfate at the surface of the stationary phase.

A typical separation of Li^+, Na^+, NH_4^+, and K^+ and H_3O^+ with conductivity detection is shown in Fig. 1. There are two negative peaks corresponding to lithium and sodium and one large positive peak corresponding to hydronium. The H_3O^+ from the sample was always detected as a positive peak with conductimetric detection. Fig. 1 differs from the separation reported by De Borba et al. [10] who used a different elution system and obtained positive chromatographic peaks for both alkali metal cations and for H_3O^+. The small negative peaks observed for Na^+ and Li^+ in Fig. 1 occurred because these ions are slightly less conducting than the K^+ ions in the eluent, and no peak was observed for NH_4^+ because its limiting equivalent ionic conductance is very close to that of K^+. The peak assigned to H_3O^+ in Fig. 1 could reasonably be attributed to displacement of K^+ ions from the dodecylsulfate aggregates at the surface of ODS since the observed retention time for this peak is close to where potassium would be expected to be eluted in such a chromatographic system (based on well-established ion-exchange selectivity coefficients). To investigate this possibility a pH-microelectrode housed in a suitable micro flow-cell was connected in series with the conductivity detector to monitor the pH of the column effluent. An intense negative chromatographic peak
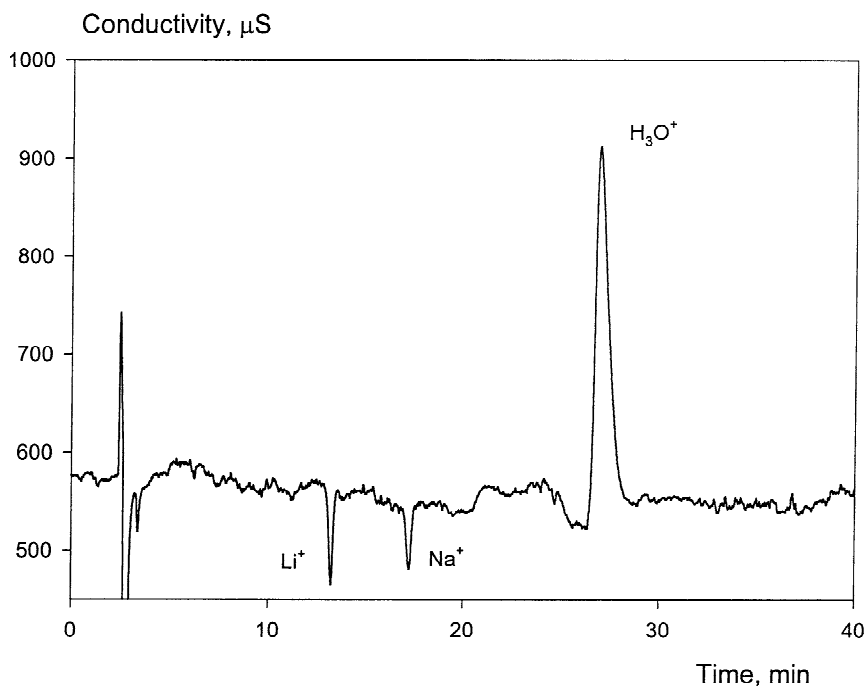

Fig. 1. Chromatogram of a sample containing 5 m*M* each of LiCl, NaCl, NH$_4$Cl, KCl and H$_2$SO$_4$ using acidified KCl solution as the eluent. Column: ODS (250×4.6 mm) coated with SDS. Eluent: an aqueous solution containing 0.3 m*M* SDS, 50 m*M* KCl and 1 m*M* H$_2$SO$_4$; flow-rate: 0.8 ml/min. Sample injection volume: 20 µl. Detection: direct conductivity.

due to a decrease of pH was observed at the retention time of the peak assigned to H_3O^+, confirming the presence of H_3O^+ in this peak.

The relationship between the logarithm of the retention factors of the alkali metal cations and H_3O^+ on the logarithm of the concentration of $(K^+ + Na^+)$ for two eluents of differing acidities is presented in Fig. 2. At the lower eluent acidity (Fig. 2A) using an eluent consisting of 0.3 mM SDS, 1 mM H_2SO_4 and varying concentrations of KCl, a set of linear relationships was obtained. The conductimetric detection of chromatographic peaks of potassium and ammonium was possible due to the presence of some sodium ions from SDS and hydronium from H_2SO_4 in the eluent. These plots all showed similar slopes (in the range -0.78 to -0.83; see Table 1), which corresponded to classical cation-exchange behaviour on strong cation-exchangers without any noticeable changes attributable to the dynamically loaded layer of SDS. In contrast, non-linear relationships were observed (Fig. 2B) for the eluent of higher acidity containing 0.3 mM SDS and 10 mM H_2SO_4. Fig. 2B shows two distinct regions. At higher concentrations of electrolyte in the eluent (log $C_{K+Na} > -2.7$), a peak for H_3O^+ was observed and the slopes of the plots were of the order -0.6. At lower concentrations of electrolyte in the eluent (log $C_{K+Na} < -2.7$), no peak for H_3O^+ was observed and the slopes of the plots decreased significantly. This could be due to a change in the surface morphology of the stationary phase caused by destruction of aggregates of SDS. Fig. 2 shows that the presence of a strong electrolyte in the eluent was necessary for the detection H_3O^+. Ito et al. observed a similar effect in their chromatography using varied concentrations of added cerium trichloride [13].

3.1.3. Effect of eluent acidity

De Borba et al. have shown that for IC determination of H_3O^+ ions at the μM level the use of acidified eluents was necessary to prevent undesirable interactions of H_3O^+ ions with residual carboxylate groups at the surface of sulfonated PS–DVB [9]. Such interactions caused strong tailing of chromatographic peaks and, consequently, their poor resolution. In the case of a silica-based stationary phase such as that used in the present study, a similar effect might occur with residual silanol groups. The role of the acidity of the eluent was therefore studied.

Any acid added to the eluent should be considered in evaluating the retention of cations since Na^+ or Li^+ (from SDS or LDS, respectively), K^+ (from potassium chloride) and H_3O^+ all contributed to the eluotropic strength of the eluent. The effect on the logarithm of retention factor of the analytes resulting from the addition of H_2SO_4 to an eluent containing 50 mM KCl is shown in Fig. 3A. Nonlinear plots were obtained and resolution of K^+, NH_4^+ and H_3O^+ was lost at the higher levels of acidity in the eluent. (>2 mM H_2SO_4). The peak area for H_3O^+ resulting from a 20-μl injection of 5 mM H_3O^+ showed a decrease from 370 to 158 V min with an increase in the acidity of the eluent from 0.5 to 5 mM H_2SO_4.

The relationship between the logarithm of retention factors of cations and the eluent pH obtained with 10 mM KCl in the eluent is shown in Fig. 3B and reflects the decrease of the eluotropic strength of the eluent with decreases in the concentration of H_2SO_4 in the eluent. The retention times were practically unchanged in the pH range 3.5 –4.5. A decrease in the concentration of the acid in the eluent (especially in the presence of a large eluent concentration of K^+) means reduced competition with sample cations for binding sites on the pseudo-stationary phase formed by aggregates of SDS at the surface of ODS and hence a fairly constant degree of retention of cations. The chromatographic peak area for a fixed amount of injected H_3O^+ ions showed the same dependence on the eluent pH as retention times and remained almost constant over the pH range 3.5–4.5.

3.2. Proposed mechanism

In proposing a possible mechanism for formation of a peak for H_3O^+ the following factors should be taken into consideration:

(i) The chromatographic peak of H_3O^+ appeared only over the eluent pH range 2–4.5 and only in the presence of a strong electrolyte in the eluent. No ion-exchange selectivity was observed for the separation of NH_4^+, K^+ and H_3O^+ at pH<2.5. The very close coincidence in retention times of K^+ and H_3O^+ might suggest the formation of a system peak
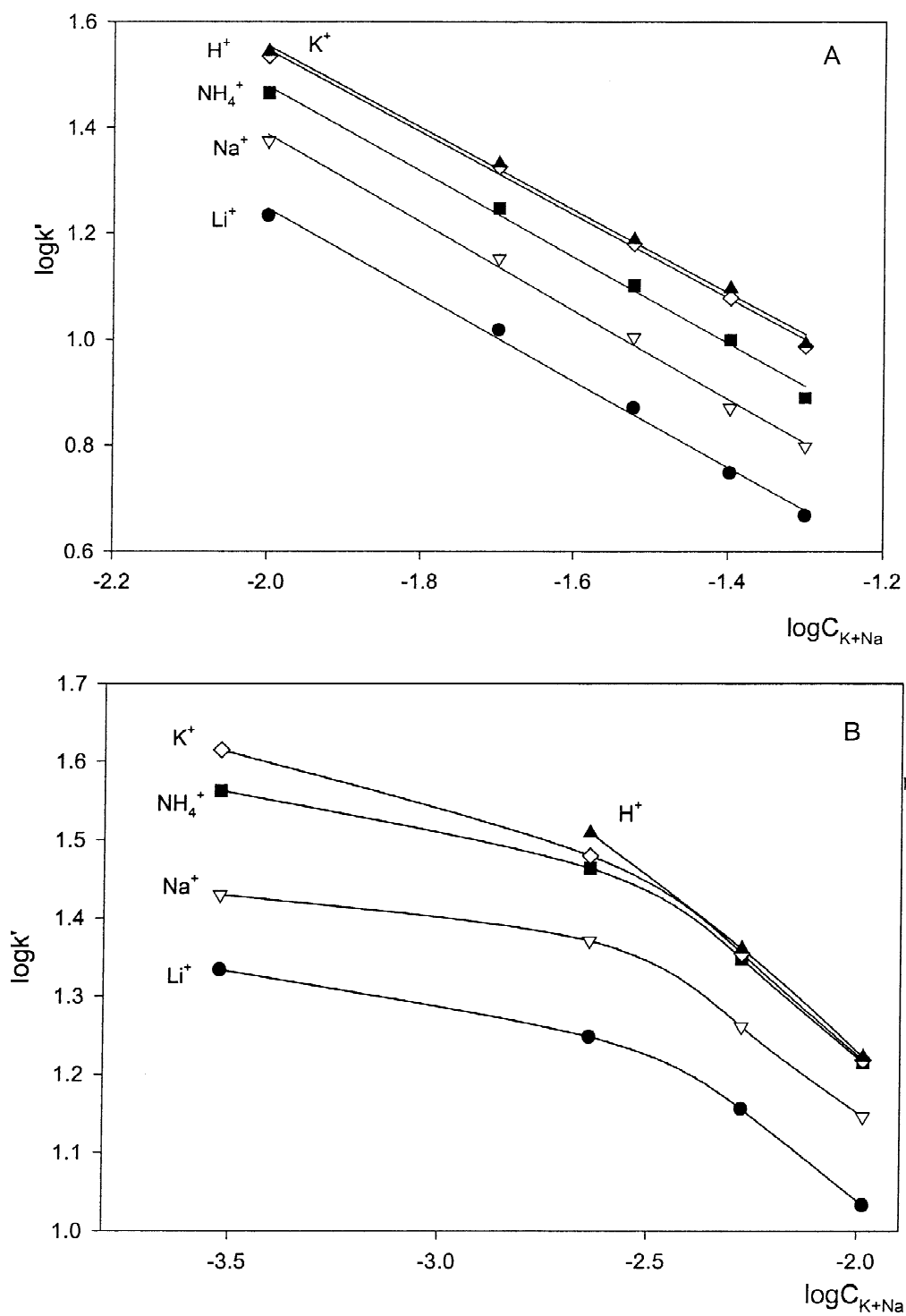
Fig. 2. Relationship between log k' and log $[K^+ + Na^+]$ in the eluent for different levels of eluent acidity. Eluent: (A) 0.3 mM SDS, 1 mM H_2SO_4 and varying concentrations of KCl; (B) 0.3 mM SDS,10 mM H_2SO_4 and varying concentrations of KCl.

Table 1

Linear regression parameters of graphs $\log k' = b_0 + b_1 \log C_{K+Na}$ (M) for analyte cations. Eluent: 0.3 mM SDS, 1 mM H_2SO_4 and (10–50 mM) KCl. ($n = 5$; $P = 0.95$)

Parameter	Li^+	Na^+	NH_4^+	K^+	H_3O^+
b_0	−0.384	−0.281	−0.143	−2.735	−0.016
b_1	−0.814	−0.834	−0.810	−0.778	−0.781
R^2	0.996	0.996	0.996	0.996	0.997

caused by displacement of K^+ from the surface of dynamically modified ODS. To investigate this possibility the chromatographic separation of four cations was performed using an eluent containing 50 mM NaCl instead of KCl (Fig. 4). The resulting chromatogram was very similar to that obtained previously with a KCl-based eluent except for the expected positive peak for NH_4^+ and the unexpected negative peak for K^+. It can be proposed that there is an equilibrium between the eluent cations (alkali metal ions and H_3O^+) in a pseudostationary phase consisting of molecules of sodium/potassium dodecylsulfate, which is responsible for the formation of a chromatographic peak for H_3O^+. At K^+/H_3O^+ ratios of ~1000 (e.g. in 0.3 mM SDS, 50 mM KCl adjusted to pH 4.5 with H_2SO_4) the peak corresponding to H_3O^+ disappeared because of saturation of the stationary phase aggregates with alkali metal cations. At a K^+:H_3O^+ ratio of ~1 (e.g. in 0.3 mM SDS, 10 mM KCl and 5 mM H_2SO_4) the altered selectivity could be connected with transformations in the phase of aggregates at the surface of the ODS phase. This hypothesis is in accordance with previously published results for the separation of alkali metal cations in an ODS–dodecylsulfate chromatographic system with varying concentrations of H_2SO_4, SDS, and $CeCl_3$, in which the appearance of system peaks was noticed for conditions promoting the formation of micelles [13].

(ii) The chromatographic peak for H_3O^+ was always positive and gave a higher conductivity response than the negative peaks obtained for other cations. Additionally, pH measurements showed a noticeable drop in pH at the retention time corresponding to the peak of H_3O^+. Both results indicate the presence of H_3O^+ in the eluted peak.

(iii) The separation selectivity of the chromatographic system differed from that expected in conventional cation-exchange chromatography. The re-

tention time of H_3O^+ was longer than for NH_4^+ and was very close to that of K^+, in contradiction to results obtained for sulfonated PS–DVB resin [9] and to ion-exchange data obtained with traditional strong cation-exchangers [17].

(iv) The chromatographic response for the H_3O^+ peak was dependent on the K^+:H_3O^+ ratio in the eluent, as shown in Table 2 which lists calibration parameters obtained using eluents with different acidity. The sensitivity of detection for H_3O^+ increased with an increase of eluent pH, with the opposite effect being noted for alkali metal cations.

The suggested mechanism involves the establishment of aggregates on the ODS stationary phase and the partitioning of eluent and analyte cations into these aggregates. Conditioning the column with acidified KCl solution as the eluent leads to the retention of both K^+ and H_3O^+ ions at the sulfonate functional groups. The K^+:H_3O^+ molar ratio in the aggregates is governed by the ratio of these two cations in the eluent. Some H_3O^+ will be used to protonate silanols at the silica surface. When the sample is injected onto the column, K^+ ions (rather than H_3O^+ ions) are replaced by cations from the sample for two reasons. First, K^+ ions have a weaker affinity than H_3O^+ ions for the stationary phase, as indicated by the elution order shown in Fig. 2 and in our previous study [10]. Second, K^+ ions can be expected to be present in the stationary phase in much larger numbers than H_3O^+ ions because the molar ratio of these species in the eluent was always strongly biased towards K^+ ions. H_3O^+ from the sample is then separated from other sample cations by conventional cation-exchange competition with K^+ ions from the eluent. The H_3O^+ ions from the sample migrate along the stationary phase in the usual manner. The conductance change detected when the H_3O^+ ions from the sample are eluted is governed by the concentration of H_3O^+ ions in the sample and the difference in equivalent ionic conductance (λ_+) between K^+ (the competing ion) and H_3O^+. A positive conductivity peak is therefore always observed for H_3O^+.

The limited eluent pH range over which the method operates can also be explained by this proposed mechanism. First, there is a need for a minimal amount of H_3O^+ (0.03 mM) to be present in the eluent to protonate residual silanol groups. On
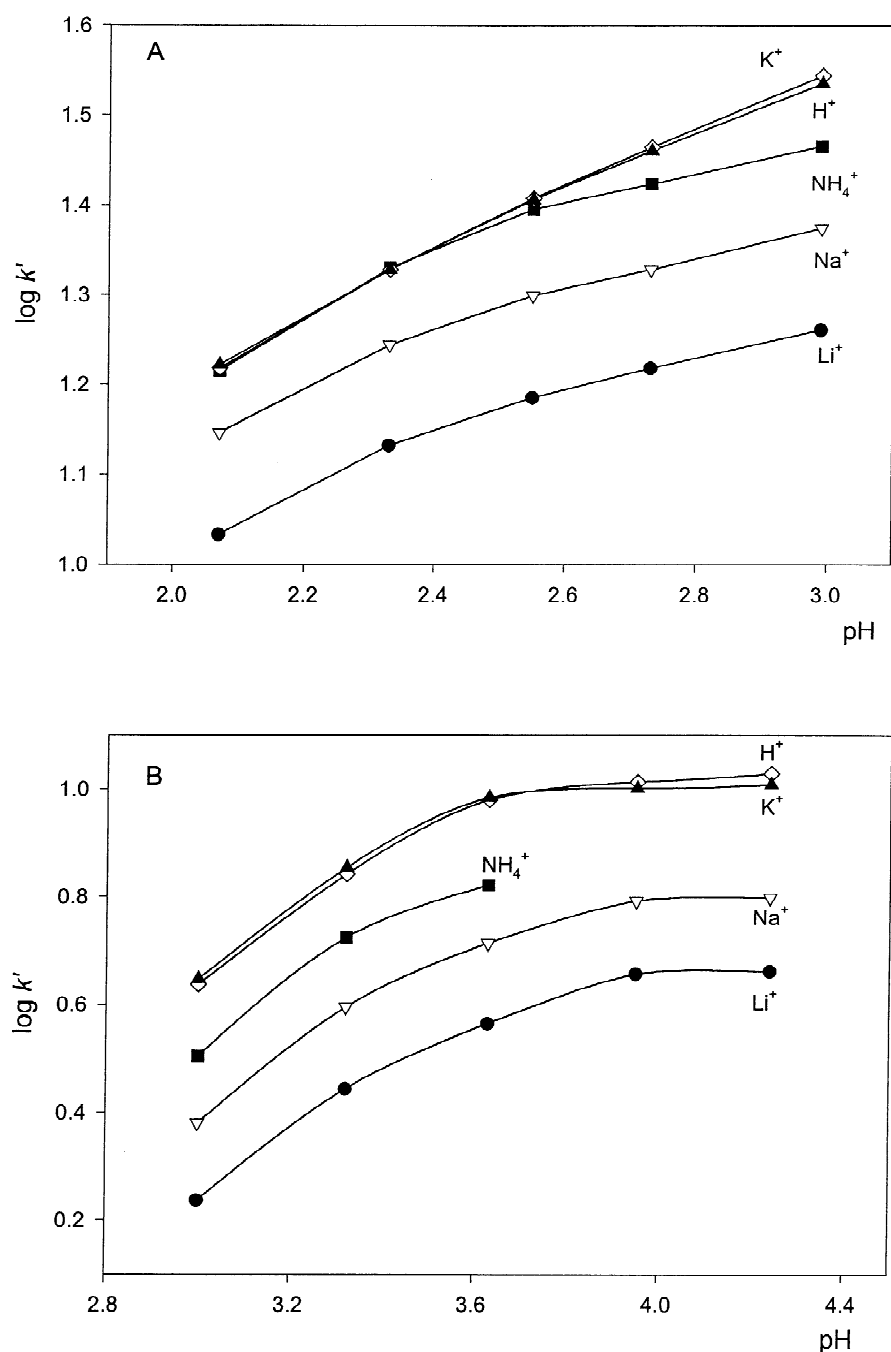
Fig. 3. Plots of log k' versus log $C_{H_2SO_4}$ for alkali metal cations and hydronium. Chromatographic column ODS L-column (250×4.6 mm) coated with SDS. Eluent: 0.3 mM SDS, 50.0 mM KCl (A) and 10.0 mM KCl (B) and varying concentrations of H_2SO_4.
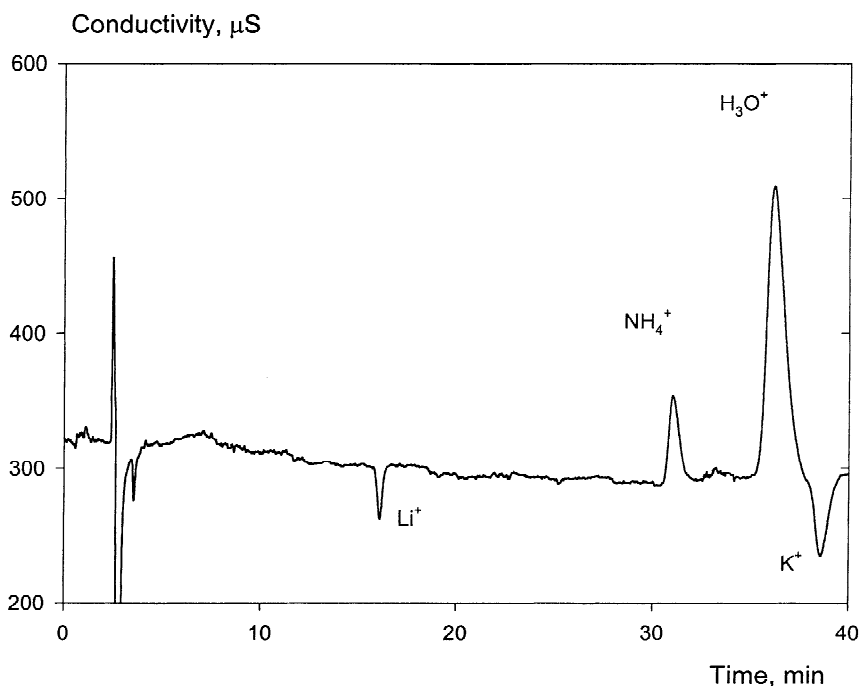
Conductivity, µS

Fig. 4. Chromatogram of a sample containing 5 mM each of LiCl, NaCl, NH$_4$Cl, KCl and H$_2$SO$_4$ using acidified NaCl solution as the eluent. Column: ODS (250×4.6 mm I.D.) coated with SDS. Eluent: an aqueous solution containing 0.3 mM SDS, 50 mM NaCl and 1 mM H$_2$SO$_4$; flow-rate: 0.8 ml/min. Sample injection volume: 20 µl. Detection: direct conductivity.

the other hand, the presence of excessive acidity in the eluent means that the stationary phase will contain appreciable amounts of both K$^+$ and H$_3$O$^+$.

Table 2
Parameters of calibration graphs S (V min) $= b_0 + b_1 C$ (mM) for the different cations obtained for eluents of composition 0.3 mM SDS, 50 mM KCl and varying acidity. Conductivity detection. ($n = 4$; $P = 0.95$)

Parameter	Li$^+$	Na$^+$	K$^+$	H$_3$O$^+$
pH 2.03				
b_0	6.515	−4.565	1.345	−4.045
b_1	6.808	5.704	4.943	25.248
R^2	0.998	0.998	0.999	0.999
pH 3.05				
b_0	1.835	0.955	1.340	−10.327
b_1	4.314	3.802	0.769	39.794
R^2	0.998	0.999	0.875	0.999
pH 4.13				
b_0	1.375	3.130	–	−3.853
b_1	3.956	3.145	–	47.370
R^2	0.999	0.998	–	0.998

H$_3$O$^+$ from the sample can therefore displace both H$_3$O$^+$ and K$^+$ ions from the stationary phase, leading to a smaller peak. The optimal K$^+$:H$_3$O$^+$ ratio in the eluent is about 25.

This mechanism suggests that the method can be also applied to the determination of OH$^-$ in alkaline samples, and we have already demonstrated this determination [18]. On injection, the OH$^-$ in the sample is neutralised immediately by H$_3$O$^+$ in the stationary phase because of the high ionic mobility of OH$^-$. H$_3$O$^+$ ions consumed from the stationary phase are then replaced by H$_3$O$^+$ ions supplied from the eluent, leaving a localised deficiency of H$_3$O$^+$ in the eluent. This deficiency of H$_3$O$^+$ leads to a negative conductivity peak which can be used as an indirect measure of the alkalinity of the sample.

3.3. Analytical performance parameters and suitability of the method

The developed method is suitable for the de-termination of hydronium in strong acid solutions.

Whilst the nature of the counter-cation in the dodecylsulfate aggregates does not play a significant role in the selectivity of separation of cations under optimum conditions, the use of LDS is preferable for quantitative determination because of the larger conductivity signals produced. Aqueous solutions containing H_2SO_4 at low-μM to mM levels were prepared and used to study the detection limits and other analytical performance parameters of this system. The detection limit for H_3O^+ ions ($S/N=3$; injection volume, 100 μl) was found to be 2.25 μM using an eluent consisting of 0.3 mM LDS, 50.0 mM KCl and 0.10 mM H_2SO_4. A plot of the area of the H_3O^+ peak versus concentration of H_2SO_4 in the sample was linear ($R^2=0.9986$) up to an injected concentration of H_3O^+ of 12.5 mM.

Standard samples comprising 0.01, 0.05 and 0.10 mM H_2SO_4 were analyzed thirty times using an eluent containing 0.3 mM LDS, 50 mM KCl and 0.10 mM H_2SO_4. The relative standard deviations (RSDs) of retention time, peak areas and peak heights were found to be <0.86% in all cases. Addition of small amounts of known concentrations of H_2SO_4 (0.01–0.04 mM) to a standard sample of 0.10 mM H_2SO_4 gave recoveries in the range 99.3–100.8%.

The suitability of the proposed method to the determination of H_3O^+ ions in solutions of organic acids is complicated by the probability of hydrophobic interactions between these analytes and the ODS phase. To investigate this the retention of C_2–C_8 alkanesulfonic acids on an ODS column dynamically modified with SDS was studied using an eluent comprising 0.3 mM SDS, 50 mM KCl and 0.25 mM H_2SO_4 (Table 3). Only hexane, heptane and octanesulfonic produced additional chromato-

graphic peaks corresponding to $AlkSO_3^-$, but the possible displacement of dodecylsulfate from the ODS surface did not affect the retention time and peak area of H_3O^+.

Changes in the degree of dissociation of weak acids in the aggregate pseudophase could restrict the applicability of the method for determination of the acidity of samples containing weak acids. This aspect was studied by the measurement of acidity of standard solutions of acetic acid, using calibration graphs obtained for dilute sulfuric acid solutions obtained with an eluent comprising 0.3 mM SDS, 50 mM KCl and 0.1 mM H_2SO_4. The pH of a 9.2 mM aqueous solution of acetic acid was determined on a pH meter to be 3.30, and triplicate analysis by the chromatographic method gave a value of 0.57 mM H_3O^+ in the sample, or pH 3.24. This value is in close agreement to that obtained on the pH meter. However, further experiments are required to fully validate the application of the chromatographic method to the determination of acidity in solutions of weak acids. Recently the possibility of determination of phthalic and glutamic acids under similar chromatographic conditions has been demonstrated [19].

4. Conclusions

The feasibility of determination of free H_3O^+ ions, together with the other common monovalent cations, by ion chromatography using ODS modified with dodecylsulfate surfactant as the stationary phase and a slightly acidified electrolyte solution as the eluent has been demonstrated. A mechanism for the separation and detection processes has been suggested. By careful control of the molar ratio of

Table 3

Retention times and peak areas for alkanesulfonic acids and hydronium. Eluent: 0.3 mM SDS, 50 mM KCl and 0.25 mM H_2SO_4

Organic acid	Concentration (mM)	Retention times (min)		Peak area of H_3O^+ (V min)
		$AlkSO_3^-$	H_3O^+	
Ethanesulfonic	5	No	17.09	17.59
Propanesulfonic	5	No	17.10	17.88
Butanesulfonic	5	No	17.07	17.29
Pentanesulfonic	5	No	17.06	17.39
Hexanesulfonic	5	3.00	17.06	18.21
Heptanesulfonic	4.63	4.36	17.03	16.89
Octanesulfonic	5	9.54	17.27	19.88

K^+:H_3O^+ in the eluent, the proposed method was found to give accurate results for the determination of μM–mM levels of H_3O^+ ions in solutions of strong acids. Preliminary results suggest that the method could also be applicable to the determination of acidity in solutions of weak acids.

References

[1] A.E. Martell, R.J. Motekaitis, in: Determination and Use of Stability Constants, VCH, New York, 1988, p. 17.

[2] R.G. Bates, Determination of pH, Wiley, New York, 1973.

[3] J.M. Davies, C. Brownlee, D.H. Jennings, J. Cell Sci. 96 (1990) 731.

[4] T.L. Legerton, K. Kanamori, R.L. Weiss, J.D. Roberts, Biochemistry 22 (1983) 899.

[5] S.J.A. Hesse, G.J.G. Ruijter, C. Dijkema, J. Visser, J. Biotechnol. 77 (2000) 5.

[6] G.L. Robert-Baldo, M.J. Morris, R.H. Byrne, Anal. Chem. 57 (1985) 2564.

[7] I. Lahdesmaki, C. Beeson, G.D. Christian, J. Ruzicka, J. Talanta 51 (2000) 497.

[8] A. Wilson, in: pH Meters, Kogan Page/Barnes and Noble, London/New York, 1970, p. 85.

[9] B.M. De Borba, C.M. Kinchin, D. Sherman, T.K. Cook, P.K. Dasgupta, K. Srinivasan, C.A. Pohl, Anal. Chem. 72 (2000) 96.

[10] W. Hu, K. Hasebe, K. Tanaka, S. Inoue, M. Nagai, Analyst 125 (2000) 2160.

[11] W. Hu, P.R. Haddad, Anal. Commun. 35 (1998) 191.

[12] K. Ito, H. Shimazu, E. Shoto, M. Okada, T. Hirokawa, H. Sunahara, J. Chromatogr. A 670 (1994) 99.

[13] K. Ito, T. Kumamaru, J. Chromatogr. A 850 (1999) 247.

[14] Y.C. Chiu, Y.C. Han, H.M. Cheng. Structure/Performance Relationships in Surfactants in: M.J. Rosen (Editor) ACS Symp. Series 253, Washington, 1984, Chapter 6.

[15] R.A. Jonson, R. Narajan, Colloids Surf. A 167 (2000) 21.

[16] M.E. Montgomery, M.J. Wirth, Langmuir 10 (1994) 861.

[17] C.E. Harward, in: Ion Exchange: Theory and Practice, RSC, London, 1994, p. 32.

[18] W. Hu, P.R. Haddad, K. Hasebe, K. Tanaka, Analyst 126 (2001) 555.

[19] W. Hu, K. Hasebe, A. Iles, K. Tanaka, Anal. Sci. 17 (2001) 1401.