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## DEPENDENCE OF THE CALCIUM DISTRIBUTION COEFFICIENT ON A STRONGLY ACIDIC CATION-EXCHANGE RESIN ON THE ANION OF STRONG ACIDS AND THEIR LITHIUM SALTS

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### SUMMARY

The dependence of the calcium distribution coefficient on the anion of strong acids ( $X^- = Cl^-, NO_3^-, ClO_4^-$ ) as well as on their lithium salts from 0.1 *M* up to high concentrations has been tested on the strongly acidic cation exchanger Dowex 50W-X12. Under the same experimental conditions, the distribution coefficient decreases in the following order:  $ClO_4^- > Cl^- > NO_3^-$ . This can be explained in terms of the different anion-calcium interactions. Using acids as electrolyte, the distribution coefficient exhibits a minimum value in the range of 4–6 *M* *HX* and rises at higher concentrations. However, no minimum value was found in systems with the lithium salts over the whole investigated concentration range. The effect on chromatographic separations of the dependence of the distribution coefficient on the anion is discussed.

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### INTRODUCTION

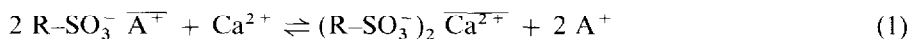
Recently we reported<sup>1</sup> that the distribution coefficient of chloride on a strongly basic anion exchanger was dependent on the cation of the electrolyte solution. Over the whole concentration range, distribution coefficient was correlated with the interaction between the co-ion (in an anion-exchange system this is the cation of the electrolyte solution) and the chloride ion.

To obtain information about the dependence of the distribution coefficient on the co-ion in cation exchanger systems, we have now studied the distribution of calcium between the strongly acidic cation-exchange resin Dowex 50W-X12 and solutions of strong acids *HX* or their lithium salts (co-ion  $X^- = Cl^-, NO_3^-, ClO_4^-$ ). In addition, the applicability of the results obtained previously with an anion exchanger system to a cation exchanger is examined to determine whether a generalization of the co-ion effect can be made. The fact that, for ion-exchange chromatography, the selection of the co-ion in the eluent has a profound influence on the separation conditions has not been considered in many previous chromatographic experiments.

Some time ago, Strelow and co-workers<sup>2–4</sup> investigated the calcium distribution coefficient with a cation exchanger. In these experiments the resin was some-

what less cross-linked (Dowex 50-X8) and the highest concentration of HCl, HNO<sub>3</sub> and HClO<sub>4</sub> was only 4 M, whereas higher concentrations are of particular interest for systematic investigations. Moreover, on plotting the calcium distribution coefficient obtained in the earlier work against the electrolyte concentration, one finds that the HCl and HClO<sub>4</sub> curves intersect. This is not in accordance with our experiments with anion exchanger systems nor with the investigations of Nelson *et al.*<sup>5</sup> on calcium distribution coefficients, and causes difficulties in interpretation. Using radionuclides, Nelson *et al.* determined the distribution coefficient of calcium and several other ions with Dowex 50-X4 in HCl and HClO<sub>4</sub> solutions. Diamond<sup>6</sup> studied the calcium distribution with Dowex 50-X12 in up to 12 M HCl solutions by column experiments. The behaviour of some alkali metal ions in hydrochloric acid, nitric acid and perchloric acid, as well as in their lithium salts<sup>7</sup>, and of some lanthanide ions in perchloric acid and different hydrohalic acids<sup>8</sup>, has also been determined. For the alkali metal ions, some results of batch experiments with LiCl as an electrolyte solution are given elsewhere<sup>9</sup>.

For the calcium exchange equilibrium investigated in our experiments



with  $\text{A}^+ = \text{H}^+, \text{Li}^+$  (counter ions). The bar denotes a cation in the resin phase. The distribution coefficient of calcium,  $K_d(\text{Ca}^{2+})$ , is defined as:

$$K_d(\text{Ca}^{2+}) = \frac{\text{mmol } \overline{\text{Ca}^{2+}} \text{ per g of dry resin}}{\text{mmol } \text{Ca}^{2+} \text{ per ml of solution}} \text{ ml g}^{-1} \quad (2)$$

In the experiments with HX, the amount of dry resin refers to the hydrogen form; in the experiments with LiX it refers to the lithium form. The two resin forms differ in weight by only about 3%, so that the corresponding  $K_d$  values are directly comparable.

## EXPERIMENTAL

Approximately 5 g of the wet, strongly acidic cation exchanger, Dowex 50W-X12 (200–400 mesh, Bio-Rad), were weighed into a 100-ml PE flask, using the hydrogen and lithium form, respectively. At the same time, the moisture content of the ion exchanger resins was determined to be 57.7% and 50.3%, respectively. Before starting the batch experiments, the resin was purified by shaking it several times with 3 M HCl, ethanol, and twice distilled water until no calcium could be detected in the hydrochloric acid washing by flame atomic absorption spectrometry. The lithium form of the resin was produced by shaking with a saturated LiOH solution. After filtration, the resin was washed with 0.1 M LiOH solution and then shaken with a few ml of twice distilled water, until the pH of the washings reached a value of 7.

A 5-ml volume of a CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> or Ca(ClO<sub>4</sub>)<sub>2</sub> solution, containing *ca.* 2 mg Ca<sup>2+</sup> per ml, was added to the PE flask. For the experiments with acids, 75 ml of a 0.1, 0.5, 1, 2, 3, 4, 5, 6, 7, 8 or 9 M HX solution ( $\text{X}^- = \text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-$ ) were then added. (When plotting the results in Figs. 1 and 2, the dilution effect of the 5 ml calcium solution on the HX solution was taken into account.) In the experiments with

LiCl and LiNO<sub>3</sub>, the lowest starting concentration was 0.1 M, whereas the highest one was 13 M for LiCl and 10 M for LiNO<sub>3</sub>. The starting concentrations for the experiments with LiClO<sub>4</sub> were 0.02, 0.3, 1.0, 1.7, 2.3, 2.7 and 3.3 M. In the experiments with LiX, the solubility of the lithium salts is the limiting factor on their concentration. All chemicals (Merck) were of "for analysis" grade.

The PE flasks were shaken at room temperature (*ca.* 20°C) until the establishment of equilibrium. Then, the resin was separated from the solution by filtering. The amount of calcium in the solutions was determined by flame atomic absorption spectrometry. For calibration, standard solutions with the same HX or LiX concentrations as those of the samples to be analysed were used. An exact matrix assimilation of the standard solutions is essential for obtaining precise  $K_d$  values.

## RESULTS AND DISCUSSION

Figs. 1 and 2 show the dependence of the calcium distribution coefficient obtained with the strongly acidic cation exchanger Dowex 50W-X12 on the concentration of the three investigated acids and their lithium salts, respectively. At lower concentrations, a strong dependence of the  $K_d(\text{Ca}^{2+})$  value on the electrolyte concentration, which is comparable for the HX and LiX systems, is found. At very high

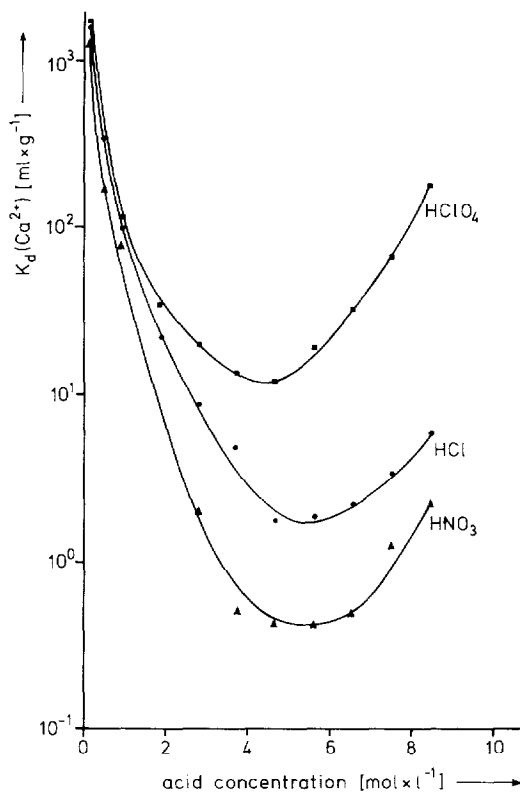


Fig. 1. Dependence of the calcium distribution coefficient on the concentration of the acids HClO<sub>4</sub>, HCl and HNO<sub>3</sub>.

concentrations, the distribution coefficient shows a small decrease with increasing concentration of  $\text{LiNO}_3$ , or reaches an approximately constant value ( $\text{LiCl}$ ). In contrast, in all systems with  $\text{HX}$ ,  $K_d$  exhibited a minimum value in the range of 4–6  $M$   $\text{HX}$ , then increased at higher concentration. The minimum value of  $K_d$  shifted to higher concentrations in the order:  $\text{HClO}_4 < \text{HCl} < \text{HNO}_3$ . In addition, the  $K_d$  value was strongly dependent on the nature of the anion  $\text{X}^-$  of the electrolyte solution over the whole concentration range investigated. For the same concentration, the calcium distribution coefficient always decreased in the order:  $\text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^-$ .

As expected, at lower concentrations, the  $K_d$  curves can be interpreted in terms of the mass balance, according to eqn. 1. The reason for the lower  $K_d$  values in the systems with  $\text{HX}$ , compared to those with  $\text{LiX}$ , is the stronger chemical bond between  $\text{H}^+$  and the cation exchanger. The significant difference between the  $K_d(\text{Ca}^{2+})$  values, obtained using various co-ions  $\text{X}^-$  can be explained by the different co-ion-counterion, *i.e.*,  $\text{Ca}^{2+}$ ,  $\text{A}^+$ , interaction and thereby by the influence of the co-ion on the activity coefficient of the counter ions. The thermodynamic equilibrium constant,  $K_a$ , corresponding to eqn. 1 is given by

$$K_a = \frac{a_{\text{Ca}^{2+}} \times a_{\text{A}^+}^2}{a_{\text{A}^{2+}} \times a_{\text{Ca}^{2+}}} = K_c \times \frac{f_{\text{Ca}^{2+}}}{f_{\text{A}^+}^2} \times \frac{f_{\text{A}^+}^2}{f_{\text{Ca}^{2+}}} \quad (3)$$

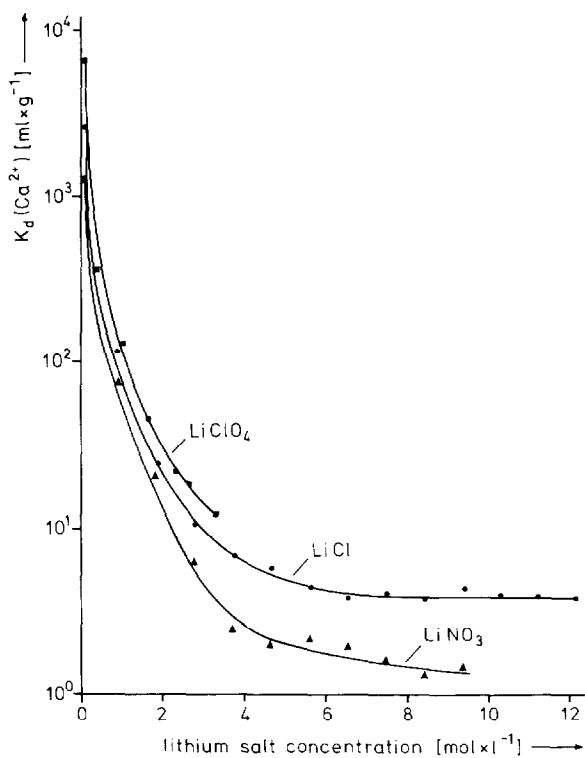


Fig. 2. Dependence of the calcium distribution coefficient on the concentration of the lithium salts  $\text{LiClO}_4$ ,  $\text{LiCl}$  and  $\text{LiNO}_3$ .

where  $a$  = activity and  $f$  = activity coefficient. As long as no co-ions enter the resin phase—which is the case with low concentrations in the free solution—the quotient

$$\overline{f_{\text{Ca}^{2+}}}/f_{\text{A}^+}$$

is constant for all systems with different anions in the free solution. Therefore, under this condition the dependence of the quotient  $f_{\text{A}^+}^2/f_{\text{Ca}^{2+}}$  on the type of the HX and LiX solution is responsible for the different  $K_d(\text{Ca}^{2+})$  values when the same electrolyte concentration is used. For example, with a 0.1 M HCl and LiCl solution the  $K_d(\text{Ca}^{2+})$  value is a factor 1.4 and 2.0 higher than it is with  $\text{HNO}_3$  and  $\text{LiNO}_3$ , respectively. According to the order of the different  $K_d$  curves in Figs. 1 and 2, the strongest interaction occurs between  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  in the free solution, the weakest between  $\text{Ca}^{2+}$  and  $\text{ClO}_4^-$ . This is in accord with the mean activity coefficient in pure  $\text{CaX}_2$  solutions which decreases over the whole concentration range investigated in the order  $\text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^-$ <sup>10</sup>. The value of  $K_C$  in eqn. 3 and thereby  $K_d(\text{Ca}^{2+})$  increases if the factor  $f_{\text{A}^+}^2/f_{\text{Ca}^{2+}}$  decreases. This is observed, *e.g.*, for a chloride or perchlorate instead of a nitrate system.

The strong interaction of calcium with nitrate and thereby the lowest  $K_d(\text{Ca}^{2+})$  values for all investigated systems can be explained by the formation of a contact ion pair corresponding<sup>11</sup>:



For high concentrations, the  $K_d$  curves can also be interpreted in terms of ion dehydration effects, *e.g.*, by Whitney and Diamond<sup>7</sup>.

The subsequent increase of the distribution coefficient in HX systems, as well as the small concentration dependence of the  $K_d$  value in LiX systems, at higher concentrations can be explained by invasion of the resin by non-exchange electrolyte. This leads to an additional uptake of counter ions (in our investigation,  $\text{H}^+$  and  $\text{Li}^+$ ) in the resin phase, which can also be exchanged by calcium ions. The amount of adsorbed electrolyte in the resin phase, determined in a system with a starting concentration of 3 M and 12 M HCl and LiCl, respectively, is summarized in Table I. In the experiments the resin ( $\text{Li}^+$  or  $\text{H}^+$ ) was treated with the starting solution of LiCl or HCl. After establishment of equilibrium, the uptake of LiCl or HCl was analysed with an ion-selective electrode by measuring the decrease in chloride content of the solution. The last column in Table I shows the ratio of the counter ion  $\text{A}^+$  ( $\text{Li}^+$  or  $\text{H}^+$ ) adsorbed as AX to that bound at the functional group of the resin. From the results,

TABLE I  
ADSORBED ELECTROLYTE IN THE RESIN PHASE

<i>Solution</i>	<i>Adsorbed amount (mol/g dry resin)</i>	<i>Electrolyte ratio, adsorbed/bound*</i>
3 M LiCl	$0.5 \cdot 10^{-2}$	1.0
12 M LiCl	$6.2 \cdot 10^{-2}$	12.0
3 M HCl	$< 0.1 \cdot 10^{-2}$	$< 0.2$
12 M HCl	$4.2 \cdot 10^{-2}$	8.1

\* Capacity =  $5.17 \cdot 10^{-3}$  mol  $\text{A}^+$  per g dry resin.

it follows that with solutions up to 3 M the amount adsorbed electrolyte is less than the amount bound at the functional groups. High concentrations in the free solution result in ratios of up to 12 between the adsorbed and bound electrolyte. The increase of the distribution coefficient in the HCl system, in contrast to the LiX system, after passing the minimum value can be attributed to the favoured exchange of  $\text{Ca}^{2+}$  with adsorbed  $\text{H}^+$ , than with adsorbed  $\text{Li}^+$ .

The trend of the  $K_d(\text{Ca}^{2+})$  curves with HX is comparable with those of the chloride distribution coefficient obtained with a strongly basic anion exchanger and alkali metal fluoride solutions<sup>1</sup>. In the latter system,  $K_d(\text{Cl}^-)$  follows the order of the mean activity coefficient of the pure alkali metal chloride solutions ( $\text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$ ). This is in accord with the results for  $K_d(\text{Ca}^{2+})$  obtained with the cation exchanger which follow the order of the mean activity coefficients of  $\text{CaX}_2$  solutions. A generalization of this co-ion effect allows predictions of the relative dependence of  $K_d$  on the electrolyte concentration.

Our results for the highly cross-linked resin Dowex 50-X12 can be compared with those obtained for the same resin with alkali metal ions in column experiments, using a radioactive tracer<sup>7</sup>. With LiCl,  $\text{LiNO}_3$  and  $\text{LiClO}_4$  solutions as eluent, the elution volume of the peak of  $\text{M}^+$  ( $\text{M}^+ = \text{Na}^+, \text{Rb}^+, \text{Cs}^+$ ), which is directly proportional the  $K_d(\text{M}^+)$  value, decreases continuously with increasing electrolyte concentration. No subsequent increase of  $K_d(\text{M}^+)$  was observed over the whole concentration range investigated, *i.e.*, up to *ca.* 4 M  $\text{LiClO}_4$ , 8 M  $\text{LiNO}_3$  and 10 M LiCl solution, respectively. This is in accord with our results for  $K_d(\text{Ca}^{2+})$  in LiX solutions. The same tendency for  $K_d(\text{M}^+)$  was found by Platek and Marinsky<sup>9</sup> with the less cross-linked resin Dowex 50-X8 and a LiCl solution. Contrary to our calcium results, the distribution coefficient of the alkali metal ions only shows a small co-ion effect. This can be explained by the smaller difference between the mean activity coefficients of the different alkali metal salts, *e.g.*, NaX. Additionally, the order of the  $K_d(\text{Na}^+)$  values for a LiCl and  $\text{LiClO}_4$  solution is opposite to that in the calcium system, and thus corresponds to the opposite order of the mean activity coefficient of NaCl and  $\text{NaClO}_4$  solutions compared with the same calcium salts.

In column experiments analogous to those with lithium electrolytes, with HCl and  $\text{HNO}_3$  the peak elution volume for  $\text{Na}^+$  exhibits a minimum value at *ca.* 6 M and 8 M, respectively. No minimum was found up to 10 M  $\text{HClO}_4$  solutions. Chopin and Dinius<sup>8</sup> analysed the  $K_d$  values for several lanthanide ions in systems with the low cross-linked resin Dowex 50-X4 and solutions of  $\text{HClO}_4$ , HCl, HBr and HI. Owing to the decreasing co-ion–lanthanide ion interaction in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$ , the distribution coefficients of the lanthanides increase within the given co-ion sequence. For all systems investigated a minimum value of  $K_d$  was found which shifted to higher electrolyte concentrations on going from  $\text{HClO}_4$  to HCl.

The calcium distribution coefficient was investigated by Diamond<sup>6</sup> in the system Dowex 50-X12–HCl solution in column experiments. Only four experimental points were used to plot the  $K_d(\text{Ca}^{2+})$  versus HCl concentration curve in the range between 2.5 and 12 M. Nevertheless, this curve is in good agreement with our results, where a minimum  $K_d(\text{Ca}^{2+})$  value was found for 5.5 M HCl. Also, Nelson *et al.*<sup>5</sup> investigated in batch experiments the calcium distribution coefficient with the low cross-linked resin Dowex 50-X4 and solutions of HCl and  $\text{HClO}_4$ . The results show the same type of  $K_d(\text{Ca}^{2+})$  curves as we obtained with Dowex 50-X12. In contrast, we

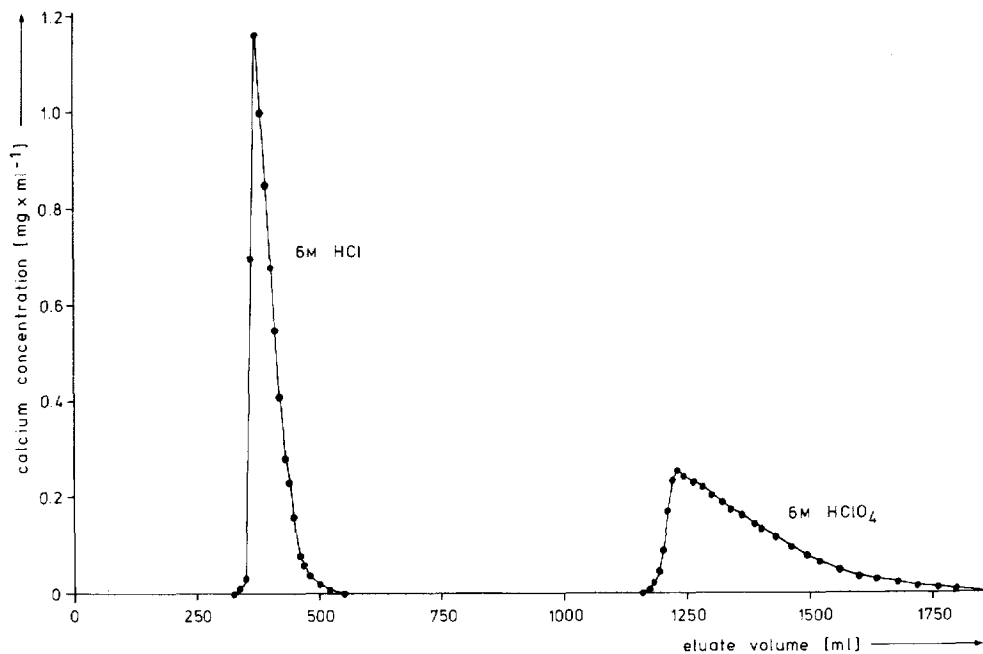


Fig. 3. Elution curves of calcium with 6 *M* HCl and 6 *M* HClO<sub>4</sub> eluents.

found higher (on average by a factor of 2–3) calcium distribution coefficients over the whole concentration range which can be attributed to the more highly cross-linked resin used in our experiments. The calcium distribution coefficients determined by Strelow and co-workers<sup>2–4</sup> with the resin Dowex 50W-X8 and HClO<sub>4</sub>, HCl and HNO<sub>3</sub> solutions up to 4 *M* show an intersection of the HCl and HClO<sub>4</sub> curves between 0.5 and 1 *M*, when the results are plotted in the same manner as in Fig. 1. This is not in accord with our results, and could not be explained by the calcium-co-ion interaction. On the other hand, with HNO<sub>3</sub>, Strelow also found the lowest  $K_d(\text{Ca}^{2+})$  values of all the HX systems investigated.

A practical aspect of the strong dependence of the distribution coefficient on the co-ion of the electrolyte system is the effect on the elution volume and therefore on the elution time in chromatographic separations as well as on the separation factor between different ions. If calcium is eluted from a column packed with Dowex 50W-X12 (height 75 cm, diameter 1.5 cm, 20°C, elution rate *ca.* 14 ml h<sup>-1</sup>) by a 6 *M* HClO<sub>4</sub> and 6 *M* HCl solution, the elution curves shown in Fig. 3 are obtained. There is a great difference in the peak elution volumes at the maximum concentration, being only 370 ml for the HCl but 1230 ml for the HClO<sub>4</sub> solution. In some cases the  $K_d$  curves show a different trend for various elements in highly concentrated electrolyte solutions. This was shown by the determination of peak elution volumes for alkali metal ions in HCl and HNO<sub>3</sub> systems<sup>7</sup> and by batch experiments for alkaline earth metal ions in HCl and HClO<sub>4</sub> systems<sup>5</sup>. This effect can be used for a better and more rapid separation in systems with high electrolyte concentrations. One example described in the literature<sup>12</sup> is the separation between magnesium and calcium with HClO<sub>4</sub> and HCl solutions. There are many more possibilities. The selection of a

suitable co-ion can result in optimization of the conditions for a chromatographic separation by ion exchangers.

## CONCLUSIONS

In batch experiments, the dependence of the calcium distribution coefficient on the co-ion was systematically investigated with a cation exchanger system up to very high electrolyte concentrations. The results increase knowledge of the dependence of the distribution coefficient on the counter ion-co-ion interaction in ion exchanger systems. A generalization of the co-ion effect shows that the  $K_d$  value follows the order of the mean activity coefficient of pure solutions comprising the investigated counter ion and the co-ion. As a result of this work, a better prediction, and optimization, of the ion-exchange behaviour in chromatographic experiments is possible.

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