Binary extracting agents as new stationary phases for the extraction chromatography of ionic compounds

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A new version of extraction chromatography with the use of binary extracting agents as a stationary phase, water as an eluent and conductometric detection was proposed for ionic compounds.

The extraction chromatography of ionic compounds based on liquid cation and anion exchangers is well known;[1] however, it is not in common use because of some limitations.[2]

In this paper, we report on binary extracting agents (the salts of organic acids and bases) as a new type of stationary phases for extraction chromatography. They are liquid or solid compounds obtained by the interaction between liquid cation and anion exchangers in stoichiometric amounts. The binary extracting agents are readily soluble in non-polar organic solvents and sparingly soluble in water.

The liquid–liquid extraction of ionic compounds (acids, bases and salts) by binary extracting agents depends on the distribution of solutes between phases and on chemical reactions in these systems.[3,4] The use of binary extracting agents as a stationary phase can form the basis for a new version of the extraction chromatography of ionic compounds.

As distinct from the initial extracting agents used for the synthesis of a binary extracting agent, the ion exchange between the components of the extraction system is accompanied by the stoichiometric phase transfer of both cations and anions from the aqueous phase to the organic phase and *vice versa*. This feature of the process is similar to the extraction by neutral extractants. The process can be described by the following reaction:

$$\mathrm{M}^{n+}_{(\mathrm{a})} + n\mathrm{X}^{-}_{(\mathrm{a})} + n\mathrm{R_4NA}_{(\mathrm{o})} = \mathrm{MA}_{n\,(\mathrm{o})} + n\mathrm{R_4NX}_{(\mathrm{o})} \qquad (1)$$

where M^{n+} and X^{-} are the extracted cation and anion, respectively, and $\mathrm{R_4NA}$ is the binary extracting agent; the subscripts (a) and (o) indicate the aqueous or organic phase, respectively. Thus, the back extraction of ionic compounds and the elution with water can also be performed using these reagents.

The extraction by binary extracting agents is characterised by linear isotherms of the distribution of ionic compounds between phases at low and medium concentrations (*i.e.*, when the solute concentration in the organic phase in much lower than the concentration of the binary extracting agent).[5] Therein is a difference between the extraction by binary extracting agents and the extraction by neutral extractants; the latter is characterised by an S-shaped isotherm and a decrease in the distribution coefficients with decreasing concentration of an ionic compound in the aqueous phase. It is well known that linear isotherms of the distribution of compounds between stationary and mobile phases are favourable to effective chromatographic separation.

A combination of the simultaneous extraction of cations and anions with the linear shape of distribution isotherms provides an opportunity to simplify the extraction-chromatographic separation and detection of ionic compounds. For instance, the same chromatographic system can be used for the separation of either cationic mixtures as salts with a common anion or anionic mixtures as salts with a common cation.

The chromatographic retention time of an ion can be changed by varying the counter-ion added to the sample. Because the elution is performed using de-ionised water, the analytes can be directly detected by conductometry, which exhibits a wide linear range.

The suggested extraction-chromatographic systems were examined in high-performance liquid chromatography. From the standpoint of selectivity, we decided on the use of dialkyl phosphates and tetraalkylammonium salts for the preparation of stationary phases. A liquid stationary phase was prepared by mixing a binary extracting agent with a non-polar organic diluent. Separon C-18 silica gel (particle size of 5 μm) was used as a solid support for the liquid stationary phase. A chromatographic column (2 mm in diameter and 64 mm in length) was sequentially washed with 150 μl of a binary extractant solution in a non-polar organic solvent and with 4 ml of water at a flow rate of 200 μl min^{-1}. The column contained 15 μl of a liquid extraction agent, and the free volume was 70 μl. A pre-column (of volume 60 μl) packed by the same procedure was used for saturating the mobile phase with the extracting agent. The pre-column was placed before the sample injector.

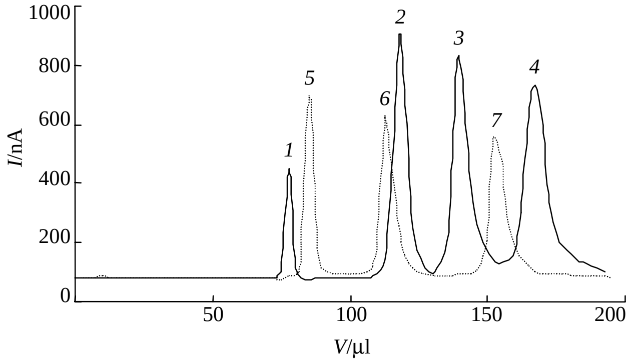

Figure 1 Chromatograms of cations mixture: (*1*) NaCl, (*2*) $\mathrm{LaCl_3}$, (*3*) $\mathrm{NdCl_3}$ and (*4*) $\mathrm{EuCl_3}$, and of anions mixture: (*5*) $\mathrm{CaCl_2}$, (*6*) $\mathrm{CaBr_2}$ and (*7*) $\mathrm{Ca(NO_3)_2}$.

The chromatograms shown in Figure 1 demonstrate the capabilities of the proposed separation technique for cationic and anionic mixtures. These chromatograms were consecutively obtained on the same column using the same eluent (de-ionised water). The sample volume was 2 μl, the concentrations of salts were 5×10^{-4} mol dm^{-3}, and the elution rate was 50 μl min^{-1}. The cations and anions were separated as chlorides and calcium salts, respectively. The relative distribution coefficients of ions between stationary and mobile phases calculated from retention volumes for the series $\mathrm{La^{3+}}$–$\mathrm{Eu^{3+}}$ are consistent with the distribution coefficients of salts under conditions of batch extraction in the water–binary extracting agent system.

Using lanthanide ions as an example, we examined the reduction of separated cations to an identical anionic form. This can be achieved by the addition of large amounts of a salt containing a low-extractable cation and a high-extractable anion to the sample.

We also tested the stability of the stationary liquid phase based on binary extracting agents in the course of the chromatographic separation of ionic mixtures. We found that, after preparing the column as described above, the relative retention volumes of lanthanide ions (taken as chlorides) decreased by less than 4% after performing 15 runs of chromatographic separation.

Thus, the use of binary extracting agents as a stationary phase is promising for extraction chromatography. The proposed technique makes it possible to develop unified procedures for the separation and analysis of cations and anions. The use of deionized water as an eluent simplifies the detection of ionic compounds.

References

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