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## Separation of ionic mixtures in sorption columns with two liquid phases

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### Abstract

A new approach to the treatment of highly concentrated solutions of electrolytes in ion exchange and sorption columns with zero bed porosity is proposed. The approach concerns reducing the inter-particle space occupied by working solutions in columns by filling them with special organic liquids immiscible with water. By a variety of examples, including the separation of nitric acid and nitrates for processing aluminium concentrates, purification of working electrolytes for copper refining, conversion of potassium chloride into chlorine-free fertilizers etc., the advantages of the proposed method are demonstrated and show that using the new method in ion exchange and acid retardation processes does not affect the equilibrium separation parameters, but significantly improves the kinetics by eliminating longitudinal dispersion effects. Also this makes it possible to reduce the duration of working cycles, thereby raising the efficiency of the use of separation columns.

**Keywords:** electrolyte solutions, sorption, separation of mixes, porosity, organic phase, ion exchange, acid retardation.

Предложен новый подход к переработке концентрированных растворов электролитов в ионообменных и сорбционных колоннах с нулевой порозностью. Подход состоит в уменьшении межзеренного пространства, занимаемого рабочим раствором в колонках, с помощью заполнения их специальными органическими жидкостями, не смешиваемыми с водой. На различных примерах, включая процесс разделения азотной кислоты и нитратов, получаемых при переработке нефелиновых концентратов, очистки рабочих электролитов для получения катодной меди, а также конверсии хлорида калия в бесхлорные удобрения, продемонстрированы преимущества предложенного способа. Показано, что в новом варианте метода удерживания кислоты не изменяются равновесные параметры разделения, но существенным образом устраняются эффекты продольной дисперсии. Кроме того, новый подход позволяет сократить длительность рабочих циклов, что повышает эффективность использования разделительных колонн.

**Ключевые слова:** растворы электролитов, сорбция, разделение смесей, порозность, органическая фаза, ионный обмен, удерживание кислоты

### Introduction

For many years after the beginning of the industrial use of ion exchangers, an opinion existed that these materials are intended only for the separation and concentration of components contained in solutions at relatively low concentrations. The most typical examples of such uses of ion exchangers are water treatment for power plants, the removal of micro-components in hydrometallurgy and various methods for solution purification of. As the rule, these technologies are characterized by prolonged filtration cycles, i.e. the

volumes of solutions processed in one sorption cycle are many times larger than the volume of a sorbent bed.

Today, along with such technologies, the treatment of concentrated electrolyte solutions with ion exchangers gains more and more practical importance. Such processes have been proposed at different times, but all are characterized by short filtration cycles, for which the volumes of processed solutions and sorbent bed are comparable. There are a number of examples of such processes; three are presented below.

In the early 1960s, one of the first publications [1] concerned the possibility of separating acids from their salts in highly concentrated solutions on ion-exchangers. The method, called Acid Retardation by its authors, was not ion exchange, because the isolation of the hydroxonium compound from the derivatives of metal ions was not performed by a cation exchanger; but an anionic resin in a ion form similar to the common anion of separated components was applied. The method proved to be attractive due to the fact that desorption was carried out with water. For a long time, this method did not find industrial application due to difficulties in organizing the flow distribution in columns to eliminate mixing of the different substances. Since the late 1970s, after process modifications, it began to be applied and is now widely used, for example, by the Canadian company Eco-Tec.[2,3] Research in Acid Retardation has expanded the range of separable components[4], and the development of new sorption materials [5].

Another example is ion-exchange conversion of chloride-containing fertilizers into chlorine-free products, as well as the production of complex NPK fertilizers, using highly concentrated solutions. Scientific research has been actively conducted since the beginning of 70s [6] and today, one can find the examples of industrial use of different variants of ion-exchange technology [7].

We also believe that using the effect of isothermal super-saturation of solutions (IXISS - effect) for inorganic electrolytes [8-10] is interesting for the practice of ion exchange technologies. The essence of this effect lies in the fact that with a dynamic ion exchange process accompanied by the formation of a slightly soluble substance, a relatively stable supersaturated solution is generated in the sorbent bed, and the spontaneous crystallization of this substance takes place in the effluent. A lot of processes in which the ion exchange reaction product is less soluble than the initial compound can be found. Among them, one can also find a lot of practically feasible processes in which the temporary stabilization of a supersaturated solution in a packed bed of ion exchanger continues for a few hours or more [9]. In the processing of highly concentrated solutions the opportunity to obtain directly a final high purity product in the solid state without additional energy consumption is very attractive. In practice, this approach proved to be indispensable in the technologies of zero-discharge processing of sea-water and sea brines [10].

As can be seen from the above examples, separation of concentrated ionic mixtures in aqueous solutions can be carried out by ion exchange or non-exchange processes on resins. For these and other processes with small cycle times for sorption and regeneration stages, as well as for processes where the solutions in these stages differ in density or temperature, we encounter a main problem: impairment of separation due to the influence of mixing effects caused by longitudinal dispersion in columns (all types of additional erosion of concentration profiles other than molecular diffusion) [11,12]. Well known approaches can be applied to eliminate dispersion effects, for example, the more concentrated solution is fed to the column in the upward direction; a hot solution from top to bottom; reduced inter-particle space and free volume under the bed. At the same time, an effect that is hard to avoid is bound up with the shrinking and swelling of resin beads. This phenomenon is illustrated in Fig.1A; previous contact of a lower bead in the column

with a more dense solution results in its shrinking, leading to the channeling and subsequent shrinking of the upper bead, and so on. One of the ways for eliminating such a progressive erosion of the concentration frontiers and improving flow distribution in resin beds is proposed by Craig Brown [2]. This is achieved by over-packing a special column with highly compressed and deformed resin beads to reduce the inter-particle space (porosity volume) of the ion exchanging bed shown by upper arrow in figure (Fig.1B).

A new approach to the organization of mass transfer processes in ion exchange and sorption beds is described in this paper. The approach consists in reducing the space occupied by water and working solutions in the columns by using an additional liquid phase [13]. The column, loaded with ion exchange granulated material, is additionally filled by an organic liquid immiscible with the aqueous solutions. No special facilities and no high pressures are required and the ion exchange materials can be used for long time. All the column processes can be carried out in down-flow mode for both sorption and regeneration stages of the working cycle. In this paper, we demonstrate the prospects of the proposed approach by a variety of actual examples for chemical engineering and elemental analysis.

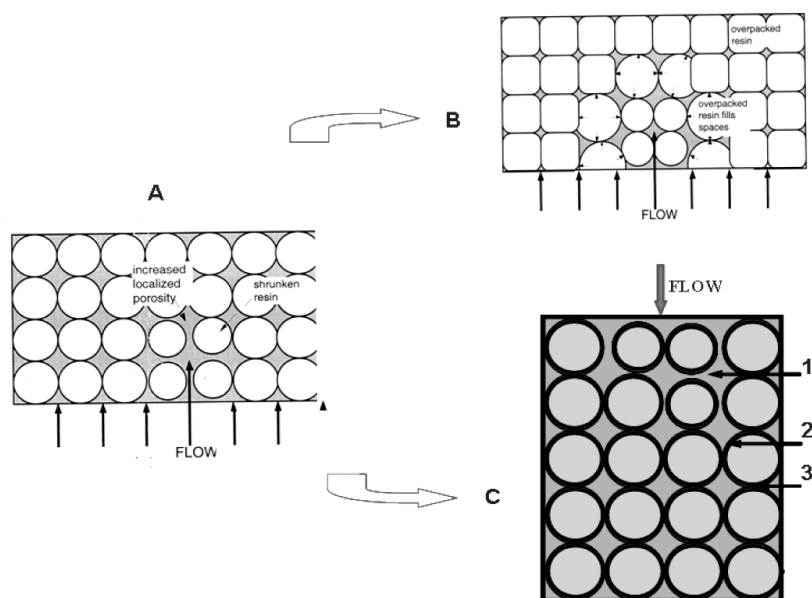


Fig. 1. Two ways of reducing longitudinal dispersion in column: A: system with progressing erosion of the concentration profile; B: over-packed bed; C: bed filled with liquid organic phase: 1, organic fluid; 2, working solution; 3: contact point.

Pictures A and B are taken from the patent publication [2]

## Experimental

A strong-base anion exchanger, AV-17x8, with quaternary ammonium functional groups, and a strong-acid cation exchanger, Ku-2x8, with sulfonic acid groups, both with polystyrene gel type matrix and produced in Russia and with grain sizes 0.5 - 0.9 mm were used.

For a variety of laboratory experiments, standard glass ion exchange columns of different sizes fitted with a single bottom drain were used. Pilot tests were carried out with a special plastic system (Figure 2). For each experiment, all the actual parameters and

conditions are listed in captions to figures and in comments in the results and discussion section.

Characteristics of organic substance, such as density and viscosity, were chosen so it always remained inside the columns during the passage of water and working solutions through the beds. Decanol was used in the columns except in identified special cases e.g. nonanoic acid.

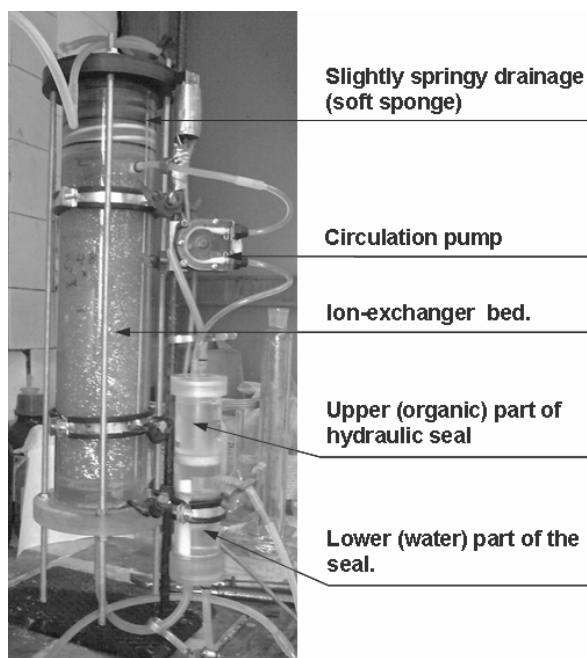


Fig. 2. Photograph of bench-scale pilot plant for separation of ionic mixtures in column with organic phase. Loading: strong base anionic resin AV-17, sulfate form; bed volume: 3150 ml, swollen in water and filled with decanol

## Results and discussion

The following interpretation of mass transfer mechanisms in the proposed system can be given. On passing ion containing solutions through a bed of granular ion exchange material in the absence of free space between the grains, as well as under conditions where the organic liquid repels water or the aqueous solution, the latter, being introduced at the interface between the organic liquid and the hydrophilic surface of the granules, forms very thin films enveloping each ion exchange bead and drains by the points of contact between them (Figure 1C). Such a steady state dynamic system of ultra-thin mobile films provides extremely well developed surface area of contact between the phases taking part in the mass exchange process.

Owing to the fact that working solutions occupy negligible space volume in the column, there is no possibility of the flows of different substances mixing, and also no problems arise with the choice of direction of these flows. The simplest variant is using a co-current downward regime.

The organic liquid always remains inside the column, but once, a very small volume can be removed on start-up of the column. For hydrodynamic reasons, such a loss can also take place on operation with too high flow rates. However, the lighter organic liquid on leaving the column seeks immediately to go up and can be returned to the column by a tube connecting bottom and top. For relatively large columns, a more complex system

shown in Figure 2 can be applied. Some examples are presented here, and they illustrate the possibilities of the proposed method, which we have called the “NewChem method” from the name of the company which played an important role in its development [13,14].

#### Simple ion exchange process with the use of the proposed method

Figure 3 shows the concentration break-through curves for the exchange of  $K^+$  and  $NH_4^+$  ions in experiments carried out entirely under the same conditions, except that a column filled with decanol was used in the experiment B.

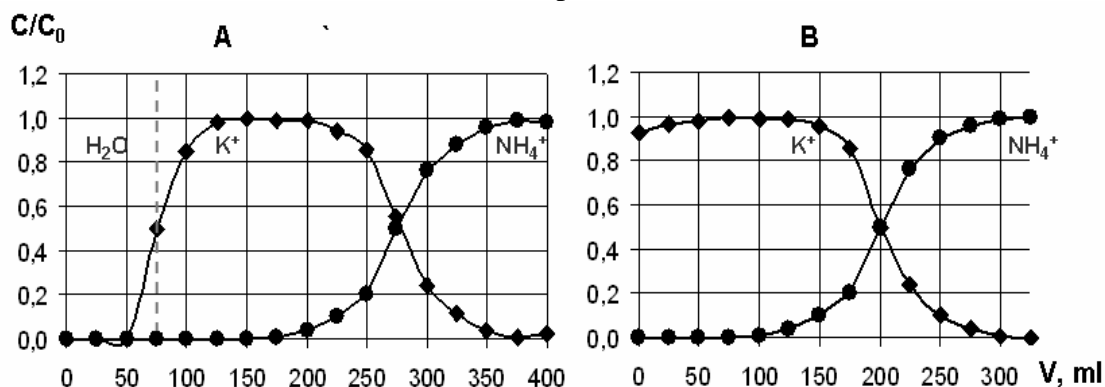


Fig. 3. Concentration histories of  $K^+$  and  $NH_4^+$  in the processes of changing the ionic form of strong acid cationic resin with the use of standard technique (A) and the NewChem method (B).

Bed volume: 110 ml KU-2 initial K-form; influent:  $1.2 \text{ mol L}^{-1}$  solution of  $NH_4NO_3$ ; flow rate: 5 bed volumes per hour ( $BV \text{ h}^{-1}$ )

Figure 3A shows that at first, as normal in the traditional experiment, water from the porosity space and free volume under the bed leaves the column, up to the volume indicated by the vertical line. Then, the salt solution of the displaced ion passes; finally, the influent component increases until equilibrium is reached. In experiment B, the displaced solution with a concentration of  $K^+$  close to the  $NH_4^+$  content in the influent appears immediately. A small difference in these concentrations is determined by the total volume of water films initially around the ion exchange beads. Comparison of the results shows that the use of two immiscible liquid phases in the processes does not affect the total exchange capacity. Under otherwise equal conditions, the new approach reduces the duration of the working cycle, thereby raising the efficiency of the ion exchange column by increasing the number of cycles within the same work period.

#### Acid Retardation processes

Consider the effect of using the NewChem method for some practical processes. Three examples are presented here. The first concerns the processing of the nepheline concentrate for production of aluminium and mineral fertilizers by treatment of solutions produced by acid leaching. The problem here is the need to separate excess acid from these solutions to return it to the head of the process, thus leading to significant savings in acid, alkali and water. It would also facilitate the purification of the aluminium solution from iron that is easier to be carried out in weakly acidic than in concentrated acid solutions.

Figure 4 shows two different concentration histories for the separation of nitric acid and aluminium nitrate on the nitrate form of a strong acid anion exchanger. The upper picture shows the results obtained using the NewChem approach while the second represents experimental results obtained with a standard column, without organic phase,

and it is given for comparison. Complete working cycles of the acid retardation method are shown there.

At the sorption stage, the actual liquid concentrate produced by acid leaching of nepheline ore is used as the feed solution, regeneration (acid desorption) is performed by deionized water. Different stages are separated in the figure by vertical dashed lines. The top picture illustrates that only the stages of sorption and regeneration take place, and the lower one shows the additional initial stage of water leaving the column bed.

With the other process conditions being equal, the new approach not only leads to a reduced duration of the working cycle, but also increases the efficiency of separation.

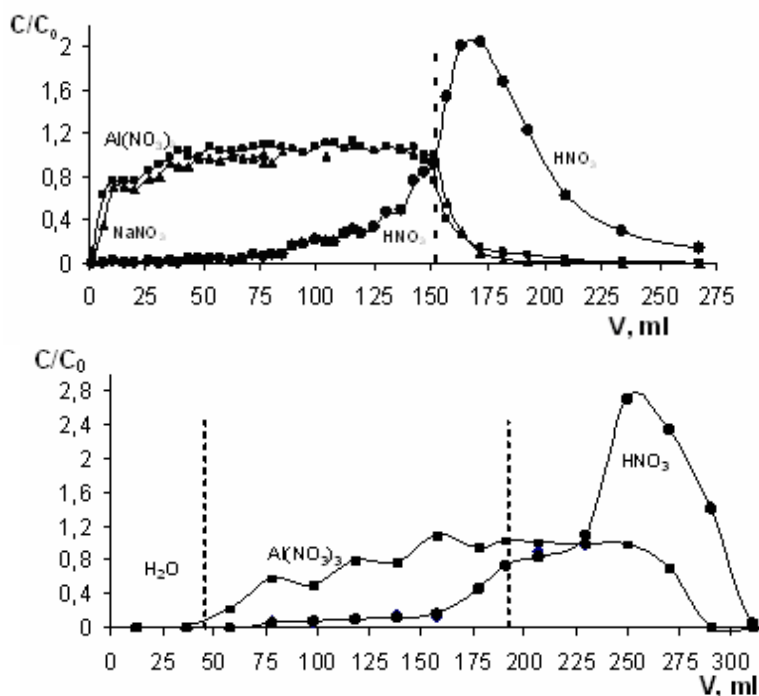


Fig.4. Break-through concentration curves of components in the separation of nitric acid and metal nitrates. Column loadings: 110 ml strong base anionic resin AV-17 NO<sub>3</sub>-form.

Composition of the influent at sorption stage (mass %): H<sub>2</sub>O: 67; Al(NO<sub>3</sub>)<sub>3</sub>: 16; HNO<sub>3</sub>: 7.3; NaNO<sub>3</sub>: 5.9; KNO<sub>3</sub>: 2.1; Fe(NO<sub>3</sub>)<sub>3</sub>: 1.2; desorbing agent: water; flow rate: 2 BV h<sup>-1</sup>.

Analysis of experimental results shows that the use of the NewChem method for Acid Retardation and separation process does not affect the equilibrium parameters of separation, but significantly influence the kinetics by the elimination of longitudinal dispersion effects.

#### Purification of a copper electrolyte

The following example concerns working electrolyte in the refining of copper. During the operation, the electrolyte is polluted by various impurity components including arsenic which seriously affects the quality of the product. Figure 5 shows the concentration curves of one of the steady-state cycles of pilot tests carried out with real electrolyte from the electrolysis section of the Balkhash copper plant (Kazakhstan). The tests were conducted on the apparatus shown in Figure 2.

To perform the separation process, the effect of competitive sorption of sulfuric acid and the As(III) and As(V) acids are used here. As seen Figure 5, arsenic derivatives are retarded much more selectively. The As concentrate produced at the desorption stage

contained not too much of the valuable component copper which could be recycled into a further operational process for arsenic utilization.

#### Preparation of samples for analysis

Finally, consider an example of sample preparation in elemental analysis, in particular, for efficient reduction of the acidity of solutions produced by the autoclave or micro-wave decomposition of difficultly soluble materials, such as geological mineral samples or biological tissue like bones. Removal of excess acid from acidic solutions is important in two cases: use of analytical instruments such as ICP MS or ISP ES, for which the samples should be not strongly acidic and using combined analytical schemes with pre-concentration where the preparation of solutions is followed by a sorption. In practice, various conventional methods are applied to separate of excess acids, for example, controlled evaporation or neutralization. The first of these is characterized by high labour intensity, the second an increase in the overall mineralization of the sample, which is also undesirable.

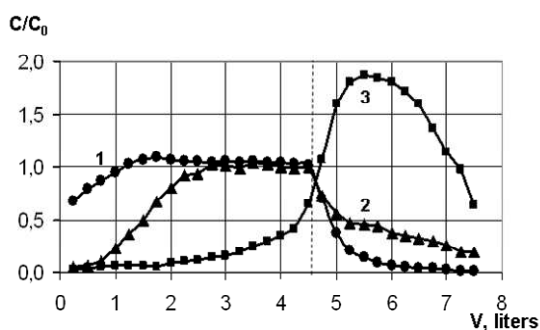


Fig. 5. Break-through curves of some components in the process of arsenic removal from copper electrolyte. 1:  $\text{CuSO}_4$ ; 2:  $\text{H}_2\text{SO}_4$ ; 3:  $\text{H}_3\text{AsO}_3 + \text{HA}_3\text{O}_3$ .

[Column loadings: 3000 ml AV-17 strong base anionic resin in initial form equilibrated with pure electrolyte and washed after with water.

Composition of the influent at sorption stage ( $\text{g L}^{-1}$ ):  $\text{H}_2\text{SO}_4$ : 220;  $\text{CuSO}_4$ : 105; Total As:  $4.5 \text{ mg L}^{-1}$ . Desorbing agent: water.

Flow rate:  $2 \text{ BV h}^{-1}$ ]

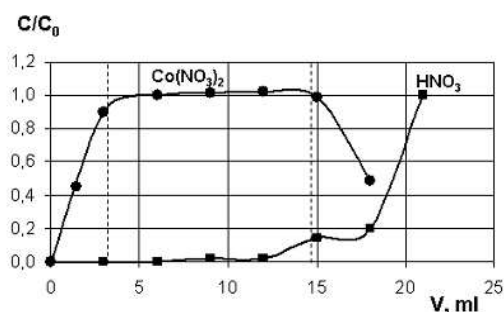


Fig. 6. Concentration curves for the separation of nitric acid and metalnitrates. Analytical column bed:  $L=25 \text{ cm}$ ,  $S = 1 \text{ cm}^2$  of strong base anionic resin AV-17 in  $\text{NO}_3^-$  form. Composition of the initial model solution ( $\text{mol/l}$ ):  $\text{HNO}_3 - 5.89$ ;  $\text{Ca}(\text{NO}_3)_2 - 1.47$ ,  $\text{Fe (II)} - 1 \cdot 10^{-3}$ ,  $\text{Mn} - 1 \cdot 10^{-3}$ ,  $\text{Cu} - 1 \cdot 10^{-4}$ ,  $\text{Zn} - 2 \cdot 10^{-4}$ ,  $\text{Co} - 1 \cdot 10^{-4}$ . Desorbing agent - water. Flow rate:  $1.2 \text{ BV/h}$

Experimental results in Figure 6 demonstrate the prospects for using the NewChem method for de-acidification of solutions before their elemental analysis. A model solution of bone decomposition with nitric acid in autoclave was used in the experiment.

All the concentration curves for micro-components appear together and are superimposed each on other, which is why only the curve for Co is shown. Two features can be noted: a) the micro-component is partially sorbed and contained in first fractions of effluent in lower concentration than the influent; b) the fractions which correspond to the interval of volume between the vertical lines in the figure can be used for analyses because they are almost free of acid and contain the analyte in concentrations very close the initial sample.

Here, we do not give the details, but can refer the article [14], which describes details of this analysis and the results of the reproducibility of analysis of an actual bone

mineralisation in repeated experiments on sorption and desorption. The results showed that with tiny columns filled with organic phase, we can practice not consuming techniques and work with small volumes of samples at significantly reduced durations of analytical experiments.

#### The process with ion exchange super-saturation (IXISS) effect

Consider the effect of using the NewChem method by the example of one of relevant to practice ion exchange processes accompanied by the formation of super-saturated solutions, namely, the conversion of potassium chloride to potassium sulfate. In case of ordinary IEX technique, two variants of the process can be used [15]: according to the first of them, strong base anion exchanger in a stationary bed is transformed from initial chloride form into sulphate one using sodium sulphate of any concentration, and then, the solution of potassium chloride close to saturation is passed through a column in the upward direction; on the second variant, strong acid cationic resin in sodium form is transformed into potassium one using the concentrated solution of potassium chloride, and then, the nearly saturated solution of sodium sulphate is passed through a column, in the same way, in the upward direction. In both variants, at the second stages of the processes, during the regeneration of resins into initial ionic forms, a parallel process takes place: relatively stable super-saturated solution of potassium sulphate is formed inside the bed. From this solution, at leaving the ion exchanging bed, a solid product crystallizes spontaneously. After insulation of the crystals of potassium sulfate, next portion of sodium sulfate (in an amount strictly equivalent to the product output) is added into the residual solution of a mixture of sulfates, and the process continues without any liquid waste. Experience shows that the problem of accumulation of sediment over the sorption bed arises often; this effect is why the process goes out of the steady state regime of repeated cycles of sorption-regeneration. When using the proposed method with the direction of flow of regenerating solution from the top down, and at the organization of the process without free volume under the ion exchanging bed, the crystallization in an effluent occurs only outside the column. This eliminates the causes that prevent the formation of a stable steady state. Concentration curves of the components for one of the completely recurring cycles for the variant with the cationic resin are shown in Fig.7.

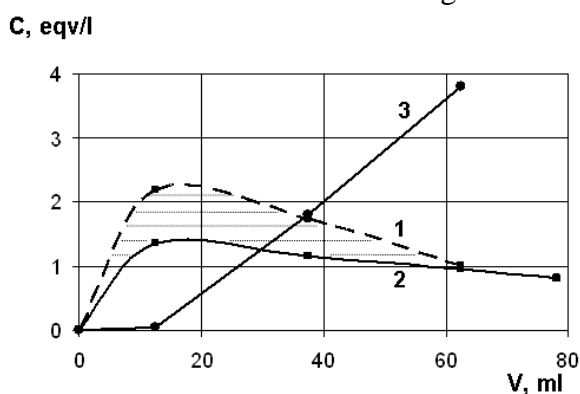


Fig. 7. Concentration histories of  $K^+$  and  $Na^+$  in steady - state process of obtaining potassium sulfate. 1- concentration of  $K^+$  in supersaturated solution. 2 - concentration of  $K^+$  in residual (saturated) solution after the spontaneous crystallization of  $K_2SO_4$ . Bed volume: 40 ml of KU-2 in initial K-form. Influent: saturated solution of  $Na_2SO_4$   $K_2SO_4$  mixture . Flow rate: 2 bed volumes per hour (BV/h). Organic phase - nonanoic acid.



## Conclusions

A new approach to the organization of mass-transfer processes in ion-exchange and sorption columns is proposed. The approach consists in the fact that the columns loaded by granulated resins are additionally filled with organic liquids immiscible with aqueous solutions. On the example of a number of actual processes for separation of ionic mixtures, the proposed method is experimentally tested and its advantages are demonstrated.

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