

# Clean Ion-Exchange Technologies. I. Synthesis of Chlorine-Free Potassium Fertilizers by an Ion-Exchange Isothermal Supersaturation Technique

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This paper reports the results of studying ion-exchange synthesis of chlorine-free potassium sulfate from KCl and Na<sub>2</sub>SO<sub>4</sub> on strong acid cation-exchange and strong base anion-exchange resins using an ion-exchange isothermal supersaturation (IXISS) effect. This effect is observed for a number of ion-exchange systems, where the ion-exchange process is accompanied by the formation of a stable supersaturated solution of slightly or sparingly soluble substances in the interstitial space of ion-exchange columns. The formation of stable K<sub>2</sub>SO<sub>4</sub> solutions in the columns has been observed by the displacement of either K<sup>+</sup> or SO<sub>4</sub><sup>2-</sup> ions from a cation or anion exchanger with concentrated Na<sub>2</sub>SO<sub>4</sub> or KCl solutions, respectively. After leaving the column, a supersaturated solution crystallizes spontaneously, which allows for the design of a practically ideal ion-exchange process where a crystalline chlorine-free potassium sulfate is obtained right after the ion-exchange conversion cycle. The process is practically wasteless and ecologically clean; hence, it can be considered as a competitive alternative to existing K<sub>2</sub>SO<sub>4</sub> production technologies based on, e.g., the Mannheim process. The flow sheet of a proposed process is presented and discussed.

## Introduction

The application of ion-exchange processes in different fields of industry is progressively growing. In many instances the ion-exchange technology can successfully substitute existing large-scale industrial processes which do not satisfy the modern ecological standards. The specific requirements that the ion-exchange technology should have to create a competitive process are high efficiency and ecological safety. However, the general scheme of the majority of known ion-exchange separation and purification processes remains, as a rule, practically unchanged during the last 40–50 years (Nachod and Schubert, 1957; Arkhangelsky and Belinskaya, 1982; Streat, 1991). The flow sheet of the "standard" ion-exchange process comprises the following auxiliary operations: (1) preparation of the solution under treatment; (2) concentration of the solution after the ion-exchange treatment, e.g., by evaporation; (3) recovery of the purified product, e.g., by crystallization; (4) regeneration of the ion exchanger and auxiliary reagents for reuse; (5) neutralization of aggressive wastes prior to their disposal; and some others.

Elimination of any of these auxiliary operations can improve the efficiency of the process due to significant savings of chemical reagents, energy, manpower, minimization of wastes produced, etc. Several approaches can be applied for achieving this purpose. One of those is based on governing the separation process by modu-

lation of some intensive thermodynamic parameters of a given ion-exchange system, such as temperature, ionic strength, pH, etc., which are known to shift the equilibrium in the system. For example, application of dual-temperature ion-exchange processes (Andreev et al., 1961; Gorshkov et al., 1977; Bailly and Tondeur, 1978, 1980; Muraviev et al., 1995, 1996, 1997a), which exploit the different affinities of the ion exchanger toward target ions at different temperatures, allows one to exclude (completely or partially) two of the auxiliary operations mentioned (4 and 5). Hence, practically reagentless and wasteless, as a result, separation processes can be designed (Muraviev et al., 1997b,c; Khamizov et al., 1995).

Another possibility for elimination of auxiliary operations (such as, e.g., 2 and 3) from the flow sheet of the standard ion-exchange process may be based on a combination of ion-exchange conversion and concentration processes in one stage. Two ion-exchange fractionation techniques such as frontal (also known as frontal ion-exchange chromatography (Bobleter and Bonn, 1991; Muraviev et al., 1992b)) and reverse frontal separation (Muraviev et al., 1992a; Gorshkov et al., 1997) are applicable for this purpose. In certain instances, both of those separation techniques allow achievement of a concentration of the target substance up to and beyond the level exceeding its solubility at a given temperature. Moreover, this supersaturated solution may remain stable within the column interstitial space for a long period. After leaving the column, a supersaturated solution crystallizes spontaneously, which allows for the design of a practically ideal ion-exchange process where a crystalline product is obtained directly after the ion-exchange treatment cycle. This phenomenon—known

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as ion-exchange isothermal supersaturation (IXISS)—was discovered for the first time by Muraviev (Muraviev, 1979).

This paper commences a series of investigations on the tailored application of the IXISS effect for the design of highly efficient and ecologically clean ion-exchange technologies which can be considered as a successful alternative to existing large-scale industrial processes. The first paper of this series is dedicated to the IXISS-based synthesis of chlorine-free potassium fertilizers.

Potassium is known to have several important functions in plant metabolism. It plays an essential role in the water economy of plants through the action of its soluble compounds on osmotic pressure. Potassium is involved in oxidative reactions as a carrier for iron required by important enzymes which convert sugar to starch and amino acids to protein. Sugarbeets, potatoes, and other plants that produce large quantities of carbohydrates use large amounts of potassium. The production of chlorine-free potassium salts (with a minimum  $\text{Cl}^-$  admixture) such as  $\text{K}_2\text{SO}_4$  and others is of particular interest since it deals with the problem of effectively cultivating some chlorophobic plants such as citrus, vegetables, herbs, etc., which are adversely affected by high chloride concentration (Slack, 1965; Scharf, 1990).

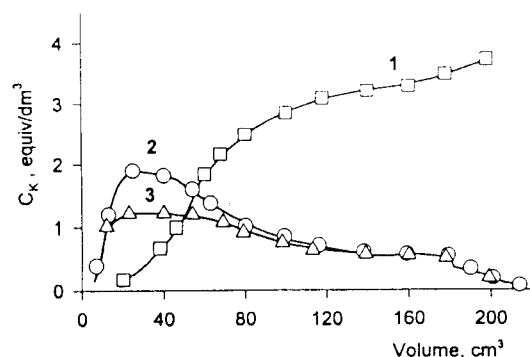
Almost 90% of  $\text{K}_2\text{SO}_4$  is for fertilizer, but it is also used for the manufacture of glass and in medicine. Potassium sulfate is produced in substantial quantities in Europe by the Mannheim process from  $\text{K}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$  or by reaction of  $\text{H}_2\text{SO}_4$  with  $\text{KCl}$  (Elvers et al., 1993). Both versions of the Mannheim process are complicated by problems of utilizing gaseous wastes ( $\text{CO}_2$  and  $\text{HCl}$ ). In the U.S. and some other countries  $\text{K}_2\text{SO}_4$  is manufactured by various exchange reactions between potassium, sodium, and magnesium salts by their dissolution and fractional crystallization (Scharf, 1990; Elvers et al., 1993). The last process requires utilization of large volumes of liquid wastes.

The ion-exchange synthesis can be successfully applied for the manufacture of potassium fertilizers such as, e.g., potassium nitrate (Senyavin, 1980). Moreover, under certain conditions this technique gives a number of advantages in comparison with traditional technologies. An example is the ion-exchange conversion of  $\text{KCl}$  and  $\text{NH}_4\text{NO}_3$  into chlorine-free  $\text{KNO}_3$  on a strong acid cation exchanger, reported by Gorshkov et al. (1987). The process is carried out in two countercurrent columns and is continuous, highly efficient, and practically wasteless. The only ion-exchange method of  $\text{K}_2\text{SO}_4$  synthesis from  $\text{CaSO}_4$  and  $\text{KCl}$  described in the literature (see Elvers et al., 1993; p 90) refers to the standard ion-exchange processes; i.e., it is characterized by the drawbacks mentioned above and does not allow one to produce chlorine-free potassium sulfate.

This study was undertaken to study the conditions of the ion-exchange synthesis of chlorine-free  $\text{K}_2\text{SO}_4$  from potassium chloride and sodium sulfate on cation- and anion-exchange resins and to find the optimal experimental conditions for formation of stable supersaturated solutions of sparingly soluble potassium sulfate in the interbed space of the column and those for crystallization of the product after collecting it from the columns.

## Experimental Section

**Materials, Ion Exchangers, and Analytical Methods.** Sodium sulfate, sodium chloride, and potassium



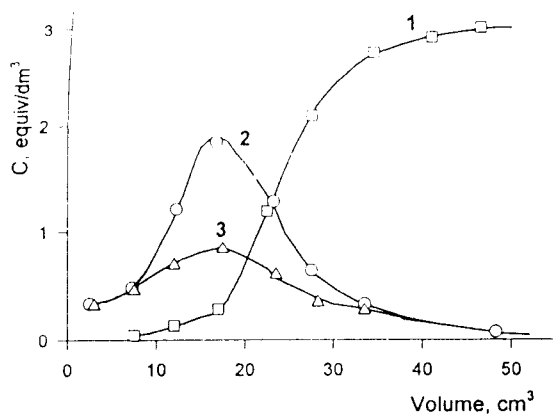
**Figure 1.** Concentration–volume history of stripping of  $\text{K}_2\text{SO}_4$  from KU-2  $\times$  8 resin in the K-form with 2 M  $\text{Na}_2\text{SO}_4$  in the first cycle (see text). Concentrations of  $\text{Na}^+$  (1) and  $\text{K}^+$  (2) in a supersaturated eluate. Curve 3 corresponds to the  $\text{K}^+$  concentration in supernatant after crystallization of supersaturated solution samples. Conditions: resin bed height,  $L = 40$  cm; column cross-sectional area,  $s = 2.5$  cm<sup>2</sup>; solution flow rate,  $\nu = 1.2$  BV (bed volumes)/h.

chloride of p.a. grade were used as received. A strong acid sulfonate cation exchanger KU-2  $\times$  8 and strong base anion exchanger AV-17  $\times$  8 (both of gel type) were poly(styrene–divinylbenzene) (PS–DVB) based commercial resins (Russian production) with total capacity values of 4.5 (KU-2  $\times$  8) and 2.1 (AV-17  $\times$  8) mequiv/g. The concentrations of  $\text{Na}^+$  and  $\text{K}^+$  were determined by flame photometry using a Saturn-4 (Russia) photometer. Concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were determined by ion chromatography using a Biotronic IC-5000 (Germany) chromatograph. The X-ray analysis was performed on a DRON-3 diffractometer (Russia). The relative uncertainty of the determination of ion concentrations in all cases was not more than 2%.

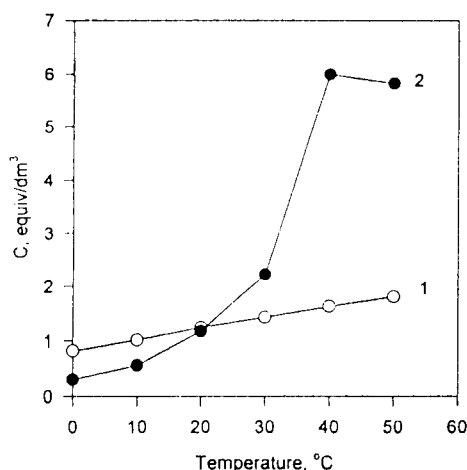
**Procedure.** All experiments on the ion-exchange synthesis of  $\text{K}_2\text{SO}_4$  were carried out under dynamic conditions in laboratory-scale jacketed thermostatic glass columns connected with a thermostat. The ion exchangers were preliminarily subjected to conventional conditioning by carrying out several ion-exchange cycles followed by their conversion into the desired ionic form (see below) and rinsing with deionized water. Then the concentrated solution of the respective sodium or potassium salt was passed through the columns, and the supersaturated eluate was collected in portions where the concentrations of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  ions were periodically determined. After complete crystallization of supersaturated solutions, the crystals were separated from the supernatant, rinsed with a small portion of cold water, and dried. The composition of the crystalline product was determined by dissolution of a certain portion of  $\text{K}_2\text{SO}_4$  obtained in water, followed by determination of  $\text{Na}^+$  and  $\text{Cl}^-$  impurities.

## Results and Discussion

The typical concentration–volume histories of the ion-exchange synthesis of potassium sulfate accompanied by IXISS of the product are shown in Figures 1 and 2, where the cation- (Figure 1) and anion-exchange (Figure 2) versions of the process are presented. As seen in Figure 1, the displacement of  $\text{K}^+$  ions from the KU-2  $\times$  8 resin with a concentrated  $\text{Na}_2\text{SO}_4$  solution leads to the formation of a zone where potassium sulfate exists in the form of a supersaturated solution with a supersaturation degree  $\gamma \approx 2$ . To achieve the maximum efficiency of the process shown in Figure 1, the stripping



**Figure 2.** Stripping of  $K_2SO_4$  from a AV-17  $\times$  8 anion exchanger in the  $SO_4$ -form with 3 M KCl at 282 K. Concentrations of  $Cl^-$  (1) and  $SO_4^{2-}$  (2) in a supersaturated solution. Curve 3 corresponds to the concentration of  $SO_4^{2-}$  in supernatant after crystallization of supersaturated solution samples. Conditions (see Figure 1):  $L = 20$  cm;  $s = 1.25$  cm $^2$ ;  $v = 1.2$  BV/h.



**Figure 3.** Temperature dependencies of  $K_2SO_4$  (1) and  $Na_2SO_4$  (2) solubilities.

with  $Na_2SO_4$  was carried out at 308 K, followed by crystallization of the product at 293 K. As seen in Figure 3, where the temperature dependencies of  $K_2SO_4$  and  $Na_2SO_4$  solubilities are shown, these conditions provide the highest difference in sodium and potassium sulfate solubilities inside the column. In other words, the solution of the displacer ( $Na_2SO_4$ ) appears to be unsaturated, while that of the product ( $K_2SO_4$ ) is supersaturated. Nevertheless,  $K_2SO_4$  does not precipitate in the column and remains as a stable supersaturated solution at least over a period of several hours. Removal of this solution from the column leads to spontaneous crystallization of the product in the form of coarse well-shaped crystals, which can be easily separated from the supernatant by filtration or sedimentation methods. The crystallization of  $K_2SO_4$  from the solution collected (which is, in fact, a supersaturated solution of both potassium and sodium sulfates; see Figure 3) is a relatively fast process which finishes within 3–5 h. At the same time, crystallization of  $Na_2SO_4 \cdot 10H_2O$  is characterized by an induction period of over 10 h.

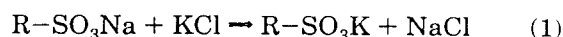
The process shown in Figure 2 appears to be more efficient when carried out at low temperature to minimize the solubility of the product in the solution collected. Hence, both stripping and product crystallization stages were carried out at 282 K. Nevertheless,

the process shown in Figure 2 was characterized by the same features as that discussed above. The crystalline  $K_2SO_4$  obtained in both processes contained less than 0.1% of  $Cl^-$  admixture.

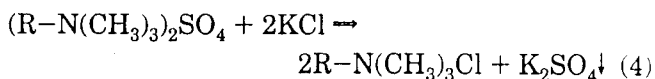
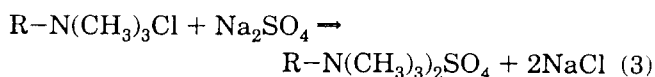
One paramount feature of the IXISS processes under consideration must be emphasized. As seen in both Figures 1 and 2, the concentration profiles of ions displacers (see curves 1 in Figures 1 and 2) are sharper than one would expect, which indicates the sufficiently high selectivity of the resins for  $Na^+$  and  $Cl^-$  against  $K^+$  and  $SO_4^{2-}$ , respectively. This conclusion may seem to contradict the conventional order of selectivity of KU-2  $\times$  8 and AV-17  $\times$  8 resins toward ionic couples under consideration. Indeed, the first resin is known to be more selective toward  $K^+$  over  $Na^+$  while the second usually preferentially sorbs  $SO_4^{2-}$  from  $SO_4^{2-}$ - $Cl^-$  mixtures.

To understand this discrepancy, consider the ion-exchange reactions applied for the IXISS-based synthesis of  $K_2SO_4$  from KCl and  $Na_2SO_4 \cdot 10H_2O$ , which can be written as follows:

#### 1. Cation-exchange process



#### 2. Anion-exchange synthesis



where R in reactions (1)–(4) denotes the PS-DVB matrix.

In the first process, a sulfonate cation exchanger is first converted from the Na-form into the K-form with a dilute KCl solution (0.1 mol/dm $^3$ ), followed by desorption (stripping) of the product ( $K_2SO_4$ ) with a concentrated  $Na_2SO_4$  solution (2 mol/dm $^3$ ). The second process starts with the conversion of a strong base anion exchanger from the Cl-form into the  $SO_4$ -form with a dilute  $Na_2SO_4$  solution (0.25 mol/dm $^3$ ). Then,  $K_2SO_4$  is produced during the stripping of sulfate ions with a concentrated KCl solution (4 mol/dm $^3$ ).

The necessity to apply dilute KCl and  $Na_2SO_4$  solutions at the first stages of both processes follows from the need to shift the ion-exchange equilibrium in both systems to the right. The equilibrium separation factor  $\alpha$  for, e.g.,  $Na^+$ - $K^+$  exchange (see reaction 1), can be written as follows:

$$\alpha_{K}^{Na} = \frac{q_{Na} C_K}{q_K C_{Na}} \quad (5)$$

where  $q$  and  $C$  are the concentrations of sodium and potassium ions in the resin and solution phases, respectively.

If a sulfonate cation exchanger (KU-2  $\times$  8 in our case) is equilibrated with a dilute solution of  $K^+$ - $Na^+$  mixtures, the respective  $\alpha$  value is known to be  $< 1$  (Dorfner, 1991a); i.e., the resin is more selective for  $K^+$ . Let us suppose that  $K_2SO_4$ , displaced from the resin by a concentrated  $Na_2SO_4$  solution ( $C_0$ , equiv/dm $^3$ ), forms a

stable supersaturated solution, where potassium sulfate exists in an associated (molecular) form at a concentration  $C_M$  (equiv/dm<sup>3</sup>) exceeding  $\gamma$  times the solubility of  $K_2SO_4$ ,  $C_S$ , at a given temperature. Formation of the molecular form of  $K_2SO_4$  can be described by the respective dissociation constant,  $K_D$ , which can be written for the conditions under consideration (for the supersaturated solution) in the following form:

$$K_D = \frac{C_K \cdot (C_0 - C_M)}{C_M} \quad (6)$$

By introducing  $C_M = \gamma C_S$  and after substituting  $C_K$  from (6) into (5), one obtains

$$\alpha_K^{Na} = \frac{q_{Na}}{q_K} \frac{K_D \gamma C_S}{C_0(C_0 - \gamma C_S)} \quad (7)$$

As follows from eq 7, at constant  $C_0$ ,  $C_S$ , and  $K_D$ ,  $\alpha$  increases with  $\gamma$  and may reach sufficiently high values ( $\gg 1$ ), as  $\gamma \rightarrow C_0/C_S$ . Note that the same reasoning can be used for interpretation of the selectivity reversal in the anion-exchange system under study (see eqs 3 and 4).

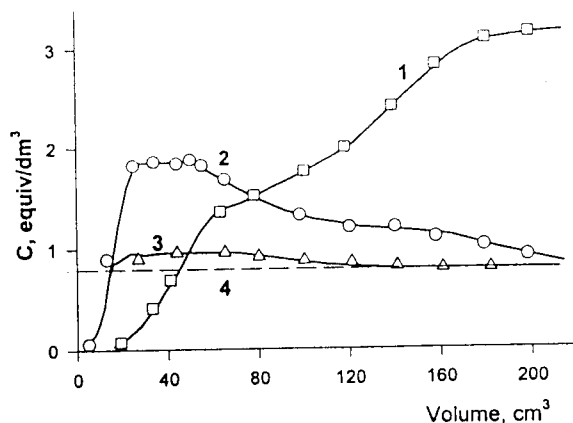
Equation 7 can be rewritten in a general form as follows:

$$\alpha_{Sss}^{Dis} = \frac{q_{Dis}}{q_{Sss}} \frac{K_D \gamma C_S}{C_0(C_0 - \gamma C_S)} \quad (8)$$

where "Dis" and "Sss" sub- and superscripts denote the displacer and the substance under supersaturation (product), respectively;  $C_0$  is the concentration of the displacer (equiv/dm<sup>3</sup>);  $K_D$  is the dissociation constant of the product (see eq 6);  $C_S$  is the solubility of the product at a given temperature (equiv/dm<sup>3</sup>) and  $\gamma$  is the supersaturation degree of the product solution.

Equation 8 represents the fundamental equation of the IXISS phenomenon, which helps to interpret the shift of ion-exchange equilibrium in supersaturated solutions obtained in different IXISS processes. The validity of this equation has been approved by the results obtained by Khamizov et al. (1996) by studying IXISS-based processes on decalcination of seawater and recovery of magnesium compounds from seawater.

Application of the IXISS effect in the flow sheets of both processes studied allows one to improve significantly the product formation stage due to the shift of the ion-exchange equilibrium in reactions (2) and (4) to the right. Another advantage of the IXISS-based processes under consideration deals with the possibility of reusing the supernatant obtained after separation of the product (crystalline  $K_2SO_4$ ) as a displacer in the second, third, etc., and subsequent desorption cycles. For example, after separation of  $K_2SO_4$  crystals, the supernatant obtained in the first process is fortified with  $Na_2SO_4$  up to the total concentration of sulfate ions of 2 mol/dm<sup>3</sup> and then is directed to the next stripping cycle (see eq 2). Figure 4 shows the concentration-volume history obtained in one of the repetitive  $K_2SO_4$  desorption cycles carried out. A comparison of the results shown in Figure 4 with those presented in Figure 1 indicates that the stripping of potassium sulfate with the  $Na_2SO_4$ - $K_2SO_4$  mixture, obtained after the first cycle, proceeds with nearly the same efficiency. Similar results were obtained in the sequential experiments on desorption of sulfate anions from the AV-17



**Figure 4.** Concentration-volume history of stripping of  $K_2SO_4$  from KU-2  $\times$  8 resin in the K-form with a 1.6 M  $Na_2SO_4$  + 0.4 M  $K_2SO_4$  mixture in the second repetitive cycle (see text). Concentrations of  $Na^+$  (1) and  $K^+$  (2) in a supersaturated eluate. Curve 3 corresponds to the  $K^+$  concentration in supernatant after crystallization of supersaturated solution samples. Dotted line 4 corresponds to the  $K_2SO_4$  content in the stripping solution used in the second cycle (after recovery of solid  $K_2SO_4$  and fortification of the solution with  $Na_2SO_4$ ). Conditions are the same as in Figure 1.

$\times$  8 resin with  $KCl$ - $K_2SO_4$  mixtures. Hence, the only waste which is produced in both versions of the process is the dilute  $NaCl$  solution, which can be readily concentrated by, e.g., reverse osmosis. The desalinated water obtained can also be returned to the process.

Another feature of IXISS-based synthesis of  $K_2SO_4$  under consideration follows from the results of a test experiment on the determination of the mechanism of potassium sulfate crystallization in the resin bed. This experiment was carried out as follows: a certain volume of a concentrated  $Na_2SO_4$  solution was passed through the column with KU-2  $\times$  8 resin in the K-form (see eq 2) until the formation of a zone of a supersaturated  $K_2SO_4$  solution in the resin bed. Then, the displacer solution flow was stopped. After completing the  $K_2SO_4$  crystallization in the interstitial space of the column, the resin was removed from the column together with potassium sulfate crystals, separated from crystals, rinsed with a small portion of water, and dried. A dry resin sample was examined by X-ray diffraction analysis, which demonstrated the absence of any crystals inside the amorphous resin phase. The main conclusion which follows from the results obtained in this experiment is that *the crystallization of the supersaturated solution obtained in the IXISS proceeds only in the solution phase* (see below).

The last conclusion becomes clearer after comparison of IXISS with other isothermal supersaturation techniques (Khamisky, 1975). Such a comparison shows that this technique is similar to those based on chemical reactions, leading to the formation of low (or sparingly) solubility substances in the solution phase (see, e.g., reactions (2) and (4)). However, several features of IXISS allow one to distinguish the ion-exchange supersaturation technique as a separate concentration method.

Formation of a supersaturated solution proceeds in an isolated interstitial space. The initial salt solution is percolated through the granulated resin bed, which serves as a highly effective chemical and physical filter, removing both chemical (ionic) and mechanical (e.g., suspended microparticles) impurities. As a result, the supersaturated solution is formed under practically ideal conditions in a highly pure state.

Since the solubility of the displacer used in the IXISS process must be far higher than that of the substance under displacement (i.e., under supersaturation), this makes it possible to achieve significant supersaturation degrees. The rate of supersaturation (or supercooling in polythermal supersaturation) is known to influence the stability of supersaturated solutions (Muraviev et al., 1982). This parameter can also be easily regulated in IXISS processes by varying both the displacer solution concentration and flow rate.

A supersaturated solution formed in the interstitial space (e.g., during the  $K_2SO_4$  desorption stage) is in contact with the granular resin until it leaves the column. The time during which this solution remains in contact with the resin phase depends on the solution flow rate (at a given height of the resin bed) and varies from several tens of minutes to several hours. The stabilization of the supersaturated solution which is observed within this period is of particular importance in designing IXISS-based processes (Muraviev et al., 1982; Muraviev and Fesenko, 1982). In the case of inorganic substances a unified interpretation of the IXISS phenomenon must be based on the general principles of the aggregative stability of dispersions of precrystalline molecular aggregates formed in the interstitial space of the column. In this context the supposition about the homogeneous mechanism of crystallization in IXISS is of particular importance. This supposition can be substantiated by the following considerations on the possibility of solid-phase formation inside the resin beads in an IXISS process.

The volume of a single micropore in a conventional ion exchanger, for example, of gel type, can be estimated to be around  $10^{-13}$  cm<sup>3</sup> (Dorfner, 1991b). Assuming that this pore is filled with a 1.0 mol/dm<sup>3</sup> supersaturated solution, the pore contains ~600 molecules or ions, which can form associates (nucleus) of radius ~10 Å. The Gibbs energy for a particle of radius  $r$  aggregated with  $g$  molecules in a solution with a supersaturation degree of  $\gamma$  can be estimated as follows (Adamson, 1976):

$$\Delta G = -gkT \ln \gamma + 4\pi r^2 \sigma \quad (9)$$

where  $\sigma$  is the surface tension and

$$gkT \approx \frac{4}{3} \frac{\pi r^3 \rho}{M} RT \quad (10)$$

Here  $\rho$  and  $M$  are the density (g/cm<sup>3</sup>) and the molecular weight (g/mol) of the substance, respectively. Crystallization of the substance starts when  $r$  exceeds  $r_{crit}$ , which corresponds to the maximum on the  $\Delta G = f(r)$  curve, i.e., to the condition  $\partial \Delta G / \partial r = 0$  (Kidyarov, 1979). At  $r \leq r_{crit}$  the supersaturated solution remains stable since the excess of the particle energy does not decrease when  $r$  rises. An estimation of  $r_{crit}$  values for  $\gamma = 5$  and  $\rho/M = 10^{-2}$  gives  $r_{crit} = 10-100$  Å. The result obtained indicates that no solid-phase formation can occur inside the resin beads. This conclusion becomes clearer if one assumes that the nuclei formed in the resin micropores are to be isolated from each other so that no interactions leading to the spontaneous crystal growth can take place. An independent confirmation of this conclusion has been obtained by Muraviev et al. (1992b) by studying the kinetics of ion exchange in polyphase systems including crystallizing substances.

Finally, we consider the results obtained in the present study from a practical viewpoint to propose a

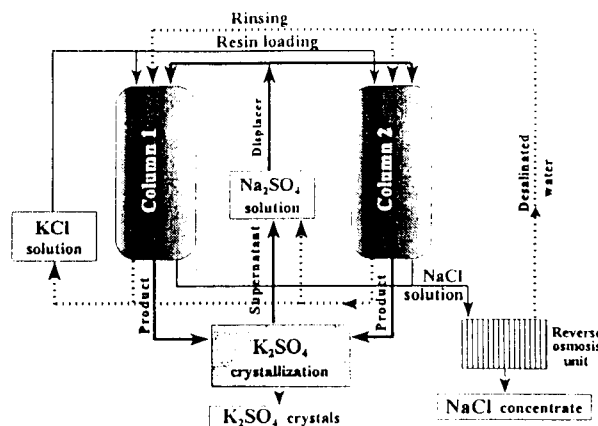


Figure 5. Flow sheet of the process for cation-exchange synthesis of chlorine-free potassium sulfate.

flow sheet of the ion-exchange process for the synthesis of chlorine-free potassium sulfate. The block scheme of the cation-exchange version of the process is presented in Figure 5. The unit comprises two ion-exchange columns operating intermittently in a loading (see eq 1) or displacement (see eq 2) mode of operation. The second stage (displacement) is carried out by using a  $Na_2SO_4$  (or a  $Na_2SO_4-K_2SO_4$  mixture) solution at 308 K. The rinsing water produced after each stage is returned to the process and is used for dissolution of either KCl (rinsing after loading) or  $Na_2SO_4$  (rinsing after displacement). The NaCl effluent obtained after the loading stage is directed into the reverse osmosis unit which produces desalinated water and NaCl concentrate, which can be, in turn, used for the manufacture of crystalline NaCl. Hence, the process appears to be practically wasteless and ecologically clean.

### Acknowledgment

A part of this work was supported by Research Grant Nos. ND-2000 and ND-2300 from the International Science Foundation and from the Science and Technology Programs of Russian Federation "Global Ocean" (Grant No. o2.08.1) and "Chemistry and Technology of Water" (Grant No. 195). D.M. thanks the Catalonian Government for the financial support of his visiting professorship at the Universitat Autònoma de Barcelona.

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Received for review September 26, 1997

Revised manuscript received January 31, 1998

Accepted January 31, 1998

IE970690O