

Note

The preparative separation of rubidium from potassium ions by a selective cation-exchange resin

RACHEL RATNER, LENI KOGAN and DAVID H. KOHN

Department of Chemistry, Technion, Israel Institute of Technology, Haifa (Israel)

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The separation of Rb^+ from K^+ is rather difficult, since both cations have quite similar physical and chemical properties. At present, the commercial production of rubidium salts is achieved by various chemical processes and rather tedious operations, such as repeated extractions, recrystallizations, etc.¹⁻³. Regarding the application of cation-exchange resins for the separation of Rb^+ from K^+ , polystyrene- and phenolic-sulphonic resins have been used in analytical work⁴⁻⁹, while macro-separations, as far as could be ascertained, have been carried out only by means of phenolic-sulphonic resins¹⁰⁻¹². The phenolic resins were probably preferred, because their selectivity coefficient is somewhat higher¹³, although their exchange rate is rather low¹⁴.

In preparative separations by means of cation-exchange resins, displacement chromatography is generally used. The main requirements of the resin are: different affinities for the cations to be separated, and suitable kinetic properties. Furthermore, a relatively cheap salt is necessary for development, whose cation has a higher affinity to the cation exchanger than the cations to be separated.

The present paper deals with the preparative separation of Rb^+ from K^+ by means of a nitrated polystyrene-sulphonic acid cation-exchange resin¹⁵, which possesses a comparatively high selectivity between the various alkali-metal cations¹⁶. Displacement development chromatography, using aqueous solutions of CaCl_2 , was applied.

EXPERIMENTAL

The following cation-exchange resins were used:

- (1) Polystyrene-sulphonic acid resin, containing 8% divinylbenzene (DVB) (52-100 mesh; capacity, *ca.* 2 mequiv./ml).
- (2) Nitrated polystyrene-sulphonic acid resin, containing 8% DVB (52-100 mesh; capacity, *ca.* 1.4 mequiv./ml).

Determination of exchange isotherms

Exchange of Rb^+ and K^+ . Exchange reactions were carried out by the static method¹⁷, shaking 1-2 g of the cation-exchange resins (K^+) with 0.2 *N* aqueous solutions (100 ml) containing KCl and RbCl in different proportions. After equilibration,

the solutions were separated from the exchanger, Rb^+ and K^+ were eluted by 2 *N* hydrochloric acid and their content was determined by use of a flame photometer (Rb^+ by atomic absorption, K^+ by the emission method). The experimental results are presented in Fig. 1.

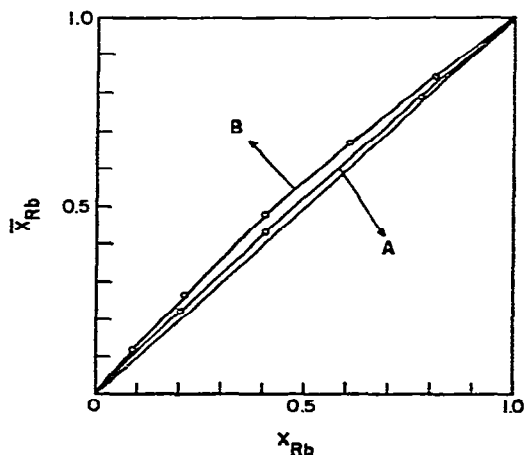


Fig. 1. Exchange isotherms for Rb^+ and K^+ on polystyrene-sulphonic acid resin (A) and nitrated polystyrene-sulphonic acid resin (B). X_{Rb} = Equivalent fraction of Rb^+ in solution; \bar{X}_{Rb} = equivalent fraction of Rb^+ in resin.

Exchange of Rb^+ and Mg^{2+} and of Rb^+ and Ca^{2+} . The isotherms were determined by the dynamic method¹⁷, by placing 2–3 g of the cation exchangers (H^+) in small columns (ca. 10 mm I.D.). The salt solutions, containing either RbCl and MgCl_2 or RbCl and CaCl_2 in different proportions at total salt concentrations of 0.1 *N*, 0.2 *N* and 0.3 *N*, were passed through the columns until equilibrium was reached, as verified by analysis of the effluents. The excess of the solutions was drawn out from the column by suction, the resins were washed with a few millilitres of distilled water and then Rb^+ and Mg^{2+} or Ca^{2+} were eluted with 2 *N* HCl and determined as described above. The experimental results are presented in Figs. 2 and 3.

Separation of Rb^+ from K^+

The separation of Rb^+ from K^+ was performed in Pyrex columns (ca. 20 mm I.D.) which were filled with the resins (Na^+) up to a height of ca. 60 cm. The total length of the resin beds of the sulphonic exchanger was ca. 120 cm and that of the nitrated exchanger was ca. 175 cm, which correspond to ca. 3.5 displacements of the loaded bands on both resins.

The loading solution consisted of a mixture (17 g) of KCl (ca. 76%) and RbCl (ca. 24%), dissolved in 1 l of water, corresponding to a total concentration of 0.207 *N* and containing 33 mequiv. Rb^+ . After loading of the solution of the mixed chlorides (1.0 l on each resin), the charged bands were eluted with an aqueous ca. 0.1 *N* solution of CaCl_2 . When Rb^+ started to appear in the effluent, fractions were collected and K^+ and Rb^+ were determined. The flow-rate was 100 ml/h for both the loading and the developing solutions. The results are given in Figs. 4 and 5.

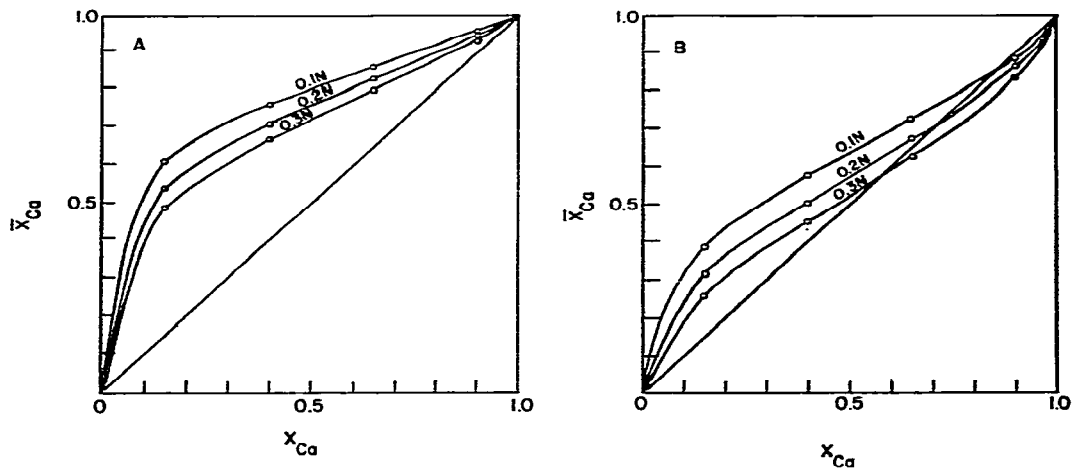


Fig. 2. Exchange isotherm for Rb^+ and Ca^{2+} . Resins as in Fig. 1. X_{Ca} = Equivalent fraction of Ca^{2+} in solution; \bar{X}_{Ca} = equivalent fraction of Ca^{2+} in resin.

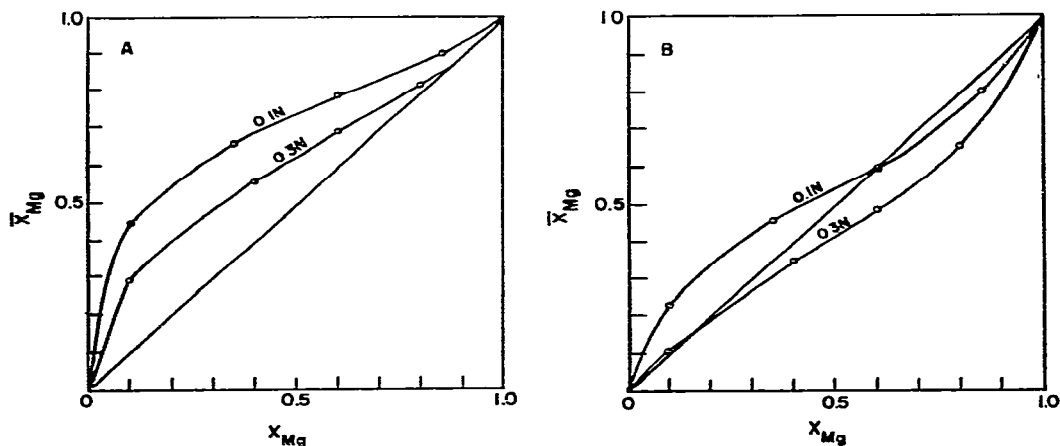


Fig. 3. Exchange isotherm for Rb^+ and Mg^{2+} . Resins as in Fig. 1. X_{Mg} = Equivalent fraction of Mg^{2+} in solution; \bar{X}_{Mg} = equivalent fraction of Mg^{2+} in resin.

RESULTS AND DISCUSSION

Selectivity coefficient K_K^{Rb}

In order to design a preparative separation by development chromatography, the selectivity coefficient (K_K^{Rb}) at the experimental conditions of concentration and ionic ratio, Rb/K , is required¹⁸, although the K_K^{Rb} values for both the resins can be calculated from the selectivity scale¹⁹. The isotherms of the $\text{Rb}-\text{K}$ exchange for both resins (Fig. 1) show that the K_K^{Rb} of the nitro resin is higher than that of the sulphonic resin at all Rb/K ratios, and that the nitro resin is suitable for separations over a wide range of Rb/K ratios. In the present study, the equivalent ratio Rb/K in the loading solution was 0.16 and the K_K^{Rb} values, found from the exchange isotherms, were 1.3 and 1.07 for the nitrated sulphonic resin and the sulphonic resin respectively.

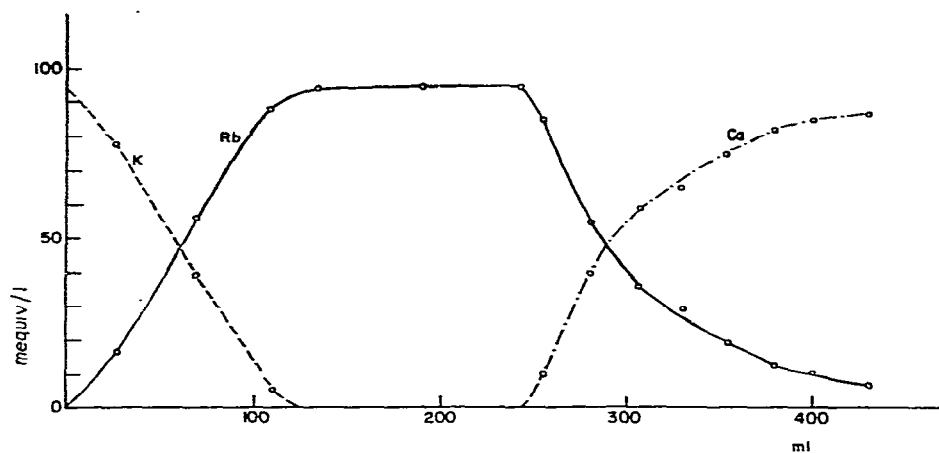


Fig. 4. Separation of Rb^+ from K^+ on the nitrated polystyrene-sulphonic acid resin.

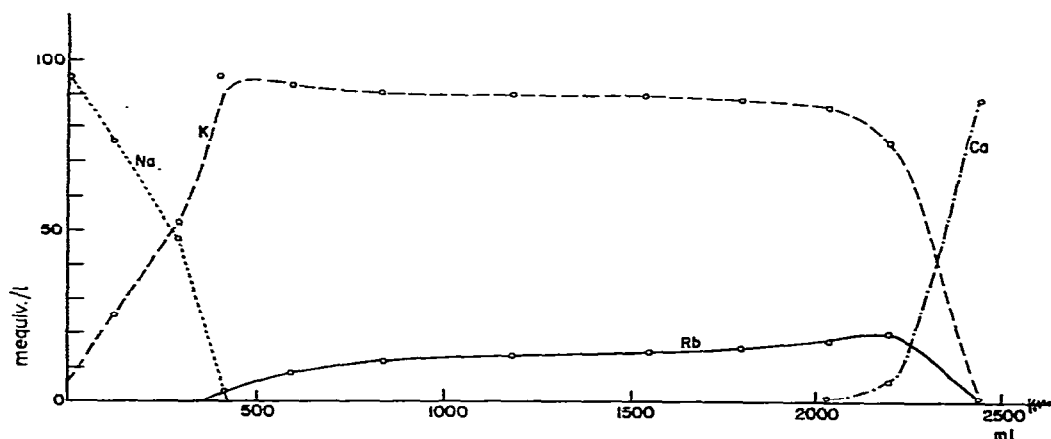
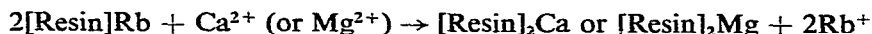


Fig. 5. Separation of Rb^+ from K^+ on the polystyrene-sulphonic acid resin.

Developing solution

For displacement, aqueous solutions of CaCl_2 and of MgCl_2 , both relatively cheap salts, were chosen for investigation.



It is known that the selectivity coefficient between ions of different valency depends on the ionic composition of the exchanger and on the concentration of the developing solution. In dilute solutions the bivalent cation is preferred, but with increasing ion concentration the selectivity is reversed^{20,21}. Therefore, in order to determine the optimal concentration of the developing solution, exchange isotherms of the cation pairs Rb^+ - Mg^{2+} and Rb^+ - Ca^{2+} were determined for solutions of 0.1 *N* and 0.3 *N* and of 0.1 *N*, 0.2 *N* and 0.3 *N* concentration respectively.

The exchange isotherms for the pairs Rb^+ - Mg^{2+} and Rb^+ - Ca^{2+} (Fig. 2 and 3) indicate that on the nitrated resin the calcium salt is a suitable developing agent at a

concentration of *ca.* 0.1 *N*. At higher concentration reverse selectivity occurs and, instead of displacement development, elution development takes place and consequently Ca^{2+} appears in addition to Rb^+ in the effluent. Solutions of MgCl_2 at the concentrations tested were found to be unsuitable as development agents.

Separation of Rb^+ from K^+

In order to resolve the loaded mixed band of $\text{Rb}^+ + \text{K}^+$ into separate zones of Rb^+ and K^+ , the mixed band must be displaced for a certain distance. The number of displacements, *i.e.*, the ratio between the total length of the resin bed (l) and the length of the loaded band (l_0), to achieve maximum separation depends mainly on the relative selectivity coefficient and to a smaller extent on the composition of the mixture to be separated. For ions of the same charge, the number of displacements can be calculated^{22,23} according to

$$v = \frac{l}{l_0} = \frac{1 + \varepsilon \cdot X_B}{\varepsilon} \quad (1)$$

X_B being the equivalent fraction of that ion of the mixture which has the highest affinity for the resin, *i.e.*, of Rb^+ , and ε being ($K - 1$). Using the appropriate K values in eqn. 1, the calculated number of displacements required to achieve maximum separation is 3–4 for the nitrated resin and 14–15 for the sulphonic resin.

Fig. 5 depicts the separation of Rb^+ from K^+ on the nitro resin, where a *ca.* 0.1 *N* solution of pure RbCl (99.5%) was obtained. The yield of pure RbCl was *ca.* 35% of the amount loaded. For comparison, under identical conditions, no separation of Rb^+ from K^+ was obtained using the sulphonic resin.

Regarding the yield of Rb^+ , this will increase with increasing quantity of the solutions to be separated, because the mixed zones of $\text{Rb}^+ + \text{K}^+$ and of $\text{Rb}^+ + \text{Ca}^{2+}$ remain quite constant and thus become smaller relatively to the pure rubidium fraction.

It can be seen from the exchange isotherm of the pair $\text{Rb}^+ - \text{K}^+$ on the nitro resin that, although the present work was carried out with a solution containing Rb^+ in an equivalent ratio of 0.16, the separation of Rb^+ from K^+ can also be achieved for other ratios. In ion separations of larger quantities it is of major importance to minimize the number of displacements, since in addition to the smaller quantities of resin, less developing solution and less time are required. The preparative separation of Rb^+ from K^+ on the nitrated resin will be of practical interest.

CONCLUSION

The efficiency of the nitrated polystyrene-sulphonic cation exchanger for preparative separation of Rb^+ from K^+ is described. The separation was achieved by ion-exchange displacement chromatography, yielding solutions of pure rubidium chloride (99.5%).

ACKNOWLEDGEMENT

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