

Selective Cation Exchange on the Cross-linked Pectin

V. TIBENSKÝ

*Institute of Chemistry, Slovak Academy of Sciences,
Bratislava*

The exchange of calcium and potassium ions on the cross-linked pectin with different content of methoxyl groups was studied. The exchange equilibrium was classified according to the selectivity coefficient and the Rothmund—Kornfeld equation. In consonance with the assumption, the lower was the degree of esterification of the cross-linked pectin, the higher was the selectivity to calcium ions. The same dependence was found with a synthetic carboxyl cation-exchanger Zerolit 226 used as a reference.

Bounding of calcium ions in potassium pectate solutions was studied by R. Kohn and I. Furda [1, 2]. It was found that at higher content of carboxyl groups esterified with methanol, the affinity of pectins from different plant sources toward calcium was lower. Consequently, the selectivity of soluble pectin to polyvalent cations decreased with decreasing electric charge of its macromolecule i. e. with increasing the average distance of free carboxyl groups. On the other hand, H. Deuel and K. Hutschneker [3] using pectin cross-linked with methylene bridges, claimed, contradicting the theoretical expectations the increase of selectivity to bivalent cations (at mono—bivalent exchange) at declining exchange capacity which reflected the charge density of the cross-linked macromolecules.

It was known from the study of synthetic ion-exchangers that cross-linked resins as a rule possessed more selective properties as the starting polyelectrolyte [4]. Concluding from pectin behaviour in solutions [1, 2] cross-linked pectin should have higher selectivity to bivalent cations and its selectivity should become more pronounced with the increasing charge density of the macromolecule. Protopectin which could be considered a special example of cross-linked molecule of so far unknown nature and degree was found to have properties similar to that of soluble pectin [5].

In some cases only the selective exchange was not directed by this rule: e. g. S. Lindenbaum and co-workers [6] dealt with this phenomenon with synthetic, laboratory prepared ion-exchangers and attempted to explain changes in their selectivity. H. Deuel and K. Hutschneker [3] assumed that the reason of the different selectivity of cross-linked pectin was due to its numerous alcoholic hydroxyl groups; if these were blocked e. g. by acetylation the selectivity of the resin decreased considerably.

Disproportions found among the properties of pectin and protopectin on one hand, and those of a cross-linked pectin on the other prompted us to study this problem. From pectin and pectic acid pectin ion-exchangers were prepared by introducing methylene bridges [7, 8]. The ion selectivity of these ion-exchangers was studied using samples of various degree of esterification E . The exchange equilibrium $\text{Ca}^{2+} - \text{K}^+$ was determined employing the static method at the room temperature. Synthetic carboxyl cation exchanger Zerolit 226 was used as a reference.

Experimental

A commercial apple pectin, washed with 60 % ethanol acidified with hydrochloric acid (5 ml of conc. HCl in 100 ml) was used throughout this work. The degree of esterification

was in an average $E = 59.3\%$ and an average molecular weight, determined viscosimetrically was $M_\eta = 58\,000$.

Pectic acid (deesterified pectin) was prepared from pectin by hydrolysis with potassium hydroxide and subsequent acidification with hydrochloric acid. The acid was removed by washing with ethanol; esterification degree 0.0% and an average molecular weight $M_\eta = 17\,000$.

To compare the properties a synthetic carboxyl cation-exchanger Zerolit 226 (United Water Softeners Ltd. London) was used.

The cross-linking of pectin and pectic acid was carried out by treatment with formaldehyde and hydrochloric acid [7, 8]. Gels or suspensions of cross-linked pectic substances were exhaustively washed with ethanol and air dried. The esterification degree of pectin upon cross-linking decreased to $E = 25\%$.

The amount of formaldehyde forming methylene bridges was determined iodometrically. Formaldehyde was split off by boiling with diluted mineral acid under simultaneous distillation [9].

The esterification of carboxyl groups of all ion-exchanger used (cross-linked pectin, pectic acid and Zerolit 226) was performed with methanolic $2\text{ N-H}_2\text{SO}_4$ to degree 70% [10]. Free carboxyl groups were neutralised with 0.1 N-KOH .

Deesterification of the highly esterified ion-exchangers in order to accomplish the different exchange capacity, was performed by adding a controlled amount of 0.1 N-KOH to a suspension of an ion-exchanger in a solution of potassium chloride, simultaneously resulting in K^+ form of the ion-exchanger.

Degree of esterification E (per-cent of carboxyl groups esterified with methanol) was calculated (by difference) from the amount of copper bound by the ionised carboxyl groups in the original sample and the amount bound after deesterification with alkaline hydroxide [11], thus at the same time establishing the exchange capacity of the sample.

To determine the exchange equilibrium, the samples of a dry ion-exchanger in K^+ form were allowed to react (under occasional shaking) with 0.05 N solutions of calcium and potassium chlorides with a known ratio of calcium and potassium ions, for 48 hours. An orientational test pointed out that the equilibrium was practically reached already after 24 hours. The equilibrium amount of calcium in solution was determined complexometrically. The amount of bound calcium was determined by difference.

The ratio of the single ions in a solution and in an ion-exchanger was expressed by equivalent fractions X and \bar{X} , respectively (i. e. by means of the ratio of the equivalents of the corresponding ion to the summation of both equivalents in the given medium). The graphic demonstration of the function $\bar{X}_{\text{Ca}^{2+}} = f(X_{\text{Ca}^{2+}})$, so called exchange isotherm, was characteristic for the selectivity of ion-exchangers to calcium ions in the presence of potassium ions.

Results

The degree of cross-linking of all prepared pectin cation-exchangers was the same. The dried cation exchangers contained 5% of formaldehyde, forming methylene bridges among the macromolecules.

The swelling of the ion-exchangers was not exactly studied; as it was observed the less swollen was Zerolit 226 (K^+) and the most swollen was the cross-linked pectin. The values of swelling were, however, very close in the range $1.5\text{--}2.0\text{ g H}_2\text{O/g}$ of

ion-exchanger. Neither the esterification with methanol nor the change of ion form ($K^+ - Ca^{2+}$) substantially influenced the swelling of the cross-linked pectin.

The cross-linked pectins are carboxyl ion-exchangers with physico-chemical properties considerably different from those of the starting materials. Whereas pectin and pectic acid could be easily titrated with alkaline hydroxides, the titration curve being steep at a point of inflexion (see [12]), pectin cation-exchangers in H^+ form practically could not be directly titrated because they reach equilibrium very slowly as a consequence of the change of their colloid status. Although the addition of 1 N-KCl to the titrated suspension considerably depresses the interaction of carboxyl groups so that direct titration can be accomplished in a shorter time, the titration curve is not so steep as was the case with synthetic carboxyl cation-exchangers [13].

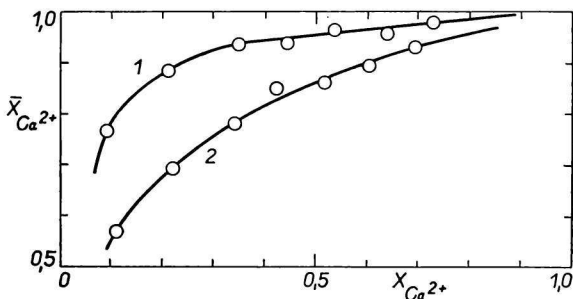
The same degree of cross-linking of pectin cation-exchangers and strictly constant equivalent concentration of electrolytes allowed us to investigate the influence of charge density upon their exchange selectivity.

Fig. 1. Isotherms of $Ca^{2+} - K^+$ Exchange on a Cross-linked Pectin.

$X_{Ca^{2+}}$ = equivalent fraction of calcium ions in solution,

$\bar{X}_{Ca^{2+}}$ = equivalent fraction of calcium ions in pectin.

1. exchange isotherm for esterification degree $E = 0.0\%$ (exchange capacity 3.01 mval/g),
2. exchange isotherm for $E = 73.0\%$ (exchange capacity 0.55 mval/g).



The cross-linked pectin exhibits a high affinity to calcium ions, as it was demonstrated from the shape of the exchange isotherms (Fig. 1). The isotherms of $Ca^{2+} - K^+$ exchange at $E = 0.0\%$ and $E = 73.0\%$ (exchange capacity 3.01 mval/g and 0.55 mval/g, respectively) moreover indicate, that the affinity to calcium at higher degree of esterification is lower. $Ca^{2+} - K^+$ exchange equilibria determined at different E values proved also that with decreasing charge density the selectivity of the cross-linked pectin to calcium ions decreases as well.

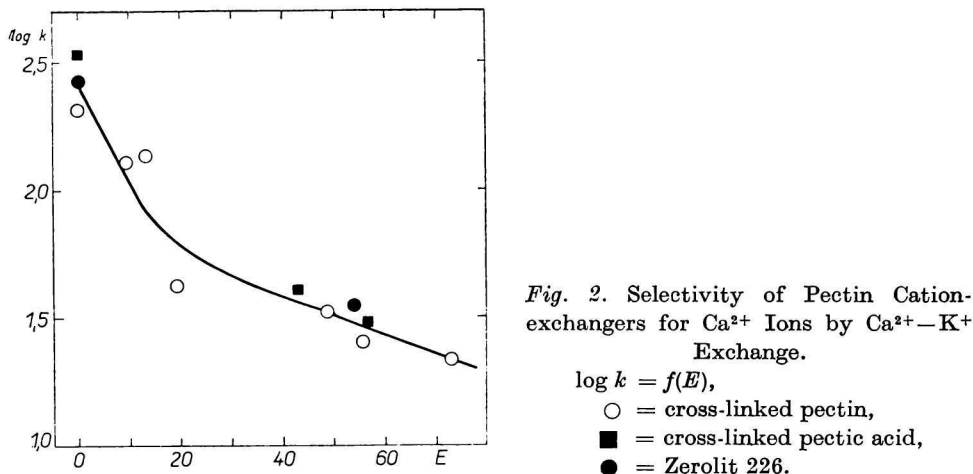
The more precise informations on the dependence of selectivity upon the esterification degree of the cross-linked pectin as it has been presented by the exchange isotherms afforded the quantitative correlation of this relation in the terms of empirical equation and selectivity coefficients, respectively.

The Rothmund—Kornfeld empirical equation being considered as the most valuable for evaluation of the multivalent equilibria [14] was used in the form:

$$\frac{\bar{X}_{Ca^{2+}}}{(\bar{X}_{K^+})^2} = k \left(\frac{X_{Ca^{2+}}}{(X_{K^+})^2} \right)^p$$

in which, instead of equivalents per liter, the concentration is given in the equivalent fractions of the corresponding cations ($X_{Ca^{2+}}$, X_{K^+}) also for water phase. This adjustment expresses more evidently the dependence of selectivity on the degree of esterification E . An exponent p , however, is the same for both ways of calculations, and, in general, close to 1.

The changes of $\log k$ as a function of the degree of esterification E of pectin ion-exchangers and Zerolit 226 is presented in Fig. 2. The consonance of $\log k = f(E)$ for Zerolit 226 and pectin ion-exchangers was not so surprising as the close resemblance of $\log k$ values.



The selectivity coefficient (also called rational equilibrium coefficient) [15, 16] was calculated from the equation:

$$K_{\text{K}}^{\text{Ca}} = \frac{\bar{X}_{\text{Ca}^{2+}} \cdot (X_{\text{K}^+})^2}{(\bar{X}_{\text{K}^+})^2 \cdot X_{\text{Ca}^{2+}}}$$

The values of K_{K}^{Ca} for $X_{\text{Ca}^{2+}} = X_{\text{K}^+}$ were compared. These data (and their logarithms, respectively), as it is obvious from the Tab. 1 and 2, are close to the parameter k from the Rothmund—Kornfeld equation and could be used for obtaining fast and reliable information on the selectivity of ion-exchangers, without the complicated construction of the whole exchange isotherm.

The affinity of the pectin cation-exchangers to calcium changes upon the dependence of the esterification degree similarly as was the case with soluble pectins (compare [1, 2]). Pectin cation exchanger, however, markedly accepts calcium ions

Table 1
 $\text{Ca}^{2+}-\text{K}^+$ Exchange on Pectin Cation—exchanger

Selectivity Coefficient K_{K}^{Ca} and Parameters k and p from the Rothmund—Kornfeld Equation in Dependence from the Degree of Esterification E

	E of cross-linked pectin						
	0.0	9.7	13.2	19.4	48.6	55.7	73.0
$\log K_{\text{K}}^{\text{Ca}}$	2.48	2.28	2.12	1.61	1.65	1.45	1.36
$\log k$	2.31 ± 0.05	2.11 ± 0.02	2.13 ± 0.02	1.62 ± 0.05	1.52 ± 0.07	1.40 ± 0.02	1.33 ± 0.00
p	1.08 ± 0.06	1.32 ± 0.07	0.97 ± 0.03	1.07 ± 0.13	1.36 ± 0.14	1.06 ± 0.03	1.06 ± 0.04

Table 2
Ca²⁺—K⁺ Exchange on Pectin and Synthetic Cation—exchangers

	<i>E</i> of cross-linked pectic acid			<i>E</i> of Zerolit 226	
	0.0	42.9	56.5	0.0	54.4
log K_{K}^{Ca}	2.84	1.63	1.53	2.54	1.53
log <i>k</i>	2.53 ± 0.05	1.60 ± 0.02	1.48 ± 0.02	2.43 ± 0.04	1.54 ± 0.02
<i>p</i>	1.52 ± 0.13	1.12 ± 0.08	0.97 ± 0.15	1.30 ± 0.10	0.94 ± 0.06

selectively, also at a high degree of esterification, where soluble pectin is no more selective. This observation is in an agreement with the fact that ion-exchanger in general exhibits higher selectivity comparing with the starting polyelectrolyte [4]. Consequently the results have not supported findings of H. Deuel and K. Hut-schneker [3] concerning the higher selectivity of the cross-linked pectin at higher degree of esterification. The pectin cation—exchanger can serve as a protopectin model for the study of exchange reactions in plants.

Mr. A. Fekete contributed to the Experimental Part.

SELEKTÍVNA VÝMENA KATIÓNOV NA ZOSIEŤOVANOM PEKTÍNE

V. Tibenský

Chemický ústav Slovenskej akadémie vied,
Bratislava

Sledovala sa výmena iónov vápnika a draslíka na zosieťovanom pektíne a zosieťovanej kyseline pektovej v závislosti od obsahu karboxylových skupín esterifikovaných metanolom. Na porovnanie sa použil karboxylový katex Zerolit 226. Výmenná rovnováha stanovená statickým spôsobom sa posudzovala podľa Rothmundovej—Kornfeldovej rovnice a podľa koeficienta selektivity. Spomenuté ionexy majú najväčšiu afinitu k vápniku za neprítomnosti esterifikovaných funkčných skupín; so stúpajúcou esterifikáciou, t. j. s poklesom elektrického náboja makromolekuly afinita k vápniku klesá. Touto vlastnosťou sa zosieťovaný pektín (rovnako i protopektín) podobá rozpustnému pektínu, jeho selektivita je však výrazná aj pri vysokom stupni esterifikácie (70 %).

СЕЛЕКТИВНЫЙ ОБМЕН КАТИОНОВ НА ПОПЕРЕЧНО СВЯЗАННОМ ПЕКТИНЕ

В. Тибенский

Химический институт Словацкой академии наук,
Братислава

Изучался обмен ионов кальция и калия на поперечно связанном нектине и поперечно связанной пектиновой кислоте в зависимости от содержания метанолом этерифицированных карбоксильных групп. Для сравнения был применен карбоксильный катионит

Зеролит 226. Обменное равновесие, определенное статическим способом, оценивалось по уравнению Ротмунда—Корнфелда и на основе коэффициента селективности. Описываемые иониты проявляют наибольшее сродство к кальцию в отсутствии этерифицированных функциональных групп; с повышением этерификации, т. е. с понижением электрического заряда макромолекулы, сродство к кальцию понижается. Этим свойством поперечно связанный пектин (а также протопектин) похож на растворимый пектин, его селективность, однако, значительна и при высокой степени этерификации (70 %).

Перевела Т. Диллингерова

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The address of the author:

Dr. Ing. Vladimír Tibenský, CSc., Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Dúbravská cesta 5.