BINDING OF LEAD AND CHROMIUM(III) CATIONS TO PECTIN

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Binding of Pb^{2+} ions to magnesium pectinates was studied by dialyzation technique in relation to their esterification degree (E) in the interval $E = 0$ to 84·7%, at an ionic strength $I = 0{\cdot}30$. It has been found that the binding of Pb^{2+} ions to pectinates proceeds according to the theory of multiple equilibria. The values of stability constant K and selectivity coefficient K_{Mg}^{Pb} evidence the high selectivity of pectinates towards Pb^{2+} ions. Both those constants are, in contrast with value corresponding to other bivalent cations (*e.g.* Ca^{2+}, Sr^{2+}), independent on the esterification degree of pectin in the $E \leqq 50\%$ range. A strong binding of Pb^{2+} to carboxyl groups takes place also at a high esterification degree of pectin.

The exchange of $Cr^{3+} \rightarrow 3\,K^{+}$ was investigated with a model preparation of potassium pectate crosslinked with epichlorohydrin by a batch method at various pH of equilibrium solutions ($I = 0{\cdot}15$). Potassium pectate was shown to be a highly selective ion exchanger towards Cr^{3+}. The binding of Cr^{3+} to pectate also occurred in a sufficient extent at a low pH of equilibrium solutions (pH ~ 3). Due to a very strong binding of Cr^{3+} to pectate a substantial shift of dissociation equilibrium of carboxyl groups in favour of further binding of Cr^{3+} ions occurred.

Pectin behaves as a highly selective intoxic ion exchanger. It has well been appreciated in prophylaxis against poisoning of living organisms with heavy metal cations including lead (for a review of older articles see[1]).

Recently, attention has been paid to the detoxication effect of pectin mainly in clinical research. The main goal was to investigate the secretion of lead in urine and excrements of laboratory animals, pathologic changes of blood and various organs[2-10]. These experiments were performed either with commercial preparations of pectin of a medium esterification degree of carboxyl groups with methanol, or with a diet enriched with produce of a higher pectin content. Positive results have been obtained in all cases thus evidencing pectin to be an effective preventive substance against lead poisoning not only through the gastrointestinal tract but also against poisoning through breathing of lead aerosols[6]. The increased secretion of lead in urine after peroral application of pectin, as well as the effective prevention against intoxication through breathing indicate that a complex reaction mechanism of lead elimination is involved, which has not been elucidated as yet.

The investigation of binding of heavy metal cations and other multiple-valent cations to pectin was so far pointed mainly towards the totally deesterified pectin,

i.e. towards insoluble pectic acid[11–14] and its salts[15] and to pectic acid crosslinked with epichlorohydrin (K^+ form)[16]. Further, the separation of cations from waste water[11] was studied and the formation of the corresponding complexes was examined by means of EPR-spectra[17] and special viscometric technique[18].

Another cation hazardous to health appearing in chemical industry is chromium(III) cation. There are only few concise notes concerning the binding of chromium to pectin as far as the effect of esterification degree of pectin and pH of solution to the precipitation of Cr-pectinates are concerned[19]; the EPR-spectrum of Cr-pectate[17] was reported.

As we have already shown[20,21]; the selectivity of $Ca^{2+} \rightarrow 2K^+$ and $Sr^{2+} \rightarrow 2\ K^+$ exchange in pectin is much dependent on its esterification degree. The highest selectivity towards Ca^{2+} (Sr^{2+}) ions exhibited the fully deesterified pectin, whereas pectin with a high esterification degree is no more selective towards these cations.

The practical utilization of pectin in protection of men working with lead and its salts is the consumption of a diet rich in the content of pectin; the acute cases would need a direct application of sodium pectate. There are no reports concerning the physico-chemical fundaments of binding of lead to pectin and the effect of esterification degree of pectin to this process. This paper deals with this problem and, orientationally, also with binding of Cr^{3+} ions to pectate.

EXPERIMENTAL

Preparations and Chemicals

Samples of pectin of various degree of esterification E (Table I) prepared from a purified citrus pectin (Genu Pectin, Pektinfabrik, København) were characterized by the same procedures as already reported[22]. Samples 5 and 6 were prepared by a partial alkaline deesterification of sample 7.

Pectic acid crosslinked with epichlorohydrin was prepared and characterized by Dr Ľ. Kuniak of this Institute. Crosslinked was pectic acid containing 90,3% of D-galacturonan in dry substance of esterification degree $E = 1\%$ and mean molecular weight $\overline{M}_\eta = 25\,000$ (determined viscometrically[31]). The crosslinked preparation (K^+ form) had a swelling volume V 5·4 ml/g, mean degree of crosslinking $\overline{DS}$ (C.L.) = 0·23 (the mean number of crosslinks per one D-galacturonic acid unit) and the mean number of side chains $—CH_2.CH(OH).CH_2OH$ per one D-galacturonic acid unit $\overline{DS}$ (S.C.) = 0·036. The capacity of ion exchange of the preparation (H^+ form) was 4·03 mmol (COOH) per 1 g of the dry sample. Used were chemicals of *p.a.* grade; redistilled freshly boiled-out water had specific electric conductance lower than $2 \cdot 10^{-4}$ S/m. Solutions of 0·05M-NaOH and 0·05M-KOH were carbonate free. Dialyzation tube was a product of Kalle A.G., Wiesbaden, (FRG).

Procedures and Analytical Methods

The equilibrium of $Pb^{2+} \rightarrow Mg^{2+}$ exchange in pectin of various esterification degree was determined at room temperature by a dialyzation method similarly, as reported earlier[23]. The solution of potassium pectate or pectinate (concentration 0·02—0·04 mol (COOK)/l) was

dialyzed against 0·1M-equilibrium solutions containing $Pb(NO_3)_2$ and $Mg(NO_3)_2$ in a various ratio (the ionic strength $I = 0{\cdot}30$). The pH value of equilibrium solutions was adjusted with a very small addition of KOH to pH = 5·0. After dialysis against redistilled water, lead and magnesium bound to pectin were expelled by dialysis against 0·1M-HNO_3. The respective dialyzation procedures were 4 times repeated after 10 and 16 h dialysis, respectively.

Concentration of free carboxyl groups in starting solution of potassium pectate or pectinate was determined by the method of precipitation of copper pectate or pectinate[24,25]. The concentration of Pb^{2+} or Mg^{2+} in starting solutions of $Pb(NO_3)_2$ and $Mg(NO_3)_2$ was determined by titration with Complexon IV on eriochrome black T, the point of equivalence being indicated spectrophotometrically (interference filter Zeiss, Jena, IF 650 nm).

Concentration of Pb^{2+} in the dialyzate was determined polarographically in acid medium (0·05—0·07M-HNO_3) at room temperature with a polarograph Radelkis OH 102 and mercury drop electrode. The calibration curve was determined prior to any analysis.

The exchange equilibrium of $Cr^{3+} \rightarrow 3\ K^+$ ions of the insoluble crosslinked preparation of potassium pectate was determined by a routine batch method at room temperature in suspensions containing *c.* 1 mmol (COOK) in 100 ml. Solutions to be tested contained $Cr(NO_3)_3$ and KNO_3 in various ratio at an ionic strength $I = 0{\cdot}15$.

The crosslinked preparation (K^+ form) was adjusted to the required pH (3 to 6) by washing with 1M-buffer solution (acetic acid/potassium acetate) of the corresponding pH and redistilled water. Capacity of the ion exchange of crosslinked pectic acid was determined acidimetrically by a potentiometric back-titration of a small excess of the hydroxide in 0·5M-KCl medium. The amount of COOH groups in preparations partly neutralized with potassium hydroxide to various pH was determined similarly.

Concentration of Cr^{3+} in an equilibrium solution was determined spectrophotometrically[26] with Complexon III in acid medium. A linear relationship between absorbance A (538 nm) and concentration of chromium in solution at 0 to 0·25 mmol (Cr^{3+})/l concentration was obtained using a compensation spectrophotometer UVISPEC Hilger. The titre of the basic solution $Cr(NO_3)_3$ was determined by a potentiometric titration with $K_3Fe(CN)_6$ solution in a strong alkaline medium in the presence of a trace amount of Tl_2SO_4 as a catalyst[27].

The selectivity coefficient of ion exchange K_{Mg}^{Pb} was calculated from equivalent fractions of the corresponding cations bound to pectin ($\bar{X}$), or in equilibrium solution (X):

$$K_{Mg}^{Pb} = \frac{\bar{X}_{Pb} \cdot X_{Mg}}{\bar{X}_{Mg} \cdot X_{Pb}} . \qquad (1)$$

The selectivity coefficient of ion exchange $Pb^{2+} \rightarrow 2\ K^+$ was calculated similarly according to the following equation:

$$K_{K}^{Pb} = \frac{\bar{X}_{Pb} \cdot (X_K)^2}{(\bar{X}_K)^2 \cdot X_{Pb}} . \qquad (2)$$

The stability constant (K) of lead pectates and pectinates was calculated employing equation (*3*) as it follows from the theory of multiple equilibria[28]:

$$\frac{1}{r} = \frac{1}{nK[Pb^{2+}]} + \frac{1}{n} , \qquad (3)$$

where r stands for the number of Pb^{2+} ions bound to the repeating segment of the macromole-

cule with n binding sites, $[Pb^{2+}]$ is the concentration of free Pb^{2+} ions in solution. The ligand unit L was assigned such a segment of the macromolecule, which bound just one Pb^{2+} ion at a full occupation of binding sites; $n = 1$ (complex of the 1 : 1 type). Such a segment involves 2 free unesterified carboxyl groups at a stoichiometric reaction. The stability constant K is given in this case by equation

$$K = \frac{[PbL]}{[(c_L - [PbL])^{2-}]\,[Pb^{2+}]}, \qquad (4)$$

where [PbL] is the concentration of the lead-ligand complex, c_L is the total concentration of the ligand and $[Pb^{2+}]$ is the concentration of free Pb^{2+} ions in the equilibrium solution.

We considered the real capacity of ion exchange of pectinates at a given pH determined experimentally for each pectin under investigation, when calculating K and K_{Mg}^{Pb}.

RESULTS AND DISCUSSION

Capacity of Ion Exchange of Pectic Acid in Relation to pH *of Solutions*

Lead nitrate and especially chromium nitrate showed, due to hydrolysis, a considerably acid reaction. Pectic acid and pectinic acids behave as a weak acid carboxyl ion exchanger. The capacity of ion exchange of those substances is strongly dependent on the pH equilibrium solutions. We investigated, therefore the capacity of ion exchange of free pectic acid in dilute solution at 0·02 mol (COOH)/l (Fig. 1 curve *1*) and that of pectic acid crosslinked with epichlorohydrin (curve *2*) in relation to pH. The capacity of ion exchange (C) at various pH is expressed in % of the full capacity of the preparation corresponding to pH 7·2–7·5. The value C in free pectic acid was determined on the basis of dissociation degree of carboxyl groups α and in the crosslinked preparation on the basis of degree of neutralization (DN) only, as the

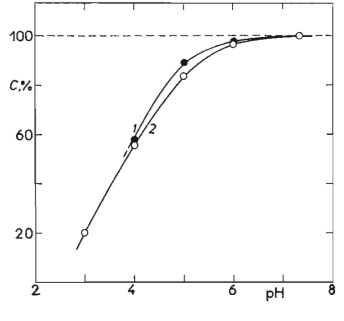

FIG. 1

Relationship Between the Capacity of Ion Exchange of Free and Epichlorohydrin-crosslinked Pectic Acids and the pH of Equilibrium Solutions

C Capacity of ion exchange in %, *1* solution of free pectic acid, *2* crosslinked pectic acid.

value α is here experimentally not attainable. The real degree of dissociation α of cross-linked pectic acid shall be in the pH 3–4 region somewhat higher than the corresponding degree of neutralization.

A very similar relationship has been found for both preparations of pectic acid. A similar feature revealed also pectinic acid of various degree of esterification (E). Results plotted in Fig. 1 show that the low pH of solutions lowers considerably the capacity of ion exchange of those substances; they are in accordance with the influence of pH on the Ca^{2+} binding at macromolecular sodium D-galacturonan[29]. The above-mentioned capacity of ion exchange relates to the partial neutralization of polyacids under investigation with an alkali metal hydroxide. A concurrent shift of dissociation equilibrium $COOH \rightleftharpoons COO^- + H^+$ to the right side takes place at a binding of multivalent cations (Cu, Pb, Cr), which are bound very firmly to carboxyl groups; this leads to the enhanced capacity of the ion exchange.

Binding of Pb^{2+} Ions to Pectin

The binding of Pb^{2+} ions and the exchange $Pb^{2+} \rightarrow Mg^{2+}$ in pectin was examined in relation to its esterification degree (E) of carboxyl groups with methanol in the $E = 0$ to 84·7% range. Characteristic data of pectin samples are listed in Table I. Content of polyuronide relates to H^+ form of pectinic acids. The mean molecular weights of pectinic acids* belong to the range in which the binding of cations depend no more on the length of the macromolecule chain[30].

Verification of the dialyzation method. Dialyzation technique was employed for the study of exchange equilibria, the application of which is correct only when exchanging cations of the same valence. Therefore, the exchange $Pb^{2+} \rightarrow Mg^{2+}$ was investigated. The magnesium salt was selected because of the weakest bond of Mg^{2+} to carboxyl groups of pectate among a great number of bivalent cations[16]. Samples of pectin are to some degree polydisperse in respect to molecular weight (the low-molecular fractions were removed during purification of preparations). Therefore, we verified whether fractions with lower molecular weight diffund through the dialyzation membrane. It was further necessary to prove that under conditions of dialysis a stoichiometric exchange of cations took place. The solution of potassium pectate (sample 1, concentration 36 mmol (COOK)/l) was dialyzed against 0·1M-$Pb(NO_3)_2$, or 0·1M-$CuSO_4$ solutions. The amount of $Pb^{2+}(Cu^{2+})$ ions bound to carboxyl groups was compared with the concentration of free carboxyl groups

* Various authors suggested different values of the coefficient k and exponent a in the equation by Mark and Houwink for conversion of the intrinsic viscosity $[\eta]$ to molecular weight; this fact can be ascribed to various heterogeneity of pectin preparations used by individual authors, *e.g.*[32].

of pectate in the starting solutions. The Pb^{2+} ions were bound to the pectate by 98% of the theoretical capacity of ion exchange, Cu^{2+} ions by 100%, what indicates the stoichiometric binding of these cations to carboxyl groups. At a great excess of Pb^{2+} (Cu^{2+}) ions in relation to COOK groups, which was used in dialysis (400: 1), the effect of hydrolysis of the respective salts to the lowering of the ion exchange capacity did not come into effect. The results evidenced the correctness of application of dialyzation method when studying the equilibria of cation exchange with pectin.

Stability constant K of lead pectinates and selectivity coefficient of $Pb^{2+} \rightarrow Mg^{2+}$ *ion exchange.* Ions Pb^{2+} are very firmly bound to carboxyl groups of pectin, what is evidenced by precipitation of a highly esterified pectin with Pb^{2+} ions[19]. We investigated the $Pb^{2+} \rightarrow Mg^{2+}$ exchange for this reason in the range of low concentrations, at an equivalent fraction of Pb^{2+} in equilibrium solutions $X_{Pb} \leqq 0{\cdot}12$. The equilibrium of ion exchange was examined at pH 5·0, the higher value being avoided for an eventual formation of basic salt of lead.

Binding of Pb^{2+} ions to pectin was first of all evaluated according to equation (*3*) following from the theory of multiple equilibria, which makes it possible to determine the number of binding sites n at the ligand unit in addition to stability constant (K) of lead pectate and pectinate. As shown, the function $1/r = f(1/[Pb^{2+}])$ has a linear course for all samples of pectin similarly as plotted in Fig. 2. This fact evidences that the Pb^{2+} binding to magnesium pectinate is well characterized by means of the theory of multiple equilibria. Sections on ordinate limited by lines ($\lim_{1/[Pb^{2+}] \to 0} 1/r = 1/n$) did not display the assumed theoretical value 1, but varied in the $1/n = 1{\cdot}08$ to $1{\cdot}25$ range (Fig. 2); $n = 0{\cdot}93$ to $0{\cdot}80$. The lower pH of unbuffered equilibrium solutions lowers the capacity of ion exchange to 93–80% of the

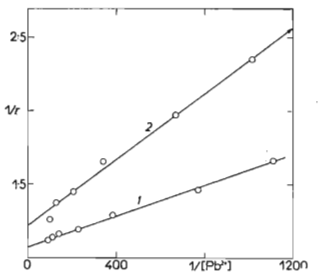

FIG. 2

Function $1/r = f(1/[Pb^{2+}])$

r Number of Pb^{2+} ions bound to the repeating segment of the macromolecule with n binding sites; *1* esterification degree E 26·8%, *2* E 73·9%; $[Pb^{2+}]$ concentration of free Pb^{2+} ions in solution.

original value individually for each experiment. A very low concentration of Pb^{2+} in equlibrium solutions is unable to shift dissociation of carboxyl groups to such an extent as to all free carboxyl groups could participate in cation exchange similarly as in the preceding case, when 0·1M-$Pb(NO_3)_2$ was applied.

In solutions of monomeric D-galacturonic acid[33], in contrast to the stoichiometric binding of Pb^{2+} ions to carboxyl groups of pectates and pectinates, which was corroborated by the above-mentioned results, the formation of PbA^+ complex was evidenced, where A^- is the anion of uronic acid. Basing upon rheological properties of transformation of lead pectate suspension to a sol by means of chelate forming reagents Schweiger[18] suggested an intramolecular chelate binding of Pb^{2+} ions to pectate. This view is also supported by precipitation of highly substituted acetyl derivatives of pectic acid with Pb^{2+} ions, ref.[34].

Values of the stability constant K of lead pectinates are listed in Table I. As shown, the stability constant (log K) for the system $Pb^{2+} \rightarrow Mg^{2+}$ does not virtually depend on the esterification degree of pectin in the E 0 to 50% range. At a higher esterification degree E the values log K slightly decrease. A completely different situation was found with the stability constant of calcium pectinates determined for binding of Ca^{2+} to potassium pectinates. The value K strongly decreases with the increasing esterification degree in a function close to a logarithmic dependence[20].

The $Pb^{2+} \rightarrow Mg^{2+}$ exchange was characterized by the selectivity coefficient K_{Mg}^{Pb} calculated according to equation (*I*). The course of function $\bar{X}_{Pb} = f(X_{Pb})$ (Fig. 3) indicates that the half-saturation of carboxyl groups of the pectate with Pb^{2+} ions (point *A*) is already attained at a very low concentration of Pb^{2+} in the

TABLE I

Stability Constant K of Lead Pectinates (system Pb^{2+}–Mg^{2+}) and Selectivity Coefficient K_{Mg}^{Pb} of Ion Exchange in Pectinates of Various Esterification Degree E

Sample	E %	Content of polyuronide %	$[\eta]$ m^3/kg	$\bar{M}_w$ [a]	$\bar{M}_n$ [b]	log K	log K_{Mg}^{Pb} ($\bar{X}_{Pb} = 0{\cdot}5$)
1	0·0	88·0	0·150	31 500	17 500	3·32	2·32
2	26·8	89·0	0·226	43 000	22 000	3·29	2·28
3	41·0	91·3	0·297	53 000	26 000	3·39	2·38
4	50·1	89·8	0·305	54 000	26 500	3·27	2·26
5	63·9					3·19	2·19
6	73·9					3·03	2·03
7	84·7	94·4	0·087	21 000	12 500	2·88	1·88

[a] Ref.[31], [b] ref.[32].

equilibrium solution, at $X_{Pb} \sim 0{\cdot}004$ ($I = 0{\cdot}30$), what evidences a high selectivity of pectinates towards Pb^{2+} ions. The values lying in the range $\bar{X}_{Pb} < 0{\cdot}5$ were for this reason no more reliably experimentally available. The selectivity coefficient of ions exchange K_{Mg}^{Pb} for $\bar{X}_{Pb} = 0{\cdot}5$ was, therefore, calculated from the corresponding stability constants K, which could well be determined using equation (*3*). Values K_{Mg}^{Pb} could be determined in a broader interval of $\bar{X}_{Pb}$ with pectin of the highest esterification degree (E 84·7%). The selectivity coefficient K_{Mg}^{Pb} does practically not depend here on the degree of saturation of carboxyl groups with Pb^{2+} ions (Fig. 4). The measured values K_{Mg}^{Pb} ($\bar{X}_{Pb} = 0{\cdot}5$), listed in Table I, display an equal dependence on the esterification degree of pectin as the stability constant K of lead pectinates.

Corrected stability constant K' of lead pectate characterizing the Pb^{2+} *binding to potassium pectate.* Values K and K_{Mg}^{Pb} (Table I) relate to Pb^{2+} binding to magnesium pectate and pectinate. Nevertheless, the Mg^{2+} ions are bound, to some extent, also to carboxyl groups. The exchange of $Pb^{2+} \rightarrow 2\,K^+$, or $2\,Na^+$, encountered at practical application of pectin, will be characterized by higher K, or K_K^{Pb} values (equation (*2*)) than in the previous case. The corrected stability constant K' could be calculated employing following equations:

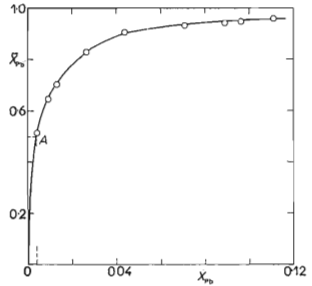

FIG. 3

Ion Exchange of $Pb^{2+} \rightarrow Mg^{2+}$ in Pectin (E 26·8%)

$\bar{X}_{Pb}$ Equivalent fraction of Pb^{2+} ions bound to pectin, X_{Pb} equivalent fraction of Pb^{2+} ions in equilibrium solution; A the point in which 50% of carboxyl groups are saturated with Pb^{2+}.

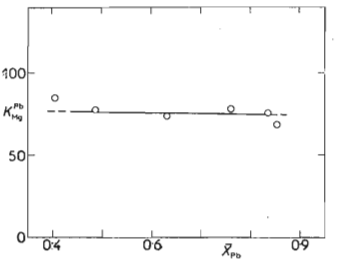

FIG. 4

Relationship of the Selectivity Coefficient of Ion Exchange K_{Mg}^{Pb} in Highly Esterified Pectin upon Equivalent Fraction of Pb^{2+} Ions Bound to Pectin $\bar{X}_{Pb}$ (E 84·7%)

$$K' = \frac{[\mathrm{PbL}]}{[(c_\mathrm{L} - [\mathrm{PbL}] - [\mathrm{MgL}])^{2-}]\,[\mathrm{Pb}^{2+}]}, \qquad (5)$$

$$K_{\mathrm{Mg}} = \frac{[\mathrm{MgL}]}{[(c_\mathrm{L} - [\mathrm{PbL}] - [\mathrm{MgL}])^{2-}]\,[\mathrm{Mg}^{2+}]}, \qquad (6)$$

where $[\mathrm{MgL}]$ is the concentration of the complex magnesium-ligand, $[\mathrm{Mg}^{2+}]$ is the concentration of free Mg^{2+} ions in the equilibrium solution, and K_{Mg} is the stability constant of magnesium pectate or pectinate corresponding to Mg^{2+} binding to potassium pectate or pectinate. Symbols c_L, $[\mathrm{PbL}]$ and $[\mathrm{Pb}^{2+}]$ are of the same meaning as in equation (*4*).

Stability constant K_{Mg} could not be determined for the ion system $\mathrm{Mg}^{2+} \rightarrow 2\,\mathrm{K}^+$ by dialyzation method due to different valence of both counterions. This constant can be, however, easily determined with a crosslinked preparation of pectin by a routine batch method. According to our results concerning the study of ion exchange $\mathrm{Mg}^{2+} \rightarrow 2\,\mathrm{K}^+$ with crosslinked potassium pectate[16] we were able at least to estimate approximately the constant K' for lead pectate ($E = 0\%$). The stability constant of magnesium pectate $K_{\mathrm{Mg}} = 209{\cdot}5$ (the equilibrium solutions contained $\mathrm{Mg(NO_3)_2}$ and $\mathrm{KNO_3}$; $I = 0{\cdot}15$) was calculated from values obtained from measurement of crosslinked preparation for $\bar{X}_{\mathrm{Mg}} = 0{\cdot}5$. The corrected stability constant of lead pectate $\log K'$ was then 4·66. Since the selectivity of ion exchange is a little higher with crosslinked preparations than with not crosslinked ones, the estimation is approximative. The difference in ionic strength of solution comes into account in a lesser extent ($I = 0{\cdot}30$ for $\mathrm{Pb}^{2+} \rightarrow \mathrm{Mg}^{2+}$; $I = 0{\cdot}15$ for $\mathrm{Mg}^{2+} \rightarrow 2\,\mathrm{K}^+$).

Binding of Cr^{3+} *Ions to Crosslinked Potassium Pectate* . The binding of Cr^{3+} to pectin was studied with potassium pectate ($E = 0\%$) crosslinked with epichlorohydrin as a model substance. The preparation is water insoluble and allows to employ a simple batch method for the study of equilibria of ion exchange. Characterization of the crosslinked preparation is given in the experimental section.

The exchange of $\mathrm{Cr}^{3+} \rightarrow 3\,\mathrm{K}^+$ ions was examined in solutions of ionic strength $I = 0{\cdot}15$. At the beginning we investigated binding of Cr^{3+} to the crosslinked preparation (K^+ form) without adjustment of pH of equilibrium solutions which, due to a strong hydrolysis of the chromium(III) salt, varied within pH 5·28 and 3·27. Equilibrium of ion exchange is characterized for this reason by the function $\bar{X}_{\mathrm{Cr}} = \mathrm{f}(X_{\mathrm{Cr}})$ only; theoretic capacity of ion exchange corresponding to K^+ form of the crosslinked preparation at pH ~7·5 was considered for calculation of equivalent fractions (X). The obtained results are characterized by curve *1*, Fig. 5. This isotherm of ion exchange is considerably asymmetric and evidences a very high selectivity of the preparation towards Cr^{3+} ions in the range of low Cr^{3+} concentration in the

equilibrium solution. The Cr^{3+} ions are bound to the pectate almost quantitatively to a half saturation capacity of the ion exchanger ($\bar{X}_{Cr} = 0{\cdot}5$).

The decrease of pH of equilibrium solutions with their increasing concentration of chromium(III) salt lowers markedly the capacity of ion exchange of the preparation. Curve 2 in Fig. 5 reflects the real capacity of ion exchange of the preparation for individual equilibrium solutions, expressed as a fraction of carboxyl groups (C'), which can immediately participate in ion exchange reactions. Comparison of curves *1* and *2* shows a successive binding of much more Cr^{3+} ions to carboxyl groups in the $X_{Cr} > 0{\cdot}005$ region, than would correspond to the capacity of ion exchange given by the pH of equilibrium solutions. The Cr^{3+} ions permanently shift the dissociation equilibrium $COOH \rightleftharpoons COO^- + H^+$ to the right side in favour of further Cr^{3+} ion binding, due to an unusual strong linkage to COO^- groups. As we have already shown[16] ions Pb^{2+}, Cu^{2+} (pH 5·0), Co^{2+} (pH 6·0) and Ca^{2+}, Sr^{2+} (pH 7·2) are bound to carboxyl groups of the crosslinked potassium pectate in an accurate stoichiometric rate, so that no mixed $RCOO^-M^{2+}A^-$ salts are formed. This fact let us assume that binding of greater portions of Cr^{3+} ions to carboxyl groups is first of all effected by a shift of the equilibrium of carboxyl group dissociation and not by formation of mixed salts. A formation of mixed (basic) chromium salts bound to pectate was observed in equilibrium solutions at pH 5·0 and more, only.

Moreover, the binding of Cr^{3+} to a crosslinked potassium pectate was investigated at pH 3·0, 4·0 and 5·0. The very diluted solutions of $Cr(NO_3)_3$ used in the analysis were adjusted to the same pH values. Measured were suspensions of a total carboxyl group concentration 12–15 mmol/l without addition of any further electrolyte.

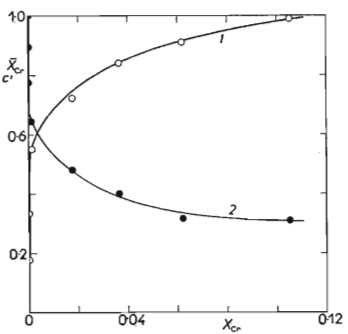

FIG. 5
Ion Exchange of $Cr^{3+} \rightarrow 3\,K^+$ in Crosslinked Potassium Pectate (E 0%)
1 Function $\bar{X}_{Cr} = f(X_{Cr})$, *2* capacity of ion exchange (C') corresponding to pH of equilibrium solutions (*cf.* the text).

The equivalent concentration of the added chromium(III) salt varied within 20 to 300% in respect to the real capacity of ion exchange corresponding to pH of equilibrium solutions. The results of measurement together with further data measured in suspensions of the preparation without adjustment of pH of equilibrium solutions ($I = 0{\cdot}15$) are summarized in Fig. 6 (curve *1*) showing the function $3[Cr^{3+}] : c_{COOK} = f(3c_{Cr}/c_{COOK})$; c_{Cr} is the total concentration of Cr^{3+} in suspension, $[Cr^{3+}]$ is the concentration of free Cr^{3+} ions in equilibrium solution and c_{COOK} the concentration of potassium salt corresponding to pH of equilibrium solution. If the equivalent concentration of added Cr^{3+} ions is less as the theoretic capacity of ion exchange ($3c_{Cr}/c_{COOK} < 1$), then practically all Cr^{3+} ions are bound to carboxyl groups of this ion exchanger (curve *1*). At an equivalent concentration ($3c_{Cr}$) greater than the concentration of (COOK) groups the concentration of free Cr^{3+} ions in solution should increase linearly according to the theoretic line 2. Due to a shift of dissociation equilibrium of carboxyl groups a further binding of Cr^{3+} takes place; this is characterized by the difference between curve *1* and line *2* (section *a* in Fig. 6).

The very high selectivity of carboxyl groups of the crosslinked potassium pectate ($E = 0\%$) to Cr^{3+}, ions, in particular at low concentrations of chromium in solution, when an almost total elimination of Cr^{3+} ions from solution takes place, is documented by the above-mentioned results. Ions Cr^{3+} also are bound to pectate at a relatively low pH of solutions (pH ~3·0). Measurements were carried out with the crosslinked preparation only. Comparison of our earlier results of ion exchange $Ca^{2+} \rightarrow 2\,K^+$ of a crosslinked[16] potassium pectate with that of not crosslinked[20] show that conclusions from model experiments with crosslinked preparations can well be applied to solutions of a not crosslinked pectate. The EPR spectra of chromium pectate[17] showed that a complex with outer-sphere structure is involved.

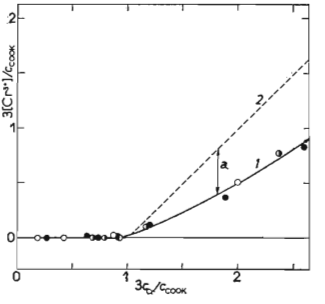

FIG. 6

Ion Binding of Cr^{3+} to Crosslinked Potassium Pectate at Various pH

1 Function $3[Cr^{3+}]/c_{COOK} = f(3c_{Cr} : c_{COOK})$, 2 theoretical course of this curve; pH: ◑ pectate and solution 3·0; ◐ pectate and solution 4·0; ● pectate 5·0, solution without adjustment of pH; ○ pectate and solution without adjustment of pH.

Finally, one can say that pectin behaves as a highly selective ion exchanger towards Pb^{2+} and Cr^{3+} ions. It was proved that binding of Pb^{2+} to carboxyl groups does not depend on the esterification degree of pectin within $E \leqq 50\%$ in contrast to other bivalent cations (Ca^{2+}, Sr^{2+}). A still relatively high value of the stability constant K of lead pectinates was found even at a higher esterification degree of pectin. This feature of pectin is especially important from the standpoint of prevention of health, in diets enriched with produce containing a higher amount of pectin characterized by medium or higher esterification degree of carboxyl groups. The capacity of ion exchange is obviously inversely proportional to esterification degree E; consequently, sodium pectate with a high capacity of ion exchange need to be directly applied in an acute poisoning with lead ions.

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