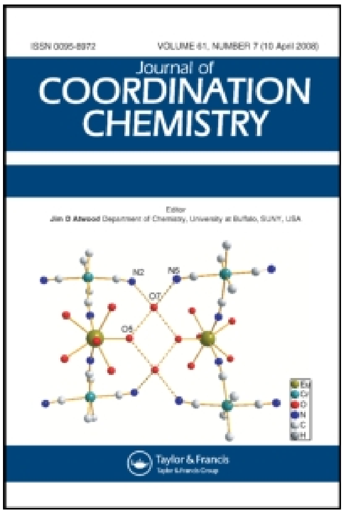

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Davarski, K. A. , Manolov, S. N. , Petrova, I. N. and Mavrov, V. D.(1994) 'COMPLEX EQUILIBRIA IN THE SYSTEM M^2 -POLYGALACTURONIC ACID (PECTIN) - H_2O (M = Co, Ni, Cu, Zn, Cd AND Pb)', Journal of Coordination Chemistry, 33: 1, 75 — 81

To link to this Article: DOI: 10.1080/00958979408024264

URL: http://dx.doi.org/10.1080/00958979408024264

J. Coord. Chem., 1994, Vol 33, pp. 75–81
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COMPLEX EQUILIBRIA IN THE SYSTEM M^{2+}-POLYGALACTURONIC ACID (PECTIN) - H_2O (M = Co, Ni, Cu, Zn, Cd AND Pb)

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(Received November 23, 1993; in final form February 17, 1994)

Ionisation constants for polygalacturonic acid (pectin) were determined by pH-metric titration in aqueous solution at different temperatures (283, 293, 303 and 313 K) and ionic strengths (0.1, 0.5, 1.0, 1.5 and 2.0), maintained with $NaNO_3$. Complexing of pectin with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} under the same conditions and M:L ratios of 1:2 or 1:4 was studied. It was found that ML complexes prevail. Stability constants were evaluated. Complexformation is a result of favourable entropy changes, whereas there is no significant change of enthalpy. The possibility of metal extraction by complex formation and ultrafiltration was examined. Selectivities in ultrafiltration and productivities of membranes for Cu^{2+} complexes of pectin were determined.

KEYWORDS: pectins, polygalacturonic acid, transition metals, complexes, stability constants, ultrafiltration

INTRODUCTION

Reactions of metal ions with synthetic and biopolymers are of considerable theoretical and practical interest. They are related to a number of biological processes, including catalysis.[1–4] Such reactions, in combination with ultrafiltration or reverse osmosis, are applied in recovering and recycling metal ions from multicomponent aqueous solutions.[5,6]

The results of a study of complex equilibria involving polygalacturonic acid (pectin) with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} in solution are discussed below. The investigation, carried out by pH-metric titration, is a continuation of our research on complex formation and ultrafiltration using polymeric ligands.[7,8] Pectins are efficient cation exchangers.[9] An understanding of their interraction with metal ions in aqueous media is of fundamental importance for understanding properties of their solutions and gels at the molecular level.[10–13] Such systems have been investigated but no satisfactory characterization of complex formation has been made.[14–16]

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EXPERIMENTAL

Materials

Apple pectin with a molecular weight over 200000 Daltons was used. Stock solutions were prepared by diluting the contents of Riedel-de Haën concentrates of the corresponding metal salt and NaOH (free of carbonate).

Apparatus and procedure

Potentiometric titrations were performed with an MV-870 potentiometer coupled with an OP-808P (Radelkis) glass-saturated calomel electrode, with an instrumental resolution of ± 0.001 pH. The measurement cell (50 cm^3) was kept at the required temperature within 0.2 K. All titrations were carried out with stirring, magnetically, and under a purified nitrogen atmosphere.

Ultrafiltration separation was performed on an SM-16526 Lab Unit (Sartorius, Germany). A UF-60 PAN membrane ("Ekofilter-AD", Bulgaria) was used. This membrane is able to separate substances of molecular weight greater than 60000. The operating conditions were pressure 0.3 MPa, stirring speed 400–450 rev. min^{-1} and T 315–318 K. The concentration of Cu^{2+} during ultrafiltration was monitored by means of atomic absorption.

Relative viscosity was estimated using an Ubbelhode viscosimeter at constant temperature (298 K) and different ionic strengths.

RESULTS AND DISCUSSION

Pectin is primarily a polymer of *D*-galacturonic acid. In all natural pectins some of the carboxyl groups are in the methyl ester form. For characterization of the apple pectin used, the total amount of carboxyl groups (K_t) as well as the free (K_f) and esterified fractions (K_e) were determined by known techniques.[17] It was found that K_t = 11.74 wt %, K_f = 3.78 wt % and K_e = 7.96 wt %. The free carboxyl groups comprise 24% of the total. These determinations show that this is a high-methoxyl pectin.[18] Such pectins do not gel so easily in the presence of divalent ions because of the low number of carboxyl groups that need to be bridged.[19] That is why they are suitable for investigating complex formation with metal ions.

The ionization constant of pectin was determined by pH-metric titration at μ = 0.1, 0.5, 1.0, 1.5 and 2.0 and at various temperatures. Values obtained are listed in Table 1.

Table 1 pk_a values for pectin at various ionic strengths and temperatures.

μ	pK_a at T			
	283	293	303	313
0.1		3.60		
0.5		3.75		
1.0	3.28	3.75	3.34	3.28
1.5		3.24		
2.0		3.09		

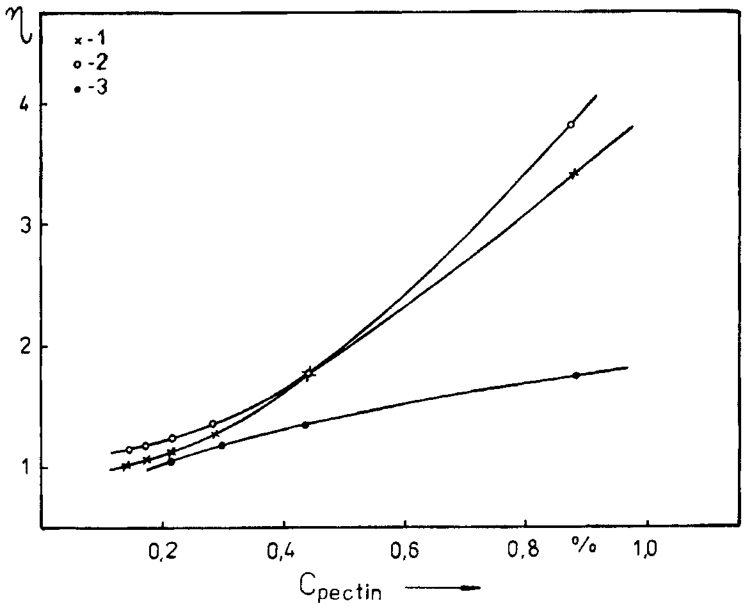

Figure 1 Effect of pectin concentration on relative viscosity: 1- pectin-H_2O (μ = o); 2- pectin-H_2O (μ = 0.1); 3- pectin-Cd^{2+}-H_2O (COOH:Cd^{2+} = 1:1).

The results obtained show that the dependence of pK on μ and T is complex. The highest pK_a value is reached at μ = 0.5 and with further increase of ionic strength it decreases. It thus was not possible to determine the thermodynamic ionization constant at μ = 0 using known functional dependences of pK_a/μ. The unusual increase in pK_a for pectin to μ = 0.5 is probably due to changes in the polymer chain (charge, conformation, *etc.*) at a higher electrolyte concentration. When μ > 0.5, pK_a decreases because of changes of activity coefficients. The pK_a values at different temperatures indicate the effect of T on pK_a, which has its maximum at 293 K. It is evident that ΔH changes sign at about room temperature. Similar changes of enthalpy are observed for a number of organic acids.[20]

Complexation of pectin with Co^{2+}, Ni^{2+} and Cu^{2+} was studied at μ = 0.1, 0.5, 1.0, 1.5 and 2.0, with M : L = 1 : 2, and at μ = 1.0 for M : L = 1 : 4 (T = 293 K). Reactions with Zn^{2+}, Cd^{2+} and Pb^{2+} were studied only at μ = 1.0 and M : L = 1 : 4 (T = 293 K). In order to determine the influence of temperature on stability constants, the system Cu^{2+}- pectin was studied at T = 283, 293, 303 and 313 K (μ = 1.0). In all cases, potentiometric titrations were carried out in the same manner as for determining pK_a. It was found that complexation causes shifting of pH curves towards lower pH-values.

Interpretation of the results for complexing with polymeric ligands is model dependent.[21] In cases of linear polymers such as pectin,[22] models in which the metal ion is a centre of complex formation are preferable. In such systems interaction depends on the chemical nature of the ligand as well as on its conformation.[23]

In this work, the metal ion was considered to be the centre of complex formation, and the polymer ligand to be a combination of *quasi*-independent monomeric ligands. In accordance, with this, the concentration of pectin (C_{eq} = 1.48×10^{-3} mol dm^{-3}) was calculated having in mind monomer fragments containing free COOH groups. In order to ensure better reliability, this concentration was measured in two ways: using the values of K_f and K_e, and by pH-metric titration.

Stoichiometry and stability constants of the complexes were determined by a Bjerrum function:

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2 \frac{(2-\bar{n})}{(1-\bar{n})}[L] + \ldots\ldots + \beta_n \frac{(N-\bar{n})}{(1-\bar{n})}[L]^{n-1}$$

The results show that $\bar{n} < 1$, *i.e.*, ML complexes prevail in solution. The Values of stability constants ($\lg\beta_1$) for these systems are shown in Table 2. Standard deviations for all $\lg\beta_1$ are within 1–3%. The results obtained for $\lg\beta_1$ of Cu^{2+} complexes at various temperatures are given in Table 3.

It was found that the volume of the system increases after interaction between pectin and divalent cations. Similar results were reported earlier[10] and may be explained by desolvation of metal ions and carboxyl groups. Complex formation is therefore characterized by a large positive entropy change.

The small changes of $\lg\beta_1$ at different temperatures show that the reactions are accompanied by endothermic enthalpy changes. This corresponds to the results obtained for the complexing of polyguluronic acid (differing from pectin only in the stereochemistry of C(3)[23]). Paolleti *et al.*,[10] have found that only the reaction of polygalacturonic acid with Cu^{2+} is exothermic. This was explained in terms of specific changes of polymer chain conformation. Our results for pectin-Cu^{2+} at different temperatures lead us to conclude that there are no significant change of enthalpy. The reason for this is probably due to the use of highly esterified pectin. In this case, the aggregation of polymer chains by bridged carboxyl groups is not as easy as for polygalacturonic acid.

From a practical point of view, the dependence $\lg\beta_1/T$ shows that in the temperature range 283–303 K the stability of the complexes does not change to any extent and complex formation-ultrafiltration studies can be undertaken without it being necessary to maintain constant temperature.

Viscosities of pectin solutions depend on the presence of metal ions in the system. Usually, monovalent ions cause reduction of viscosity but di- and trivalent cations have an opposite effect.[10,24]

Our results (Fig. 1) show that M^{2+} causes a decrease in viscosity of aqeuous pectin

Table 2 Values of $\lg\beta_1$ for complexes of pectin with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} at a ratio of M:L = 1:2 (1:4) and at T = 293 K.

μ	$\lg\beta_1$					
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
0.1	3.14	3.44	4.38			
0.5	3.49	3.78	4.58			
1.0	3.40	3.71	4.15			
	(3.57)	(3.90)	(4.34)	(4.01)	(3.93)	(3.74)
1.5	3.31	3.65	4.12			
2.0	3.15	3.57	3.92			

Table 3 Values of $\lg\beta_1$ for Cu^{2+} complexes of pectin at different temperatures (μ = 1.0).

T,K	$\lg\beta_1$	
	M:L = 1:2	M:L = 1:4
283	4.08	4.21
293	4.15	4.34
303	4.16	4.33
313	4.11	4.18

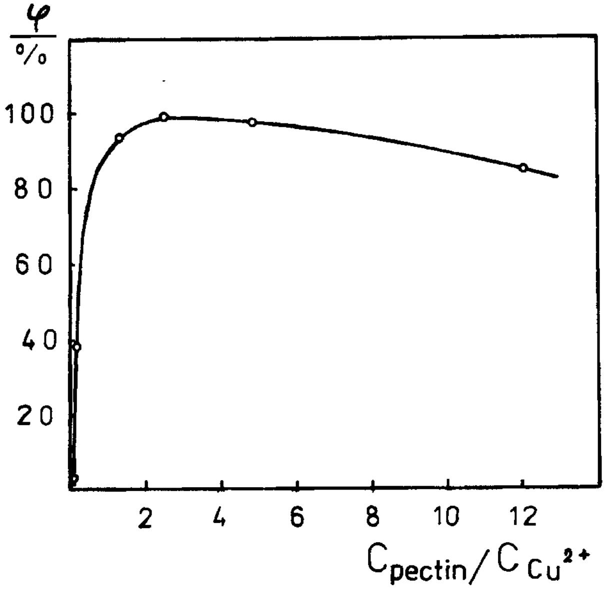

Figure 2 Effect of the ratio $C_{pectin} : C_{Cu^{2+}}$ on selectivity of UF.

solutions. This can be explained by the fact that after complexing the carboxyl groups exist as $-COOM^+$. The distribution of these charges along the molecule tends to keep it in an extended form because of coulombic repulsion, thus preventing aggregation of polymer chains. These results correspond to the conclusion (made on the basis of circular dichroism measurements[10,25]) that pectins with degrees of esterification more than 40% exist in different conformations in their acidic and salt forms. In the case of low-methoxyl pectins, as used by Thibault and Paoletti,[10] intermolecular bonding of M^{2+} to carboxyl groups of two macromolecules leads to the formation of dimers or multichain aggregates.

The possibility of extracting Cu^{2+} from its aqueous solutions by ultrafiltration (UF) after complexing with pectin was studied. One of the most important characteristics of UF is selectivity (φ). For Cu^{2+}this is calculated by the formula

$$\varphi_{Cu^{2+}} = \frac{C_i - C_p}{C_i} 100\%$$

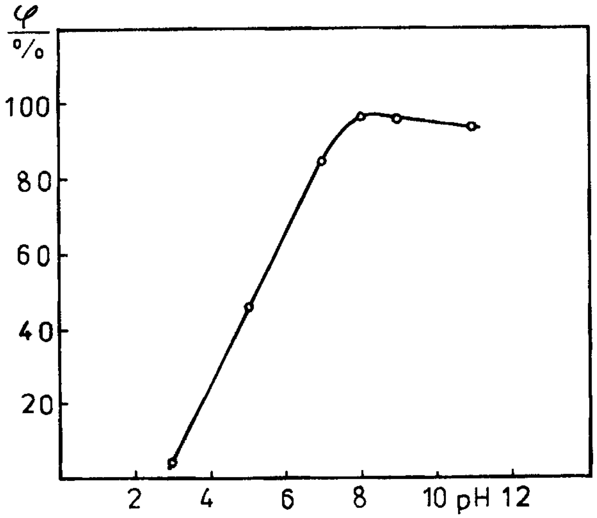

Figure 3 Effect of pH on selectivity of UF ($C_{Cu^{2+}}$ = 1.57 × 10^{-4}; C_{pectin} = 1.88.10^{-4} mol dm^{-3}).

where C_i is Cu^{2+} concentration in the initial solution, and C_p the corresponding concentration in the permeate. In all runs, C_i was 1.57 × 10^{-4} mol dm^{-3}. The concentration of pectin, calculated for fragments having nonesterified carboxyl groups, varied from 1.88 × 10^{-5} to 1.88 × 10^{-3} mol dm^{-3}. The dependence of $\varphi_{Cu^{2+}}$ on the ratio C_{pectin}: $C_{Cu^{2+}}$ at pH = 7 is shown in Figure 2. It is seen that at a ratio of COOH : Cu^{2+} of about 1:1 selectivity is about 90%. This shows that the stability of the Cu^{2+} complex with pectin is high enough to ensure efficient extraction of Cu^{2+} from the system. When there is a small excess of COOH $\varphi_{Cu^{2+}}$ becomes partically 100%. At a ratio > 3, the characteristics of the membrane process are poorer. The most probable reason for this may be due to concentration polarization caused by a thick layer of pectin on the membrane.

The influence of pH on $\varphi_{Cu^{2+}}$ is shown in Figure 3. The optimum pH range is 6.5–7.5. A further increase in pH decreases UF selectivity due to possible formation of hydroxides or hydroxo complexes. At pH < 3–4 selectivity is less than 10%, *i.e.*, the complex is practically destroyed. This shows that it is possible to recover the pectin ligand from the permeate in a form suitable for a further cycle of complex formation-ultrafiltration. These results lead us to conclude that complex formation-ultrafiltration with pectin ligands is a promising process for extracting metal ions from aqueous solutions.

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