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Interphase Distribution of Pectinate Calcium and Alginate Calcium in a System of Two Immiscible Liquids

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ABSTRACT

In comparison with the sugar beet pectin and sodium alginate, was studied interphase distribution of pectinate calcium and alginate calcium in the system "water: octanol-1" (1:1) at different temperatures. On the basis of the equilibrium concentrations of pectin, sodium alginate (technique neutralize), pectinate calcium, calcium alginate (complexometry) identified in the aquatic and oktanoles phases, graphically the calculated degree of Association of compounds in non-polar solvent, the calculation method of the distribution coefficients. The dependence between the process temperature and the degree of Association management: Video for sodium alginate, the inverse of pectin and pectinate of calcium; no effect on alginate calcium. Direct dependence between the temperature and distribution coefficients for pectin, pectinate calcium, alginate calcium, the alginate sodium. In descending order of the distribution coefficients of the substances in the following order: pectin>pectinate calcium>alginate calcium>alginate sodium. Calculation of thermodynamic functions (enthalpy, entropy, Isobaric-isothermal potential) according to the established distribution coefficients and known formulas showed a decisive contribution to the change of the Gibbs free energy entropy factor. The data obtained allowed to conclude that under standard conditions the spontaneous transition of pectin, pectinate calcium, alginate calcium from the polar phase to nonpolar phase, and for alginate sodium this transition can be carried out in the presence of activators of the process.

Keywords: Interfacial distribution, Pectinate calcium, Calcium alginate, The degree of Association thermodynamic functions.

INTRODUCTION

Polyuronide as polyuronides coordination compounds with metal ions have structural features: multiple electron-donor oxygen atoms capable of coordinating with metal ions; quantitative binding of metal cations, the tendency of cyclic uronic acids for coordination with the metal centers in the tetrahedral or octahedral configurations [1]. High capacity oxygen atoms polyuronides (pectins, alginates), along with covalent bonds to form with calcium ions coordination as intermolecular and intermolecular (such as "egg boxes") [1] leads to the formation of large conglomerates. Despite the knowledge of their structure, open questions remain for theoretical and experimental nature: The possibility of spontaneous distribution of these macromolecules in the system of immiscible polar and nonpolar solvents, thermal stability at phase transitions, and the change in aggregate stability. These problems led to the purpose of the work.

The aim of this work was to study the thermodynamic potentials of the process of distribution of pectinate calcium and alginate calcium in comparison with the initial reagents (pectin and alginate sodium) in a system of two immiscible liquids.

EXPERIMENTAL PART

The objects of study were pectinate calcium and alginate calcium, is obtained by reaction of interaction of calcium chloride with the appropriate polyuronides (pectin, alginate sodium). Used beet pectin produced by "Pekto" (Nalchik) the quality conforms to the requirements of a temporal pharmacopoeial article 42-3433-99 "Pectin" and is a polymer with an average molar mass of 3.2 kg/mol, consisting of 1→4-linked residues of α -D-galacturonic acid containing 14.4% of the free carboxyl groups, 9.2% of methylated carboxylic groups. Pectin is characterized by a content of total ash of 1.4%, ash insoluble in hydrochloric acid –0.4% pH of 2.0% aqueous solution of 3.5, the dissociation constant in water of 3.2×10^{-4} [1].

Used sodium alginate production in Arkhangelsk experimental seaweed plant, isolated from the sugar kelp *Laminaria asagba* (L.), corresponds to the quality requirements of State standard 26185-84 "Marine Algae, sea grasses and products of their processing. Methods of analysis" and is a polymer with an average molar weight of 89.7 kg/mol, consists of alternating blocks of 1→4-linked residues of β-L-guluronic and α-D-mannuronate acids (in the ratio 1:2) containing 9.1% of the ionized carboxylic groups, with 0.9% methylated carboxyl groups. Content in the sodium alginate ash total is 25.7%, ash insoluble in hydrochloric acid-0,8%, pH of 1.0% aqueous solution of 7.6 [1].

We used calcium chloride with a purity qualification "pure for analysis".

Polyuronide calcium in a solid state obtained by blending 0.1 mol/l aqueous solution of calcium chloride with 7.8×10^{-4} mol/l aqueous solution of pectin or 2.8×10^{-5} mol/l aqueous solution of sodium alginate in the volume ratio 1:10, intensive mixing of the mixtures and incubation at 293 K for 3 h to establish equilibrium. The separated gel-like precipitation of calcium poliuronate centrifuged, washed three times with water (1:4, 15 min), dried at a temperature of 333 K until reaching constant weight [2]. The average molar mass of pectinate calcium was 3.57 kg/mol, alginate calcium-a 99.97 kg/mol.

Due to the high permittivity (80 at 293 K [3]), water is selected as the polar solvent. Among the various non-polar solvents: octanol-1, butanol-1, butanol-2, pentanol-1, pentanol-3, butyl acetate, heptane, xylene, etc. choice made in favor of octanol-1, which has an optimum balance of hydrophilic and lipophilic properties [4].

For the study we prepared aqueous solutions (or suspensions) of pectin, pectinate calcium, alginate sodium and alginate calcium with an initial concentration (C_0) of 8.7×10^{-4} mol/l. The Solutions were mixed with an equal volume of octanol-1, kept at temperatures (T): 283 K, 293 K, 313 K during the day (to establish equilibrium), shaking occasionally.

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In aqueous solutions (suspensions) were determined by the equilibrium concentration (C_1) of pectin by the method of alkalimetry (titrant 0.1 mol/l hydroxide sodium solution, the indicator phenolphthalein) [5], alginate sodium by the method of acidimetry (titrant 0.1 mol/l solution hydrochloric acid, methyl red indicator) [5], pectinate calcium and alginate calcium by the method of chelatometric titration (titrant 0.01 mol/l solution of chelating agent III, indicator eriochrome black T, pH 10) [6]. The equilibrium concentration of pectin, sodium alginate, pectinate calcium and alginate calcium in solutions of octanol-1 (C_2) were calculated as the difference between C_0 and C_1 . Further, in the graphics coordinate system " $\lg C_2=f(\lg C_1)$ " on the tangents of the angle of inclination of the obtained straight to the x-axis determined the degree of Association (n) of the test substances in a solution of octanol-1 [4]. The distribution coefficients (K_p) calculated from the known equation [4] (equation 1):

$$k_p = \frac{C_2^n}{C_1} \quad (1)$$

Given that the interfacial distribution is accompanied by changes in thermodynamic functions: enthalpy (ΔH°), entropy (ΔS°), Gibbs energy or the Isobaric-isothermal potential (ΔG°) and the possibility of spontaneous occurrence of the process depends on the ratio of contribution to the Isobaric-isothermal potential enthalpy (ΔH°) and entropy ($T\Delta S^\circ$) components, we have determined the values of these thermodynamic potentials. Taking into account that the studied solutions (suspensions) are sufficiently diluted, the change in enthalpy and entropy can be equated to changes in the relevant standard potentials [7].

Thermodynamic potentials of the process of distribution of investigated substances from the aqueous layer in the organic layer calculated from the known equations. Value ΔH° calculated using the equation of Vant Hoff on the K_p , determined at different temperatures (K_{p1}, K_{p2}) [7] (equation 2):

$$\Delta H^\circ = \frac{\ln(K_{p2} / K_{p1}) \cdot (T_2 T_1 R)}{T_2 - T_1} \quad (2)$$

Where R-is the gas constant, $8,3144 \times 10^{-3}$ kJ/(mol × K) [7].

The value of ΔS° calculated according to the equation (3), ΔG° is the equation of Gibbs-Helmholtz (equation 4), and K_p (equation 5) [7,8]:

$$\ln K_p = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\Delta G^\circ = -RT \ln K_p \quad (5)$$

The relative error of all definitions was 3.6/4.8%.

RESULTS AND DISCUSSION

For polyuronides and calcium salts in the system "water: octanol-1" (1:1) experimental data n, C1 and C2 at different temperatures for which the calculated values of Kp (Table 1).

Table 1: Experimental data and calculated values of distribution coefficients polyuronides and their salts at various temperatures

| These | The Pectin | Pectinate calcium | Alginate sodium | Calcium Alginate |
|---------------|-----------------------|-----------------------|-----------------------|-----------------------|
| T=283 K | | | | |
| n | 0.90 | 1.08 | 0.98 | 1.03 |
| C_1 , mol/l | 2.58×10^{-4} | 1.34×10^{-4} | 4.80×10^{-4} | 1.96×10^{-4} |
| C_2 , mol/l | 6.12×10^{-4} | 7.36×10^{-4} | 3.90×10^{-4} | 6.74×10^{-4} |
| K_p | 4.97 | 3.08 | 0.95 | 2.76 |
| T=293 K | | | | |
| n | 0.87 | 1.05 | 1.00 | 1.02 |
| C_1 , mol/l | 2.51×10^{-4} | 1.28×10^{-4} | 5.05×10^{-4} | 1.88×10^{-4} |
| C_2 , mol/l | 6.19×10^{-4} | 7.42×10^{-4} | 3.65×10^{-4} | 6.82×10^{-4} |
| K_p | 6.44 | 4.04 | 0.72 | 3.14 |
| T=313 K | | | | |
| n | 0.80 | 1.02 | 1.06 | 1.03 |
| C_1 , mol/l | 2.48×10^{-4} | 1.15×10^{-4} | 5.46×10^{-4} | 1.76×10^{-4} |
| C_2 , mol/l | 6.22×10^{-4} | 7.55×10^{-4} | 3.24×10^{-4} | 6.94×10^{-4} |
| K_p | 10.98 | 5.69 | 0.37 | 3.17 |

Data indicate that with increasing temperature the degree of Association of pectin and pectinate calcium reduced. Apparently, this is due to the partial destruction of hydrogen bonds associated units, which helps them, transition into the layer of organic solvent. Along with this, the optimal distribution of pectin and pectinate calcium in non-polar solvents favored by the fact that both substances are weak electrolytes. In comparison with pectin, K_p pectinate of calcium depending on the temperature in the 1.6-1.9 times lower, which is probably due to the conglomeration of calcium pectinate type "egg boxes", where each cation calcium contact with ten oxygen atoms of the four monomers of uronic acids (two from each polymer molecule) (Figure 1) [1].

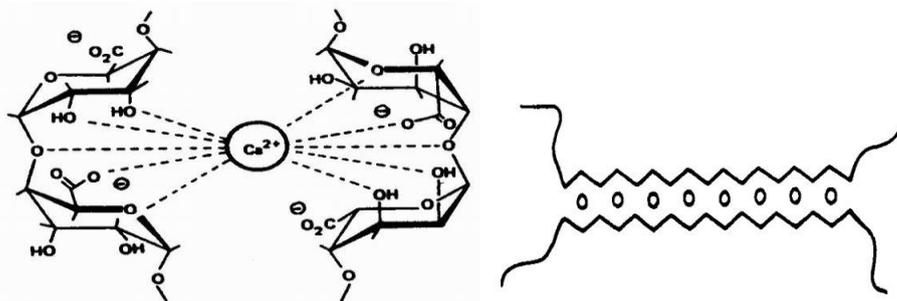


Figure 1: The structure of pectinate calcium type "egg box": a – formula, b – external view

For alginate sodium the increase in temperature leads to an increase of the degree of Association, probably due to solvation formed by the dissociation of ions. Macromolecules of alginate sodium, significantly larger in comparison with pectin, with labor moving into the organic layer, as evidenced by the low values of K_p . The temperature increase is not conducive to the transition of alginates in organic layer.

In contrast to alginate sodium, the temperature rise has virtually no effect on the degree of Association of alginate calcium, but significantly affects the value of K_p for which the range 283-294 K the rise of the K_p , and at 313 K–stabilization value. It can be assumed that the transition in the organic layer when 283-294 K is due to the partial destruction of the more labile unit alginate – polymannuronate of calcium, in contrast to the more solid block polyguluronate calcium, not undergoing thermolysis. Compared with sodium alginate, which is a strong electrolyte, calcium alginate, structured according to the type of "egg box" is similar to pectinata calcium, depending on the temperature 2.9-8.6 times more is distributed in a layer of octanol-1.

In General, the obtained results can be explained as follows. Change "best" of the solvent (water) to "worst" solvent (octanol-1) for pectin and alginate sodium leads to aggregation of the molecules and the intermolecular displacement of the adsorption equilibrium from the system "polyuronic \leftrightarrow water" to "polyuronic \leftrightarrow polyuronic". A certain influence on the aggregation of the molecules of polyuronic have individual properties octanol-1, which is expressed in the interaction of molecules with water molecules and polymer [4]. As the binding energy of the molecules with each other and their solvation energy depends on the mass fraction of free carboxyl groups of polyuronic, the degree of their saturation with calcium cations. To some extent the influence of these factors can be taken into account: the molar energy of cohesion of the groups $-\text{COOH}$ is 376.6 kJ/mol, whereas groups COOCH_3 only 23.4 kJ/mol [9]. Depending on the structure of molecules containing these groups, the values of the molar energy of cohesion may vary somewhat, but the ratio values for the groups $-\text{COOH}$ and $-\text{COOCH}_3$ is generally preserved.

The presence of carboxyl groups polyuronides cations of sodium increases the degree of dissociation and repulsion of similarly charged anions, resulting in intermolecular Association is impossible. In case of incomplete dissociation of the binding energy between the dipoles RCOOMe (Me-metal) should be apparently the same as between the ether groups RCOOCH₃. However, for salts of calcium, the formation of ionic bonds of the type RCOO-Ca-OOCR, energy which, as any ion must be several times higher energy hydrogen bond [10]. Probably, the binding energy of the molecules polyuronides increases in the series: -COONa<-COOCH₃<-COOH<-(COO)₂Ca; in a slightly different sequence changes the energy of hydration [9]: -COOCH₃<-COOH< (COO)₂Ca<-COONa. Because the high energy of the molecules polyuronides increases their ability to Association, and at high values of the solvation energies of the associated power drops, the total result of these effects is not always possible to foresee. However, it is clear that the mutual binding of the molecules polyuronide should help, as the increase in the number of calcium cations, and displacement of metal cations (I) hydrogen ions. These conclusions are confirmed by the fact that if sodium alginate is soluble in water, sparingly soluble pectin, the calcium salts of pectin and alginic acid is not soluble [1].

The results of determining of the thermodynamic functions of the process distribution of the investigated substances in the system "water: octanol" is presented in Table 2.

Table 2: The thermodynamic functions of the process distribution polyuronides and their salts in the system "water: octanol" at different temperatures

| T, K | Pectin | Pectinate calcium | Alginate sodium | Alginate calcium |
|--|-----------------------|-----------------------|------------------------|-----------------------|
| ΔH°, kJ/mol | | | | |
| 283 | 17.86 | 18.71 | -19.11 | 8.89 |
| 293 | 19.46 | 15.07 | -23.15 | 3.40 |
| 313 | 20.34 | 13.06 | -25.38 | 0.36 |
| ΔS°, kJ/(mol K) | | | | |
| 283 | 7.64×10^{-2} | 7.55×10^{-2} | -6.80×10^{-2} | 3.99×10^{-2} |
| 293 | 8.20×10^{-2} | 6.30×10^{-2} | -8.17×10^{-2} | 2.11×10^{-2} |
| 313 | 8.51×10^{-2} | 5.62×10^{-2} | -8.94×10^{-2} | 1.07×10^{-2} |
| $T \cdot \Delta S^\circ$, kJ/mol | | | | |
| 283 | 21.62 | 21.37 | -19.24 | 11.29 |
| 293 | 24.03 | 18.46 | -23.94 | 6.18 |
| 313 | 26.64 | 17.59 | -27.98 | 3.35 |
| ΔG° (according to equation 4), kJ/mol | | | | |
| 283 | -3.76 | -2.66 | 0.13 | -2.40 |
| 293 | -4.57 | -3.39 | 0.79 | -2.78 |
| 313 | -6.30 | -4.53 | 2.60 | -2.99 |
| ΔG° (according to equation 5), kJ/mol | | | | |
| 283 | -3.77 | -2.65 | 0.12 | -2.39 |
| 293 | -4.54 | -3.40 | 0.80 | -2.79 |
| 313 | -6.24 | -4.52 | 2.59 | -3.00 |

CONCLUSION

The calculated values of the thermodynamic functions of the process distribution polyuronides of the aqueous phase in the organic phase suggests that the enthalpy change favors the transition of only sodium alginate ($\Delta H^\circ < 0$) and for pectin, pectinate calcium and alginate calcium indicated the transition from the point of view changes not favorable enthalpy ($\Delta H^\circ > 0$). The found values indicate the solvation of alginate sodium ($\Delta H^\circ < 0$) and the destruction of the associates of pectin and calcium salts polyuronides ($\Delta H^\circ > 0$) in the organic layer. With the position change of the entropy factor in the situation is the opposite: adverse transition for sodium alginate ($T \cdot \Delta S^\circ < 0$) and favorable for the other test substances ($T \cdot \Delta S^\circ > 0$). The contribution of the entropy factor in the change in the Isobaric-isothermal potential of the process of distribution of all substances exceeding the enthalpy contribution component, so the resultant value of the change of Gibbs energy is negative for pectin, pectinate calcium, alginate calcium, a positive value for alginate sodium. Obtained according to the equation of Gibbs-Helmholtz values of changes of Gibbs energy are fully confirmed by the values of the function calculated according to the amounts of K_p . Therefore, we can conclude that under standard conditions the spontaneous transition of pectin, pectinate calcium, alginate calcium from the polar phase to nonpolar phase, and for alginate sodium this transition can be carried out in the presence of any activators of the process.

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