



Complexes of anionic polysaccharides with metal salts. Part II. κ -Carrageenan

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Abstract

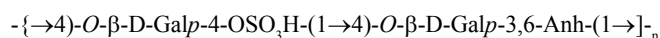
Properties of κ -carrageenan complexes with paramagnetic transition metal cations [Co(II), Cu(II), Fe(III), Mn(II), and Ni(II)] were evaluated using the EPR spectrometry, conductivity measurements, thermogravimetric (TG), and differential scanning calorimetric (DSC) studies as well as computations with involvement of the ZINDO-1 method. The formation of the Werner-type complexes with metal central atom and polysaccharide as the ligand was proven. Ligation of the central atom involved lone electron pairs of the polysaccharide hydroxyl groups and the SO_3^- groups of carrageenan.

Key words: Computations, electron paramagnetic resonance, differential scanning, calorimetry, thermogravimetry, Werner complexes.

Introduction

Carrageenans are natural carbohydrate polymers of seaweeds. About 80,000 tons of dry red seaweeds are needed to produce 20,000 tons of carrageenans. Carrageenans are particularly widely used in food, cosmetic, and pharmaceutical industry to modify textural attributes of the products¹⁻³. They are regulated food additives, and current health concerns focus on the minimum safe molecular weight for carrageenan when eaten. Carrageenans of the molecular weight below 100 kDa are claimed⁴ toxic. However, high-molecular weight carrageenans do not hydrolyse under physiological conditions to such fractions. The conformation of carrageenans is essential in this case⁵. Microencapsulation is another application of carrageenans^{6,7}.

Carrageenans constitute a group of mono-, di-, and tri-sulfated polymers of β -D-galactose. They may be naturally contaminated with cellulose⁸. Among carrageenans, monosulfated κ -carrageenan has received the most attention.



The NMR spectra⁹, cryo-transmission electron microscopic¹⁰, small-angle X-ray scattering¹¹⁻¹², conductometric¹³⁻¹⁴, and matrix assisted laser desorption/ionization and electrospray ionization mass spectrometric¹⁵ studies indicated an ordered conformation of carrageenans. Formation of their structure in solutions proceeds through multistage associations of macromolecules that, in many instance, lead to a micro-heterogeneous structure of semi-dilute liquid solutions as well as thermotropic gels. In aqueous solution, κ -carrageenan behaves as a normal polyelectrolyte⁴. Therefore, along with hydrogen bonds and hydrophobic interactions, metal ions can be crucial for the formation of gel networks. Indeed, in numerous studies carried out on κ -carrageenan solutions^{7,10,11,14-27} the role of the salt cations in the coil-to-helix transition was documented. Also importance of salt counterions in such transition was proven^{7,13,28}. In these

studies attention was paid mainly to the effect of the metal ions from the first and second non-transition groups.

Only randomly, interactions of κ -carrageenan with the transition metal atoms attracted attention. It has been shown that zinc was bound electrostatically to this carrageenan²⁹. However, a stabilisation of iron hydroxides and oxides in κ -carrageenan even at high pH and effect of the nickel and cobalt salts upon the precipitation of iron oxide showed that a coordination of carrageenan to these metal ions could take place^{30,31}. Also the effect of the Cu(II) ion on the dynamic rheology of κ -carrageenan suggested coordination of that ion by carrageenan²⁴. The interaction of κ -carrageenan with Fe(II) and Fe(III) ions facilitated depolymerization of that polysaccharide already at room temperature³². Comparative studies of the ability of alginates, chitosanalginates, and κ -carrageenan to trap the cadmium ion from solutions showed a superior ability of κ -carrageenan as the cadmium collector³³. Interaction between metal ions and ligands containing the alcoholic hydroxyl groups, this is, such as these present in saccharides and polysaccharides have received increasing attention in recent years, since the metal complexes with saccharides and polysaccharides may play important role also in living organisms. Effect of the complexes on the metabolism as well as distribution and excretion of the metal ions from the organism can be taken under consideration^{34,35}. Several metal-polysaccharide complexes have industrial, medical and agricultural application³⁶.

Interactions of κ -carrageenan with transition metal salts may either extend or limit a range of practical applications of this polysaccharide. These arguments rationalise recognition of the structure and properties of potential carrageenan complexes with heavy metals. Formation of intra- and inter-molecular metal complexes of anionic κ -carrageenan seems likely.

In this paper interactions of κ -carrageenan with salts of Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) are presented together with properties of the products resulting from such interactions.

Experimental

Materials: κ -Carrageenan, was purchased from Fluka (Switzerland). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{OCOCH}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot \text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, all of analytical grade, were purchased from POCh Gliwice (Poland).

Methods

Formation of complexes: Aqueous solutions (7 w/w%) of carrageenans were prepared by one-hour heating and agitation at 90°C of corresponding suspensions. Blending with salts was performed by admixture of a 0.1 M aqueous anhydrous salt solution (10 cm³) into the suspension containing 5 g of κ -carrageenan followed by 24-hour agitation at room temperature. Sedimented complexes were separated by decantation of the mother liquor and dried at 50°C. Received κ -carrageenan was taken as the primary control sample and the same carrageenan separated from its 7 w/w% aqueous solution prepared by one-hour heating and agitation at 90°C was the secondary control sample.

EPR spectra: The EPR spectra were recorded for powdered samples in the X-band region ($\nu = 9.5$ GHz, $\lambda = 3.2$ cm) at room temperature. Diphenyl picrylhydrazide (DPPH) was taken as the standard for g-factor ($g = 2.0036$). The apparatus was manufactured by Politechnika Wroc³awska (Poland). The spectral curves were processed using the 2.8 b MicroCal Origin program.

Thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC): The thermal DSC-TG-DTG analysis was carried out with a NETZSCH STA-409 simultaneous thermal analyzer calibrated with standard indium, tin, zinc, and aluminium, all of the 99.99% purity. Samples (approximately 0.020 g) were heated in corundum crucibles with non-hermetic lids. Corundum was the standard. The heating was performed under static conditions in the air in the range of 20–400°C with the temperature rate increase of 5 K min⁻¹. Measurements were duplicated. They provided the $\pm 0.5^\circ\text{C}$ precision in reading of temperature.

Conductivity measurements: The conductivity measurements at room temperature were performed for aqueous suspension of κ -carrageenan (0.5 g of dry residue in 10 cm³ of water), salt solutions (0.1 M calculated for anhydrous salt), and aqueous blends of κ -carrageenan with salts (0.5 g of dry residue of carrageenan in 10 cm³ of 0.1 M aq. salt solution). Results were proven stable within 24 hours. Measurements were run in triplicates. Conductometer (inoLab, Pol-Eko-Aparatura, Poland) provided precision of $\pm 1\%$ of recorded value.

Computations: The computations were carried out with involvement of the SCF LCAO MO ZINDO-1 method with the Cache 4.4. program (evaluation version).

Results and Discussion

Conductivity of particular solutions was between 14.8 and 24.5

mS/cm. The original conductivity of salt solutions differently responded to the admixture of the κ -carrageenan solution (Table 1). The decrease in the conductivity of solutions, which was observed, was not unexpected because admixed κ -carrageenan was a sodium and/or potassium salt of the polysaccharide monosulfate of the conductivity of 0.464 mS/cm. Because of poor solubility of the heavy metal salts of carrageenan, the process of the ion exchange at the sulphate group could be completed. The extent of the reduction of the conductivity required acceptance of more refined approach to rationalise the observation. Thus, the polysaccharide–ion (cations and their counterions) interactions might influence the coil-to-helix transformations of carrageenan and, in this manner, the ability of that polysaccharide to trap the ions by the formation of salts, Werner, cage, and surface sorption complexes could be affected to the extent dependent on admixed salt. This study focused on the structure and properties of solid products separated after blending solutions of κ -carrageenan with salt solutions.

Inspection of Table 1 revealed that invariably, metal acetates provided very strong decrease in the conductivity of solutions. Except the cobaltous salt, nitrates performed similarly, and except manganous salt, chlorides produced the smallest reduction of the conductivity. The admixture of three cobaltous salts gave relatively the smallest decrease in the conductivity suggesting that either the complexes might be best water soluble.

Table 2 contains results of the computation of the enthalpy of formation of the coordination spheres around metal cations. In these computations the coordination number of 4 was adopted for the Cu(II) and Ni(II) ions whereas the coordination number of 6 was accepted for Co(II), Fe(II) and Mn(II) ions.

The stability of hydrated cations decreased in the following order: $\text{Mn}(\text{H}_2\text{O})_6^{2+} > \text{Fe}(\text{H}_2\text{O})_6^{3+} > \text{Cu}(\text{H}_2\text{O})_4^{2+} > \text{Ni}(\text{H}_2\text{O})_4^{2+} > \text{Co}(\text{H}_2\text{O})_6^{2+}$. Among assumed complexes of the Co(II) ion with carrageenan and water in the inner coordination sphere, the complex with one carragenate and five water ligands was the most stable species. It might explain remarkably small changes in the conductivity in the solutions of cobaltous chloride, nitrate and, to a certain extent, also acetate. According to the results of the computation the Cu(II) complex with two carragenate and two water ligands in the inner coordination sphere were the most stable. The most stable Fe(III) complex comprised of two carragenates and four water molecules in the inner coordination sphere, Mn(II) had its inner coordination sphere built of five carragenates and one water molecule and Ni(II) held only four carragenate ligands.

The strongest effect of acetates upon changes in the conductivity of the salt solutions might be associated with an unrecognised effect of that counterion upon the coil-to-helix transformation and possible aggregation of the polysaccharide. Alternatively, the acetate ion could be incorporated into the inner coordination sphere of the complexes. It should also be underlined that in remained complexes, the postulated water molecules ligating the central metal atom could be repulsed by the hydroxyl groups of the β -D-galactose units and the second of three oxygen atoms of the sulphate groups. In non-anionic polysaccharides the formation of complexes with metal ions (Cu(II), Co(II), Zn) involved the hydroxyl groups of C2 and C3 atoms in the monosaccharide mers³⁷. Comparison of the changes in EPR g-factor of particular salts after the coordination

of carrageenan (Table 3) showed relatively large shifts for complexes of carrageenan with all metal acetates informing on a fairly efficient delocalisation of unpaired spin from the central atom to the ligand. In those complexes and in complex with FeCl_3 , a tetrahedral rather than square planar arrangement structure of the polysaccharide ligand could be postulated because such structure of the complex provided structural conditions facilitating the spin delocalization. In other complexes the square planar structure of the complex seemed to be likely. The value of g -factor close to 2.000 pointed to the degeneration of the orbitals in all complexes. Results of the thermogravimetric analysis of κ -carrageenans and its metal complexes are presented in Table 4. The thermogram and diagram of the differential scanning calorimetric measurements (DSC-gram) of received (Fig. 1) and from aqueous solution recovered (Fig. 2) carrageenan showed a different pathway of the water loss in the preliminary stages up to approximately 150°C and also different course of further thermal transformations. As received sample was slowly thermally dehydrated ($\text{tg } \alpha = 0.13$). Some stages of dehydration in this temperature region could be distinguished in the DTG curves in form of shoulders and broad, low peaks. A sharp DTG peak at 127.6°C reflected the loss of 11% clathrated water. This stage was relatively fast ($\text{tg } \alpha = 0.55$). Totally, the sample contained 22% of water.

The sample of κ -carrageenan recovered from its paste held totally 24% water. Approximately 18% of surface sorbed water was lost up to 120°C in a more uniform but faster manner ($\text{tg } \alpha = 0.34$). The loss of 6% clathrated water was manifested by sharp peak at 125.5°C. Subsequent regions of the diagrams for both samples were distinctly different. Thus, pasting caused essential changes in a macrostructure of carrageenan. Original sample showed relatively fast transformation between 171 and 188°C after which a slow decomposition followed. It resulted in the total 57% weight loss up to 400°C. Except a weak exothermic effect at 382.5°C all thermal effects were endothermic. The sample recovered from its paste behaved differently. After a series of weak endothermic transformations of varying rate there was a very fast ($\text{tg } \alpha = 1.54$) exothermic transformation completing the total 64% weight loss and after which the decomposition product was completely stable and did not lose its weight anymore.

The coordination of κ -carrageenan to the metal ions introduced dramatic changes to the pattern of thermograms and DSC-grams. Taking the pattern of the TG-grams as the criterion the diagrams could be accounted into a group of anhydrous and hydrated species, a group of complexes with CoCl_2 , $\text{Co}(\text{OCOCH}_3)_2$, CuCl_2 , $\text{Cu}(\text{OCOCH}_3)_2$, $\text{Mn}(\text{OCOCH}_3)_2$, NiCl_2 , and $\text{Ni}(\text{OCOCH}_3)_2$, and a group of complexes with $\text{Co}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, FeCl_3 , MnCl_2 , and $\text{Ni}(\text{NO}_3)_2$, respectively. There were in both groups complexes, which were either moderately or very stable. Fig. 3 presents the diagram for the complex with NiCl_2 . This anhydrous complex began to decompose around 136°C. After moderately fast decomposition ($\text{tg } \alpha = 0.57$) there was almost steady slow decomposition resulting in the 61% loss of the weight up to 400°C.

The thermal behaviour of the complex with cobaltous acetate (Fig. 4) delivered an example for anhydrous and very stable compound. The slow ($\text{tg } \alpha = 0.07$) thermal decomposition of

the complex began above 340°C. The decomposition accelerated ($\text{tg } \alpha = 0.83$) above 425°C and slowed down above 500°C resulting in the loss of 55% weight. Because of its thermal properties (Fig. 5), the complex with $\text{Co}(\text{NO}_3)_2$ illustrated behaviour of hydrated moderately thermally stable complex and the decomposition pattern of the complex with $\text{Ni}(\text{NO}_3)_2$ (Fig. 6) exemplified the hydrated, thermally very stable complex. These results spoke in favour of the coordination of carrageenan to the central metal atoms with involvement of its hydroxyl groups.

In pasted κ -carrageenan exothermic transition appeared at 382.5°C. As given in Table 4, in some cases, its coordination to the metal atoms shifted this exothermic transformation to a lower temperature. It could not be considered as a rule because in the DSC-grams of the complexes with CoCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{OCOCH}_3)_2$, MnCl_2 , $\text{Mn}(\text{OCOCH}_3)_2$, and $\text{Ni}(\text{OCOCH}_3)_2$ no exothermic processes could be observed in the region up to 400°C. The absence of this exothermic effect was in no relation to the thermal stability of the complexes.

A confrontation of the results of the thermal studies with computations led to certain conclusions. The computation indicated that the Ni(II) central ion should not contain water molecules in its inner coordination sphere. Indeed, the thermograms of the complexes of nickel chloride and acetate showed that the complexes were anhydrous. In contrast to that, complex of nickel nitrate contained water (Fig. 6). The inspection of the relevant diagram and Table 4 indicated that the water present in the complex was, perhaps, the surface sorbed water. It was readily evolved below 100°C. The thermal analysis of complexes and computation implied that the hydroxyl groups of carrageenan did not ligate the central Ni(II) atom.

The computation suggested that the Mn(II) cation should be ligated by one water molecule as one of six ligands in the inner coordination sphere of that central atom. The course of the weight loss up to 150°C from these complexes (Table 4, Figs. 7 and 8) was in accord with results of the computation. Both complexes contained also the surface sorbed water.

The computation pointed to the ferric complex as that containing four water molecules in the inner coordination sphere. The thermal analysis (Fig. 9) produced evidence that there was only small amount of surface sorbed water in that complex. Therefore, one might accept that central atom was ligated by the hydroxyl groups of carrageenan. The pattern of thermograms of the cupric complexes suggested that only the complex with cupric nitrate might contain coordination water. There was a clear shoulder on the low-temperature side of the intensive peak of the complex decomposition (Fig. 10). Also relevant region of a slow weight loss ($\text{tg } \alpha = 0.24$) in that diagram supported this suggestion. The thermograms of the complexes of cupric chloride (Fig. 11) and acetate (Fig. 12) showed that the first complex was anhydrous and the second contained a small amount of the surface sorbed water. In conjunction with the computation results one might accept ligation of the central atom with the carrageenan hydroxyl groups.

Conclusions

1. Pasted κ -carrageenan formed the Werner-type complexes with the Co(II), Cu(II), Fe(III), Mn(II), and Ni(II) central atoms.

2. Ligation of the central atom involved lone electron pairs of the polysaccharide hydroxyl group and the OSO_3^- group of carrageenan.

3. Complexes of all metal acetates and FeCl_3 with carrageenan were tetrahedral whereas other complexes were square planar.

Table 1. Conductivity of aqueous suspensions of κ -carrageenan and its metal complexes.

| Conductivity [mS/cm] ^a | | |
|--|-------|----------------------|
| Salt | | Complex ^b |
| Cobaltous salts | | |
| Chloride | 16.58 | -36.7 |
| Nitrate | 17.69 | -21.5 |
| Acetate | 20.01 | -60.5 |
| Cupric salts | | |
| Chloride | 24.51 | -46.9 |
| Nitrate | 23.58 | -63.1 |
| Acetate | 21.54 | -69.8 |
| Ferric salts | | |
| Chloride | 22.56 | -46.9 |
| Manganous salts | | |
| Chloride | 23.54 | -63.8 |
| Acetate | 18.95 | -63.2 |
| Nickelous salts | | |
| Chloride | 14.79 | -56.1 |
| Nitrate | 18.25 | -64.5 |
| Acetate | 19.46 | -63.6 |

^aConductivity of κ -carrageenan is 0.464 mS/cm .

^bGiven as a change (in %) in the original conductivity of the salt solution resulting from admixture of κ -carrageenan.

Table 3. g -Factors for salts and their complexes with κ -carrageenan.

| | g -Factor | | | |
|-------------------------------|-------------|--------|---------|---------|
| | Salt | | Complex | |
| CoCl_3 | 2.2448 | | 2.0399 | 2.2386 |
| $\text{Co}(\text{NO}_3)_2$ | 2.2423 | | 2.0311 | 2.2418 |
| $\text{Co}(\text{OCOCH}_3)_2$ | 2.0011 | | 2.0418 | 2.2391 |
| CuCl_2 | 2.1073 | | 2.0892 | 2.2101 |
| $\text{Cu}(\text{NO}_3)_2$ | 2.0946 | 2.3148 | 2.0948 | 2.1201 |
| $\text{Cu}(\text{OCOCH}_3)_2$ | 2.0231 | 2.1652 | 2.0123 | 2.2341 |
| FeCl_3 | 2.2109 | | 1.9926 | 2.1344 |
| MnCl_2 | 1.9884 | | 2.0017 | |
| $\text{Mn}(\text{OCOCH}_3)_2$ | 2.0125 | | 2.0821 | A = 96G |
| NiCl_2 | 1.9876 | | 2.0026 | 2.0884 |
| $\text{Ni}(\text{NO}_3)_2$ | 2.2576 | | 2.0216 | 2.2592 |
| $\text{Ni}(\text{OCOCH}_3)_2$ | 2.2452 | | 2.0121 | |

Table 2. Computed enthalpy of formation of the coordination sphere around the metal central atoms.

| Ion | Enthalpy of formation, $-\Delta H$ [kJ/mole] | | | | | | | | | | | |
|-----|--|------|------|------|------|------|------|------|------|------|------|------|
| | Structure of the coordination sphere (Carrageenan + H_2O) | | | | | | | | | | | |
| | 0+4 | 0+6 | 1+3 | 1+5 | 2+2 | 2+4 | 3+1 | 3+3 | 4+0 | 4+2 | 5+1 | 6+0 |
| Co | | 2212 | | 1995 | | 1896 | | 1870 | | 1975 | 1664 | 1905 |
| Cu | 2242 | | 1978 | | 2099 | | 1933 | | 2064 | | | |
| Fe | | 2295 | | 1883 | | 2171 | | 2175 | | 1935 | 1796 | 1855 |
| Mn | | 2356 | | 2042 | | 2146 | | 1922 | | 1931 | 2498 | 1927 |
| Ni | 2237 | | 2089 | | 1805 | | 2052 | | 2109 | | | |

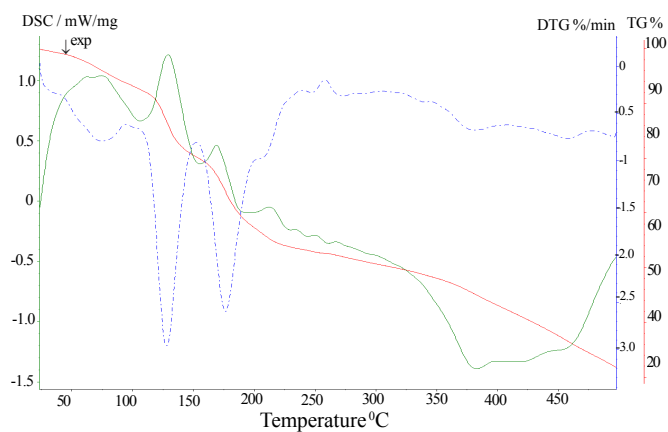


Figure 1. The thermogram and DSC-gram of received κ -carrageenan.

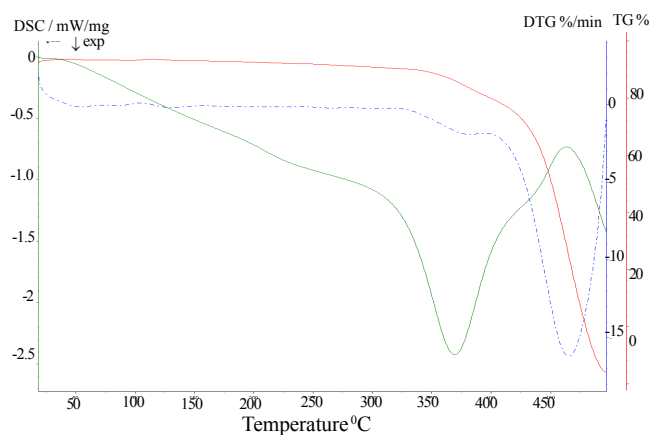


Figure 4. The thermal decomposition of the κ -carrageenan- $\text{Co}(\text{OCOCH}_3)_2$ complex.

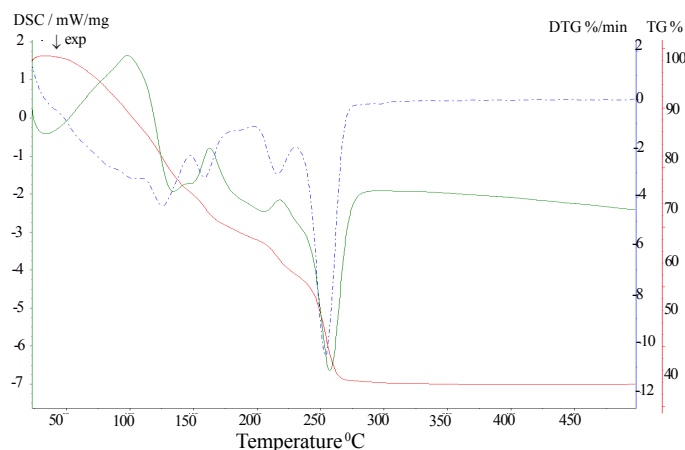


Figure 2. The thermogram of κ -carrageenan recovered from its 7 w/w% aqueous paste.

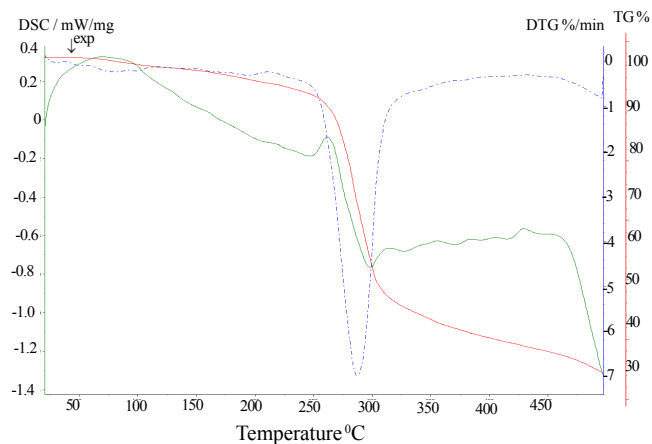


Figure 5. The thermal decomposition of the κ -carrageenan- $\text{Co}(\text{NO}_3)_2$ complex.

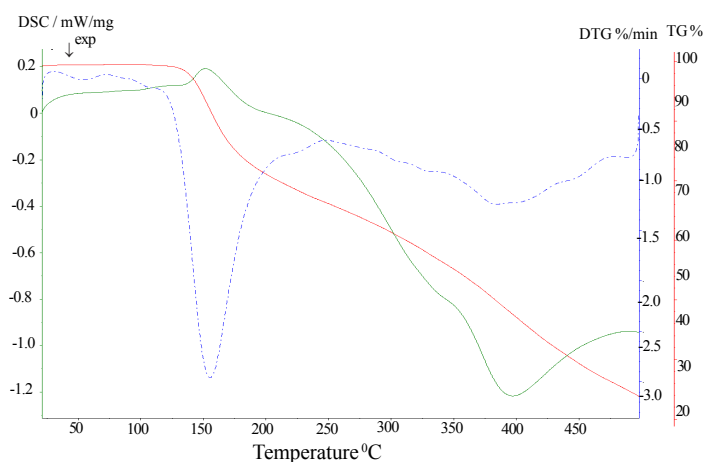


Figure 3. The thermal decomposition of the κ -carrageenan- NiCl_2 complex.

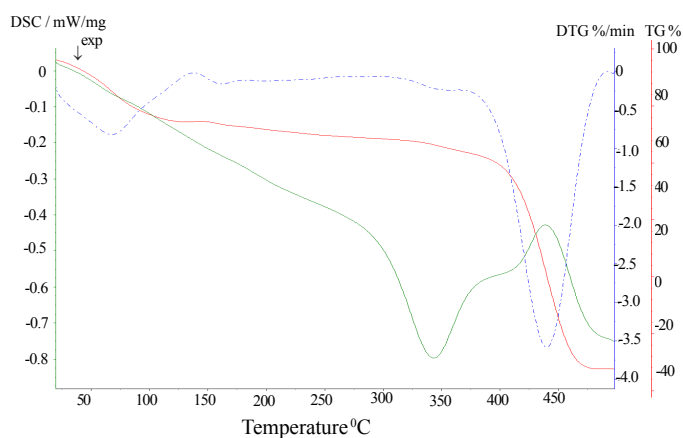


Figure 6. The thermal decomposition of the κ -carrageenan- $\text{Ni}(\text{NO}_3)_2$ complex.

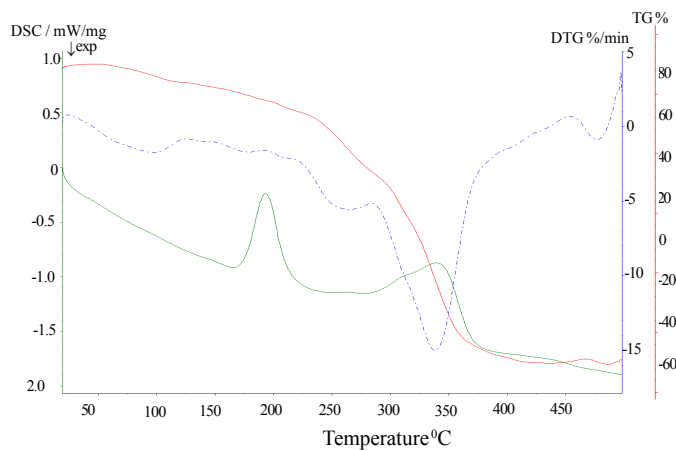


Figure 7. The thermal decomposition of the κ -carrageenan-MnCl₂ complex.

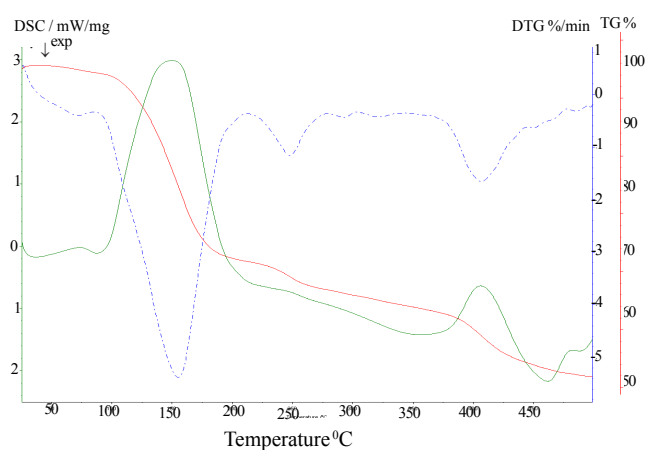


Figure 10. The thermal decomposition of the κ -carrageenan-Cu(NO₃)₂ complex

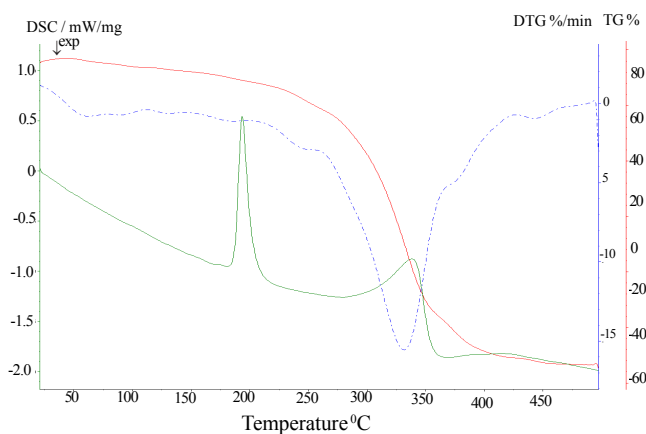


Figure 8. The thermal decomposition of the κ -carrageenan-Mn(OCOCH₃)₂ complex.

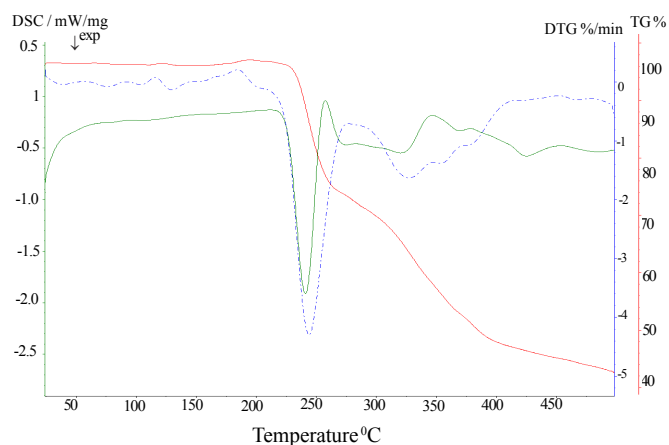


Figure 11. The thermal decomposition of the κ -carrageenan-CuCl₂ complex.

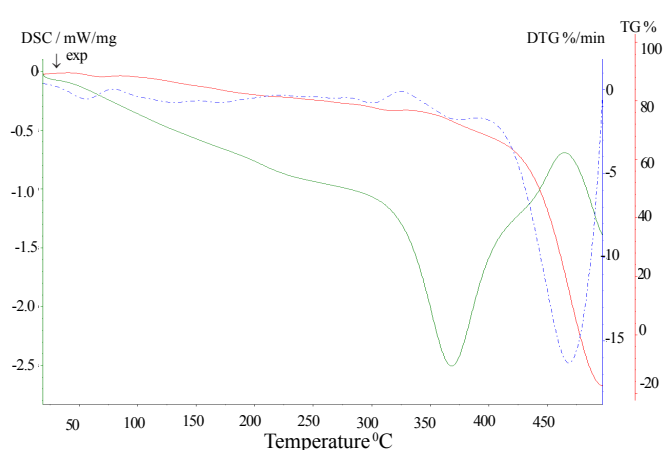


Figure 9. The thermal decomposition of the κ -carrageenan-FeCl₃ complex.

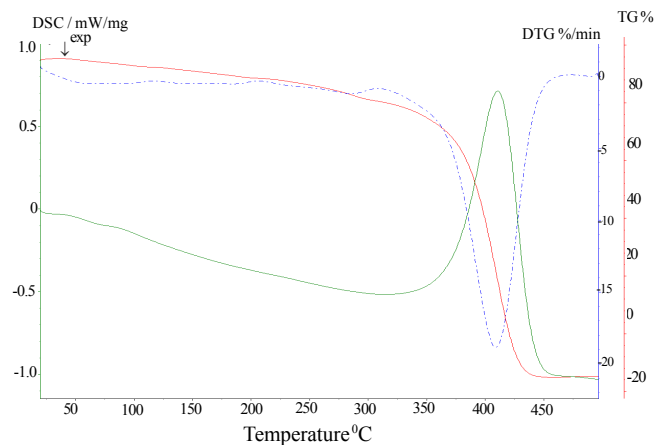


Figure 12. The thermal decomposition of the κ -carrageenan-

Table 4. Thermal studies of κ -carrageenan and its metal complexes.

| Salt | TG | | | DTG ^a | | DSC | |
|-------------------|------------------|------------------------------|--------------|------------------|----------------------|------------|-----------------------|
| | Temp. range [°C] | Weight loss ^b [%] | Slope [tg α] | Complex [°C] | Salt [°C] | Temp. [°C] | ΔH ^c [J/g] |
| None ^d | 25 - 51 | 2 | | | | | |
| | 51 - 119 | 11 | 0,13 | 73 | | 62,4 | +96.2 |
| | | | | | | 74,0 | +85.8 |
| | 119 - 139 | 22 | 0,55 | 128 | | 128,8 | +97.4 |
| | 139 - 171 | 27 | 0,17 | | | | |
| | 171 - 188 | 36 | 0,53 | 176 | | 168,7 | +32.1 |
| | 188 - 220 | 43,5 | 0,23 | 211 | | 11,9 | +19.2 |
| | | | | | | 233,4 | +7.2 |
| | 220 - 354 | 51 | 0,06 | | | 249,5 | +6.9 |
| | 354 - 400 | 57 | 0,13 | 380 | | 382,5 | -374.9 |
| None ^e | 25 - 67 | 0 | | | | | |
| | 67 - 120 | 18 | 0,34 | 100 | | 97,8 | +267.8 |
| | 120 - 137 | 24 | 0,35 | 126 | | | |
| | 137 - 158 | 29 | 0,23 | | | 143,4 | +11.7 |
| | 158 - 162 | 31 | 0,50 | 159 | | 162,2 | +97.2 |
| | 162 - 211 | 37 | 0,12 | | | | |
| | 211 - 224 | 41 | 0,31 | 215 | | 217,5 | +48.5 |
| | 224 - 249 | 45,5 | 0,18 | | | | |
| | 249 - 261 | 64 | 1,54 | 254 | | 257,4 | +176.4 |
| | 261 - 400 | 64 | 0,00 | | | | |
| Cobaltous | | | | | | | |
| Chloride | 25 - 188 | 7,5 | 0,04 | | 107, 148 | 105,1 | +5.6 |
| | 188 - 205 | 8 | 0,05 | | 191 | | |
| | 205 - 249 | 9,5 | 0,03 | | | | |
| | 249 - 275 | 12 | 0,10 | 265 | | | |
| | 275 - 304 | 13 | 0,03 | | | | |
| | 304 - 327 | 17,5 | 0,20 | | | | |
| | 327 - 350 | 28 | 0,46 | | | | |
| | 350 - 400 | 67 | 1,02 | 365 | | 365,9 | +107.4 |
| Nitrate | 25 - 60 | 0 | | | | | |
| | 60 - 125 | 9 | 0,14 | 82 | | 82,9 | +89.4 |
| | 125 - 257 | 9 | 0,00 | | 130, 160, 210, 225 | | |
| | 257 - 287 | 47 | 1,27 | 273 | 248 | 237,2 | +61.1 |
| | 287 - 340 | 60,5 | 0,25 | | 288 | 336,2 | -48.1 |
| | 340 - 400 | 72 | 0,19 | | | | |
| Acetate | 25 - 150 | 0 | 0,00 | | 129 | | |
| | 150 - 340 | 5,5 | 0,03 | | 190, 273, 332 | | |
| | 340 - 370 | 7,5 | 0,07 | | | 368,7 | -407.2 |
| | 370 - 439 | 14,5 | 0,10 | 382 | | | |
| | 439 - 500 | 55 | 0,83 | 465 | | 463,0 | +117.2 |
| Cupric | | | | | | | |
| Chloride | 25 - 230 | 0 | 0,00 | | 117 | | |
| | 230 - 255 | 21,5 | 0,86 | 244 | | 240,8 | +206.4 |
| | 255 - 311 | 30,5 | 0,16 | | | 274,5 | -19.6 |
| | 311 - 352 | 45 | 0,35 | 327 | | 320,1 | -28.6 |
| | 352 - 381 | 50 | 0,17 | 353 | | 369,2 | -12.6 |
| | 381 - 400 | 53,5 | 0,18 | | | | |
| | Nitrate | 25 - 60 | 0 | | | | |
| 60 - 110 | | 2,5 | 0,05 | 75 | | 74,7 | +12.4 |
| 110 - 135 | | 8,5 | 0,24 | | | | |
| 135 - 177 | | 30 | 0,51 | 156 | 150sh | 142,9 | +272.1 |
| | | | | | | 153,3 | +318.4 |
| 177 - 237 | | 32 | 0,03 | | 179 | | |
| 237 - 260 | | 34,5 | 0,11 | 248 | 249, 259 | 244,5 | +8.7 |
| 260 - 388 | | 40 | 0,04 | 300 | | 36,2 | +11.6 |
| 388 - 400 | | 42 | 0,16 | | | 81,0 | +8.2 |
| Acetate | | 25 - 50 | 0 | | 58 | | |
| | 50 - 255 | 10 | 0,05 | | 152 | | |
| | 255 - 296 | 12 | 0,06 | 287 | 274 | | |
| | 296 - 383 | 15,5 | 0,05 | | | 412,8 | +126.4 |
| | 383 - 428 | 61,5 | 1,02 | 409 | | | |
| | | | | | | | |
| Ferric | | | | | | | |
| Chloride | 25 - 50 | 0 | | | | | |
| | 50 - 106 | 5 | 0,06 | 60 | | | |
| | 106 - 175 | 8 | 0,04 | | | | |
| | 175 - 300 | 10 | 0,02 | | 200 | | |
| | 300 - 308 | 11 | 0,13 | 308 | | | |
| | 308 - 337 | 11 | 0,00 | | | | |
| | 337 - 360 | 12,5 | 0,07 | | | | |
| | 360 - 386 | 14,5 | 0,08 | 374 | | 368,2 | -902.6 |

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