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Structure formation in liquid solutions and gels of polysaccharides A review of the authors work[☆]

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Abstract

Structure formation in solutions of polysaccharides proceeds through multistage associations of macromolecules that lead in many cases to micro heterogeneous structure of semi-dilute liquid solutions as well as thermotropic gels. Along with hydrogen bonds and hydrophobic interactions, intermacromolecular coordination bonds of metal ions can be of crucial importance in the formation of gel networks. © 1998 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Polysaccharides play a substantial role in food systems, in particular as structure-forming agents. By the investigations of the behaviour of polysaccharides in solutions the emphasis is on their conformational helix-coil transitions as well as interactions with metal ions. Less attention is paid to association processes in solution. In this paper some examples of polymer–polymer interactions in dilute as well as semi-dilute and concentrated solutions will be given, which contribute, to the structure formation of solutions, including their gelation.

2. Dilute solutions

Polysaccharides, especially semi-rigid ones, such as pectic substances, have extended conformations in solution. Their macromolecules bear various polar and non-polar groups, and also in the backbone there are fragmented differing in their polarity and, thus affinity to water. These features predetermine the tendency of pectic substances to form associations in solutions. This is typical of polysaccharide solutions (Schmidt & Burchard, 1985).

In Table 1 there are shown elastic light scattering data of a series of pectic substances produced by the methylation of sodium pectate with diazomethane. This procedure precludes chain degradation. Experimental methods and calculation procedures are described in Plashchina, Semenova, Braudo, and Tolstoguzov (1985). It is seen that the increase in the degree of esterification leads to the growth of the mass of solute particles, i.e. to the increase in the degree of association.[1] At the same time the radius of gyration remains constant and the second virial coefficient, although decreases slightly, does not become less than $10^{-3}\,\mathrm{mol\,m^3\,kg^{-2}}$. These results show that pectinate macromolecules align parallel forming associations which retain high affinity to the solvent. The last feature likens these associations to micelles of surface-active substances. It is also evident that methoxyl groups play an important role in the formation of associations. However, the nature of this effect is not clear yet.

It is natural to suggest that there are hydrophobic interactions of methoxyl groups that results in the formation of associations of pectinate macromolecules. Characteristic features of hydrophobic interactions are non-monotonous dependence of the excess chemical potential of the solvent on temperature and a negative value of the partial molar heat capacity of the solvent. These characteristics are determined according to the following equations:

$$\Delta\mu_1^E = -\mathrm{RT}A_2V_1c_2^2,$$

[☆] Dedicated to the memory of Professor S. A. Glikman who contributed significantly to the understanding of association phenomena in polymer solutions and the nature of polysaccharide solutions and gels.

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[1] These values differ from published earlier (Plashchina et al., 1985). They are obtained through the recalculation of the experimental data presented there.

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Table 1
Characteristics of solute particles of pectic substances at 25°C (data of light-scattering)

Degree of esterification (%)	M_w (kD)	Second virial coefficient and its components (10^{-3} mol m^3 kg^{-2})			$[< R_\rho^2 >_z^{1/2}]^b$(nm)
		A_2	Coulombic component[a]	Excluded volume component	
0	150	11.0	1.1	9.9	64
14	140	3.6	0.8	2.8	60
58	260	1.3	0.0	1.3	71
69	290	1.4	0.0	1.4	80
78	420	3.1	0.0	3.1	—
95	500	1.6	0.0	1.6	61

Solvent—0.09 M NaCl + 0.01 M NaF.

[a] Method of calculation (cf. Plashchina et al., 1985).

[b] Corrected taking into account non-linearity of the reversed Debye scattering function (Plashchina et al., 1985).

where $\Delta\mu_1^E$ is the excess chemical potential of the solvent, A_2 is the second virial coefficient of the solvent, V_1 is the partial molar volume of the solvent and c_2 is the polymer concentration, kg m^{-3};

$$(\Delta C_p)_1 = \delta(\Delta H_1)/\delta T$$

$$\Delta H_1 = -\mathrm{RT} A_{2H} V_1 c_2^2$$

$$A_{2H} = -T[\alpha_1^* A_2 - (\delta A_2/\delta T)].$$

Here $(\Delta C_p)_1$ is the partial molar heat capacity of the solvent, ΔH_1 is the partial molar enthalpy of the solvent, A_{2H} is the enthalpic component of the second virial coefficient, α_1^* is the temperature expansion coefficient of the solvent ($257.05\ 10^{-6}$ K^{-1} at 298 K) (Schulz, Inagaki, & Kirata, 1960; Comper & Laurent, 1978).

As is seen in Fig. 1, the excess chemical potential of the solvent in solutions of a high-esterified pectinate increases linearly in the temperature range from 10 to 60°C and the partial molar heat capacity is positive, being as small as less than 7.10^{-6} J mol^{-1} grad^{-1}. However, investigations over a greater temperature range are necessary to conclusively establish the contribution of hydrophobic interactions into the association of pectic substances in solution.

The formation of micelle-like associations in dilute solutions is characteristic also of an amphiphylic microbial exocellular polysaccharide—ethapolan or simusan, produced by *Acenitobacter* sp. (Braudo, Danilenko, An, & Antonov, 1996a). Macromolecules of this polysaccharide contain hydrophobic acyl groups C_{12}–C_{18}. Measurements of elastic light scattering showed (Braudo, Danilenko, & Vetrov, 1996b) that ethapolan forms in 0.01 M NaCl uniform associations which contain 10 parallel aligned macromolecules. These associations are characterized by the extremely high chain stiffness, the value of Kuhn segment being about 430 nm. Despite of the occurrence of hydrophobic groups in macromolecules, solutions of ethapolan show only faint surface activity, that may point to the tight packing of hydrophobic groups in the interior of associations. The second virial coefficient of ethapolan solutions is as low as $< 10^{-4}$ mol m^3 kg^{-2}, and solutions of ethapolan in 0.01 M MaCl are unstable due to the further aggregation of solute particles. A characteristic property of ethapolan solutions is also the high cooperativity of an endothermic, presumably, conformational transition, which occurs by the heating (Braudo et al., 1996a). The removal of hydrophobic groups through hydrolysis results in the dissociation of micelle-like solute particles, the lowering of the temperature and the cooperativity of the endothermic transition and the decrease of the rate of falling out of insoluable aggregates.

3. Semi-dilute solutions

The transition from dilute to semi-dilute solutions of polyuronides is accompanied by the formation of associations presumably of a higher hierarchial level. It is evident from the concentration dependences of an intensive property of solutions namely relative activity coefficients of counter-ions[2] (Yuryev, Plashchina, Braudo, & Tolstoguzov, 1981). It is seen from the Figs. 2 and 3 that by the increase in the concentration of a polyuronide relative activity coefficients of counter-ions reach constant values. It was shown by the measurements of viscosity (Yuryev et al., 1981) that the attainment of the constant value of the relative activity coefficient corresponds to the crossover, i.e. the transition from a dilute to semi-dilute solution.

The constant values of the relative activity coefficients evidence for micro heterogeneous structure of the solution. Well-known examples are micellar solutions of surface-active substances. In such systems the enhancement of

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[2] Relative activity coefficient of a counter-ion is the ratio of its activity coefficients in the polyelectrolyte solution and the solution of a low-molecular mass salt, usually chloride, with the same equivalent concentration, this value reflects the contribution of the polymer nature of the polyion into the activity coefficient of the counter-ion.

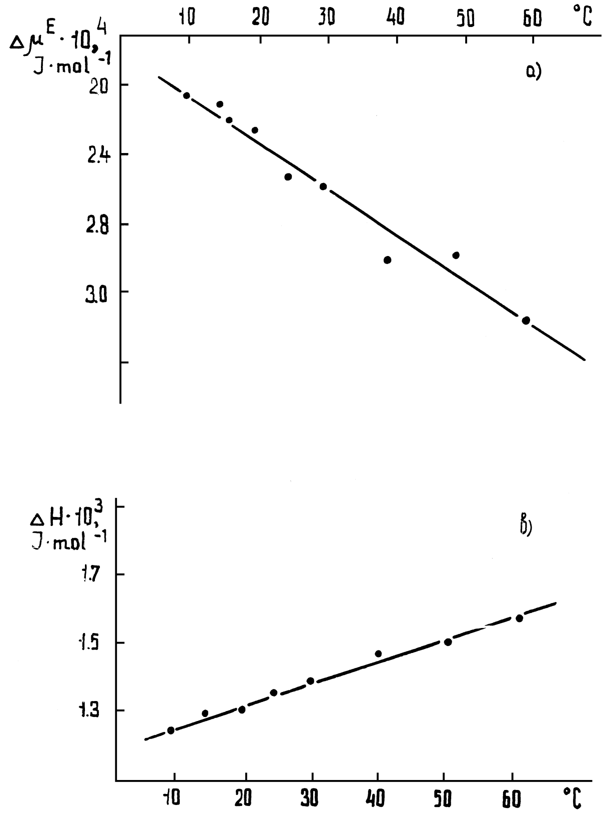

Fig. 1. Temperature dependences of the excess chemical potential (a) and the partial molar enthalpy (b) of the solvent in solutions of a high-esterified pectinate (unpublished). Degree of esterification—76%; 0.1 M NaCl; pH 7.0.

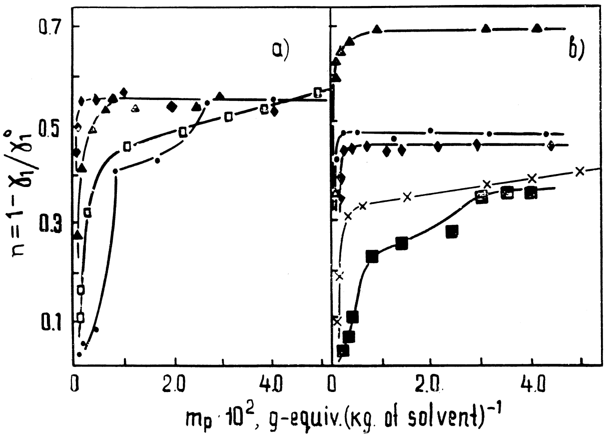

Fig. 2. Concentration dependences of the relative activity coefficients of counter-ions (γ_1/γ_1^0) in aqueous solutions of sodium salts of polyuronic acids (Yuryev et al., 1981). (a) Sodium alginates: ●, A1 (content of blocks of residues of α-L-guluronic acid (GG)-20%, blocks of residues of β-D-mannuronic acid (MM)-30%, blocks of mixed composition (MG)-50%); ▲, A2 (GG-30%, MM-33%, MG-37%); ◆, A3 (GG-47%, MM-33%, MG-20%); □, A1 + 8 M urea. (b) Sodium pectinates: degree of esterification, %; ●, 0 (pectate); ◆, 14: ■, 58; ▲, 78; χ, pectate + 8 M urea.

the concentration leads to the increase in the number of solute particles, whereas the structure of the particles, in particular the surrounding of counter-ions, does not change.

This may be also characteristic of interactions between polyuronides and polyvalent metal ions. Thus, the binding isotherm of Ca^{2+} ions with sodium pectate does not change by varying the concentration of the polyuronide in the range 1–6 mg-equiv l^{-1} (Braudo, Soshinsky, Yuryev, & Tolstoguzov, 1992).

Some characteristics of micro heterogeneous semi-dilute solutions of polyuronides (constant activity coefficients of components with the concentration of solute; thermodynamic stability of solutions) liken them to ideal organized solutions, as they are defined by Shinoda (1996).

In the presence of 8 M urea the relative activity coefficient of counter-ions changes over the, whole range of concentrations studied (Fig. 2). Apparently urea weakens polymer–polymer contacts and results in the loss of micro heterogeneous structure of the solution.

It is also seen in Figs. 2 and 3 that the relative activity coefficient of counter-ions in semi-dilute solutions of alginates is independent of the monomer composition. On the other hand, for pectic substances this parameter changes non-monotonously with the degree of esterification, the minimal value corresponding to the pectinate with the degree of esterification 58%. As is seen in Table 2, similar dependence was established for the thermodynamic chain rigidity of pectinates, the sample with the degree of esterification 58% being characterized by the maximal chain flexibility (Yuryev et al., 1981). It is obvious that in both cases we observe a manifestation of the competition between various kinds of interactions typical of either low- or high- esterified pectinates.

Chain rigidity of pectate and low-esterified pectinates appears to be determined by coulombic interactions between negatively charged carboxylate groups. Depending on the mixing entropy of counter-ions, these interactions can lead either to mutual attraction of like charged groups of a polyelectrolyte, if counter-ions are arranged in the vicinity of the polyion (cf. Ise, 1986), or their repulsion, if counter-ions go away into the solvent. The high values of relative activity coefficients of counter-ions may point to the prevailing repulsive interactions between monomer units in aqueous solutions of polyuronides.

As to the nature of interactions which operate in high-esterified pectinates, we suggest the great contribution of intramolecular hydrogen bonds formed by carbonyl oxygens belonging to ester groups (Plashchina, Semenova, Slovokhotov, Yu, Struchkov, Yu, Braudo, & Tolstoguzov, 1986b).

Similar to chain rigidity, some characteristics of pectinate-based gel-forming systems depend extremely on the degree of esterification of the pectinate (Fig. 4). Also in this case the competition between various kinds of interactions is manifested. Thus, the degree of esterification

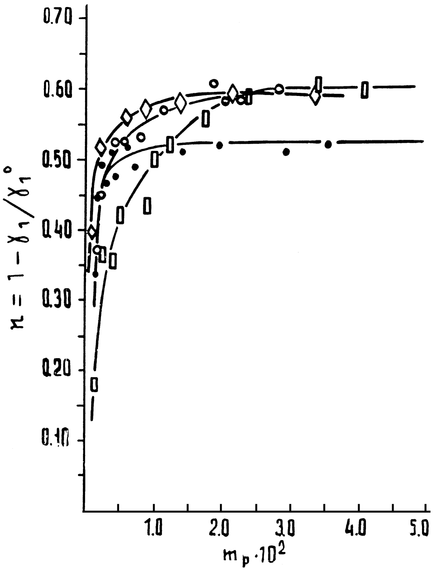

Fig. 3. Concentration dependences of the relative activity coefficients of counter-ions (γ_1/γ_1^0) in aqueous solutions of potassium salts of polyuronic acids (unpublished). (a) Potassium alginates; ○, A1; ◇, A3. (b) Potassium pectinates: degree of esterification, %; ●, (pectate); □, 58.

Table 2
Concentration range corresponding to the transition from limit-diluted to semi-diluted, microheterogeneous aqueous solutions of sodium salts of polyuronides

Polyuronide	$\Delta\gamma_1$	m_p'	m_p''	Δm_p
Alginate[a]				
A1	0.29	0.25	2.75	2.50
A2	0.20	0.20	0.80	0.60
A3	0.12	0.05	0.15	0.10
Pectic substance. Degree of esterification (%):				
0	0.23	0.12	0.18	0.06
14	0.25	0.17	0.25	0.08
58	0.41	0.30	3.10	2.80
78	0.02	0.05	0.90	0.85

Notations:

$\Delta\gamma_1$—parameter which correlates with the thermodynamic chain flexibility (Yuryev et al., 1981).

m_p'—polymer concentration which corresponds to the limit-diluted solution (Yuryev et al., 1981), 10^{-2} g-equiv. (kg of solvent)$^{-1}$.

m_p''–minimal polymer concentration which corresponds to the micro heterogeneous solution, 10^{-2} g-equiv. (kg of solvent)$^{-1}$.

$\Delta m_p = m_p'' - m_p'$.

[a] Composition of the alginates (cf. Fig. 1).

ca. 50% corresponds to the minimal degree of association of macromolecules in solution, the minimal rate of gelation and the maximal elasticity modulus of gels. The two latter characteristics are favourable for the use of pectinates as gel-forming agents in the production of fruit jellies. The high elasticity modulus evidently stems from the low-grain structure of pectinate gels. In this regard the analogy with hardened steel can be drawn.

The difference between the concentrations which correspond to the limit-dilute solution (Yuryev et al., 1981), on the one hand, and the point of attainment of the constant value of relative activity coefficient, on the other hand, characterizes the transition range from dilute to semi-dilute, micro heterogeneous solutions of polyuronides. This range depends on the thermodynamic chain rigidity of a polyelectrolyte. For a series of polyelectrolytes with the same kind of prevailing interactions (alginates of different monomer composition, high-charged pectic substances) the transition becomes more abrupt by the increase in the chain rigidity (Table 2). The thermodynamics of small systems applied to micelle formation predicts the decrease of the abruptness of the transition by the reduction of the degree of association (Hall & Pethica, 1967).

4. Associations in gels

The micro heterogeneous structure, which manifests itself in the independence of intensive properties on concentration, occurs also in concentrated solutions, such as thermotropic gels of polysaccharides: rate of mechanical relaxation in these gels does not depend on concentration (Braudo, Plashchina, Tolstoguzov, 1984; Braudo & Plashchina, 1995). It holds both for hydrogels of sulfated galactans and gels of high-esterified pectinates in mixtures of water with sucrose or glycerine. Processes of mechanical relaxation in these gels appear to be localized in associations of macromolecules, which form the gel network (Braudo et al., 1984). Gels of agarose in a 1:1 mixture of 0.75 M aqueous solution of KCl and dimethyl sulfoxide are not fully micro heterogeneous: the rate of mechanical relaxation in these gels depends on the concentration (Braudo & Plashchina, 1995). Apparently, the addition of dimethyl sulfoxide to water increases the solubility of agarose. This manifests also in the transparency of gels.

Under conditions of thermotropic gelation additional association in solution can occur leading to the formation of structural elements of the next hierarchial levels. It is, in particular, characteristic of high-esterified pectinates. They form gels in acid media, in the presence of so-called dehydrating agents. Thus, the addition of glycerine to a solution of high-esterified pectinate and especially the subsequent acidification of the solution leads to the appearance of hysteresis of temperature dependence of the elipticity corresponding to the Cotton effects of carboxyl groups (Fig. 5). Similar results for solutions of high-esterified pectinate in a mixture of water with ethylene glycol are obtained by Morris et al. (Morris, Gidley, Murray, Powell, & Rees, 1980; Thom, Dea, Morris, & Powell, 1982). According to these authors, the jump of the elipticity by cooling can reflect the decrease of the rotational mobility of carboxyl

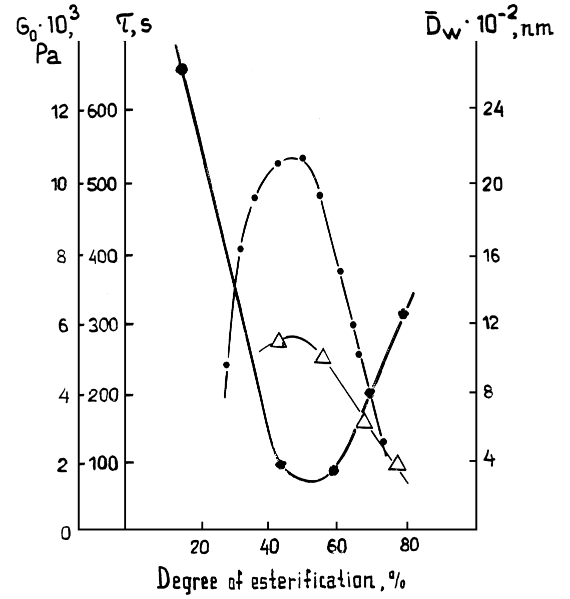

Fig. 4. Dependences of characteristics of gelling systems on the degree of esterification of pectinate (unpublished). Polymer concentration—1.0%; solvent–mixture 1:1 of water and glycerine; pH 2.0; 25°C. ○, diameter of equivalent sphere of scattering centers (D_w), nm, determined by the method of spectroturbidimetry (Heller, Bhatnagar, Nakagaki, 1962). ●, gelation time (τ), *s*, determined according to Janus, Tabor, and Darlow, (1965); Δ, conventionally instantaneous shift modulus (G_0), Pa, determined according to Plashchina, Fomina, Braudo, & Tolstoguzov, 1979.

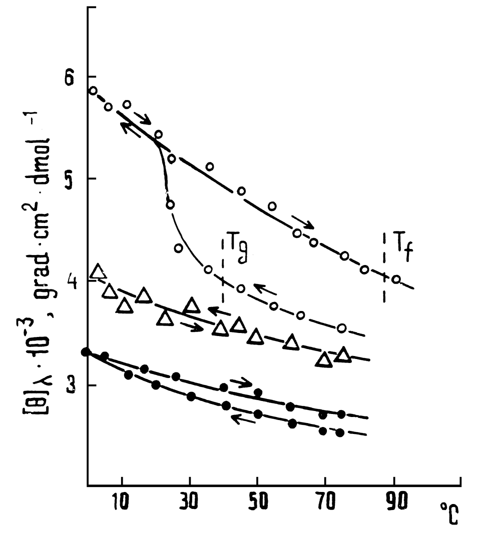

Fig. 5. Temperature dependence of molar ellipticity of a high-esterified pectinate (unpublished). Degree of esterification—58%; polymer concentration—0.5%; rates of heating and cooling—0.3 grad min^{-1}. Solvent: △, water, pH 2.5; ●, mixture 1:1 of water and glycerine, pH 7.5; ○, mixture 1:1 of water and glycerine, pH 2.5. T_g—temperature of gelation; T_g—temperature of gel fusion.

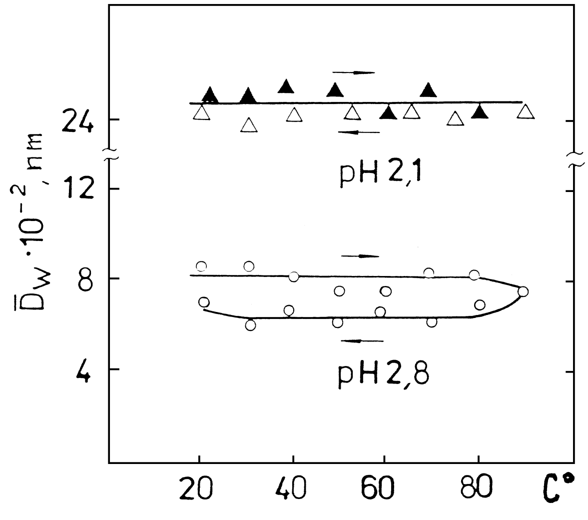

Fig. 6. Temperature dependence of the diameter of equivalent sphere of scattering centers in gels of a high-esterified pectinate (unpublished). Degree of esterification—58%; polymer concentration—1.0%; solvent—mixture 1:1 of water and glycerine; rate of heating—0.3 grad min^{-1}; cooling at the air at 22°C. Determined by the method of spectroturbidimetry (Heller et al., 1962).

chromophores due to the formation of associations. Such associations withstand subsequent heating up to 80–90°C (Figs. 5 and 6).

So, we distinguish three levels of associations in solutions of polyuronides (1) micelle-like associations in dilute solutions, (2) associations, which give rise to the micro heterogeneous structure of semi-dilute solutions, and (3) associations, which are formed in concentrated liquid solutions under the conditions of thermotropic gelation.

It should be noted that the formation of associations does not necessary lead to gelation. Thus, similar jumps on the temperature dependences of the elipticity were observed in the case of both gel-forming pectinates and completely esterified pectinate, which does not gel (Fig. 7). Moreover, the formation of gel network hinders the growth of associations. Thus, spectroturbidimetric measurements showed that the dimensions of associations of the high-esterified pectinate diminish as the system passes the gelation threshold (Fig. 8).

The formation of associations in liquid polymer solutions under conditions, which correspond to thermotropic gelation, is a general phenomenon, known since the beginning the century (Zhigmondi, 1905, 1914; Arisz, 1915; Backmann, 1912; Menz, 1909; Moore & Roaf, 1907). Both the formation of associations in liquid polymer solutions and their linking together to form the network of a thermoreversible gel originate from the deterioration of the thermodynamic quality of the solvent, which favours the formation of polymer–polymer contacts in expense of contacts polymer–solvent. However, the formation of the gel network can impose limitations for the growth of associations. We suggest that such limitations cause the lack of optically detectable inhomogeneities in some concentrated thermoreversible gels (Pines & Prins, 1973).

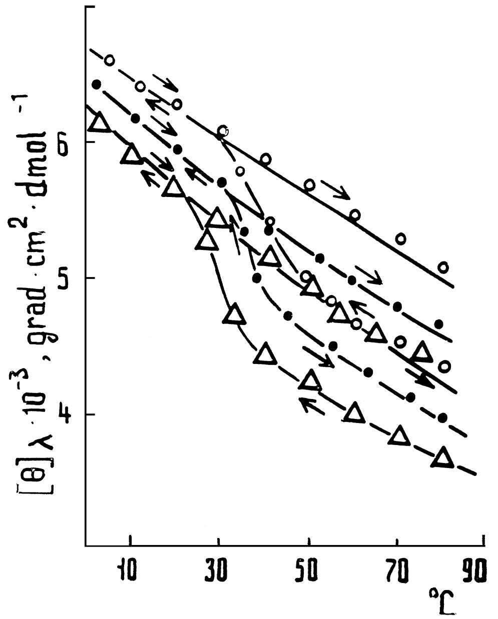

Fig. 7. Temperature dependence of molar ellipticity of high-esterified pectinates (unpublished). Polymer concentration—0.5%; solvent—mixture 1:1 of water and glycerine, pH 2.5; rates of heating and cooling—0.3 grad min^{-1}. Degree of esterification: Δ, 69%; ●, 78%; ○, 95%.

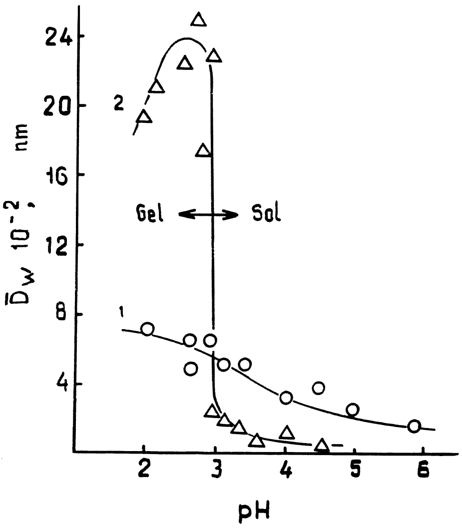

Fig. 8. pH-dependence of the diameter of equivalent sphere of scattering centers in solutions of a high-esterified pectinate (unpublished). Degree of esterification—58%; polymer concentration—1.0%; 25°C. Solvent: ○, water; Δ, mixture 1.1 of water and glycerine. Determined by the method of spectroturbidimetry (Heller et al., 1962).

5. Interactions at thermotropic gelation

Mechanisms of thermotropic gelation of polysaccharides are still a matter of discussions. Thus, the dominating conceptions proceed from the postulate that for helix-forming polysaccharides the conformational transition is a prerequisite and a first step of the formation of the gel network (Morris, 1979; Morris, Rees, & Robinson, 1980; Morris & Norton, 1983; Picule, Nilsson, Viebke, & Wei Zhang, 1993; Rees, 1969, 1981; Rees, Morris, Thom, & Madden, 1982; Rees & Welsh, 1977; Robinson, Morris, & Rees, 1980; Smidsrød, 1980; Smidsrød, Andresen, Grasdalen, Larsen, & Painter, 1980; Smidsrød & Grasdalen, 1982). This idea is attractive because it allows reconstruction of events, which originate from the deterioration of the thermodynamic quality of the solvent. It also coincides with general ideas about the nature of physical gels formed by flexible-chain polymers. Thus, according to Flory (1974), only cooperatively formed domains of interchain bonds, such as crystallites or multistrand helical segments, can provide the stability of gel networks formed by relatively weak, fluctuating bonds, such as hydrogen bonds.

We showed (Braudo, 1992; Braudo, Muratalieva, Plashchina, & Tolstoguzov, 1991a; Plashchina, Muratalieva, Braudo, & Tolstoguzov, 1986a) that the processes of gelation and helix formation of galactans, namely κ-carrageenan and agarose, proceed independently, both being the consequences of the deterioration of the thermodynamic quality of the solvent. Depending on the chemical structure of a polysaccharide and conditions of the process, gelation can both precede or coincide with helix-formation. If the gel network is formed by macromolecules in a disordered conformation, the formation of a great number of local interchain contacts is necessary to bind the macromolecules into a network. The fluctuating nature of these contacts is evident from the fact that the conformational transition of κ-carrageenan or agarose is not accompanied by drastic changes in properties of gels. Moreover, it is seen from Figs. 9 and 10 that the changes in optical rotation by the heating of gels proceed even in more narrow temperature ranges than the changes in the elasticity modulus.

The nature of secondary bonds, which connect macromolecules of polysaccharides into a gel network, can be revealed using the analysis of effects of additives. Regretfully, it is impossible to find an absolutely selective additive. Thus, urea in high concentrations suppresses both hydrogen bonding and hydrophobic interactions. Therefore only comparative investigations of effects of various additives can be informative.

It is seen in Fig. 11 that urea depresses the temperature of gelation and onset of the coil-helix transition of agarose in the a 1:1 mixture of 0.75 M KCI with dimethyl sulfoxide, as well as the temperature of agarose gelation in 0.75 M KCl. At the same time non-ionogenic surfants, differing in chemical structure (polyoxyethylene (Zhigmondi, 1905) sorbitan monolaurate–Tween-80, and a block copolymer of ethylene oxide and propylene oxide—Proxanol-305) do not effect gelation of agarose in 0.75 M KCl.) These results show that hydrogen bonding, not hydrophobic interactions, governs the formation of gel network of agarose.

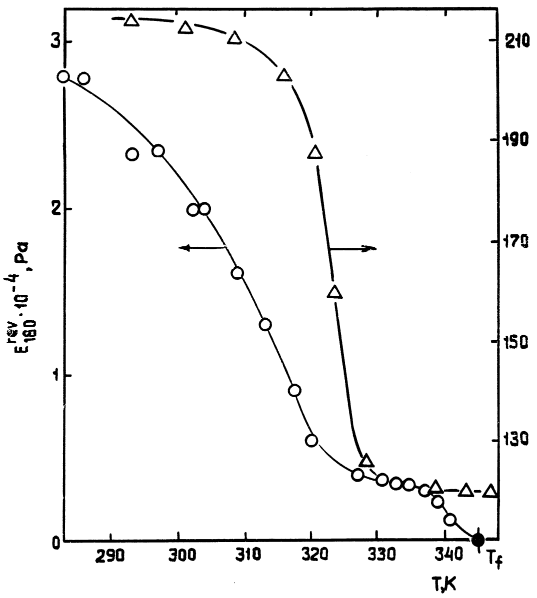

Fig. 9. Temperature dependences of Young modulus corresponding to the reversible deformation after 3 h loading and specific optical rotation of a 1.5% gel of Na-form of κ-carrageenan in 0.11 M KCl (Rees & Welsh, 1977). Rate of heating–0.3 grad min^{-1}. T_f—temperature of gel fusion.

Hydrogen bonding appears also to contribute to thermotropic gelation of high esterified pectinate. It is suggested (Pashchina et al., 1986) that pectinate macromolecules are crosslinked through hydrogen bonds formed by molecules of so-called dehydrating agents, such as sucrose or glycerine. These bonds are developed between carbonyl oxygen atoms of ester groups in pectinate macromolecules and hydrogen atoms belonging to relatively acidic hydroxyl groups of molecules of dehydrating agents.

For the gelation of a sulfated galactan–κ-carrageenan, hydrogen bonding plays only a minor role and hydrophobic interactions are of no importance (Fig. 12). Thus, both the gel network and helical conformation can develop even in 8 M urea.

There are interactions with some cations, such as K$^+$ions, which govern the gelation and helix-formation of κ-carrageenan. Both the gelation temperature and the temperature of the midpoint of the coil-helix transition raise linearly with the logarithm of the concentration of K$^+$ ions but the temperature of gelation increases faster than the temperature of the conformational transition (Fig. 13). Different effects of the concentration of K$^+$ ions on gelation and helix formation suggest that these processes are controlled by different kinds of interactions.

We showed that K$^+$ ions form contact ion pairs with sulfate groups of κ-carrageenan independent of the conformational state of macromolecules (Braudo, Muratalieva, Plashchina, Tolstoguzov, & Markovich, 1991b). It is suggested that the cooling of κ-carrageenan solutions is accompanied by the increase in the number of contact ion pairs, which, in its turn, triggers the gelation. The capability of K$^+$ ions to form contact ion pairs with sulfate groups seems to be also the cause of the stabilizing action of these ions on the helical conformation of κ-carrageenan. The relatively high affinity of K$^+$ ions as well as other high-polarizable, low-solvated alkali metal ions to sulfate groups, the both being ‘weak-field’ ions, meets the conception of hard and soft acids and bases.

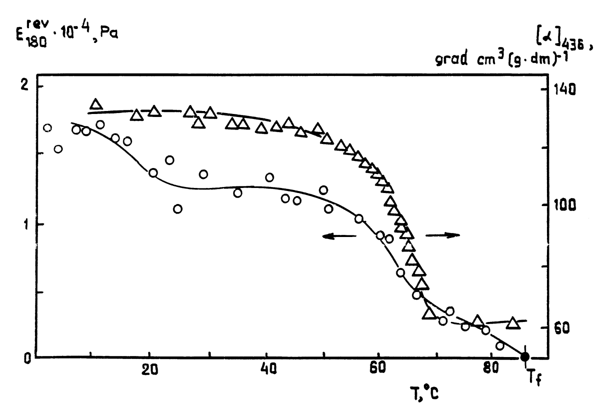

Fig. 10. Temperature dependences of Young modulus corresponding to the reversible deformation after 3 h loading and specific optical rotation of a 1% gel of agarose in the mixture 1:1 of 0.75 M KCl and dimethyl sulfoxide (Morris, 1979). Rate of heating—0.3 grad min^{-1}. T_f—temperature of gel fusion.

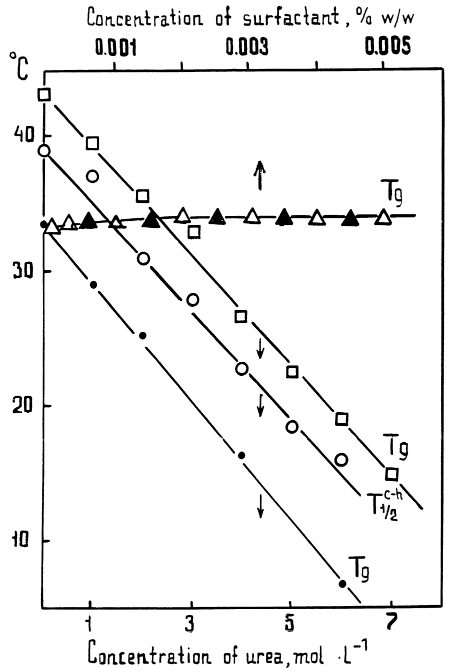

Fig. 11. Dependences of characteristics of 1% agarose solutions on the concentration of an additive (according to Morris, Rees, & Robinson, 1980). Rate of cooling—0.3 grad min^{-1}. $T_{1/2}{}^{c-h}$—the midpoint temperature of the coil-helix transition; T_g—temperature of gelation. Solvent: □, and ○, mixture 1:1 of 0.75 M KCl and dimethyl sulfoxide; ●, △ and ▲, 0.75 M KCl. Additive: □, ○ and ● urea; △, Tween-80; ▲, Proxanol-305.

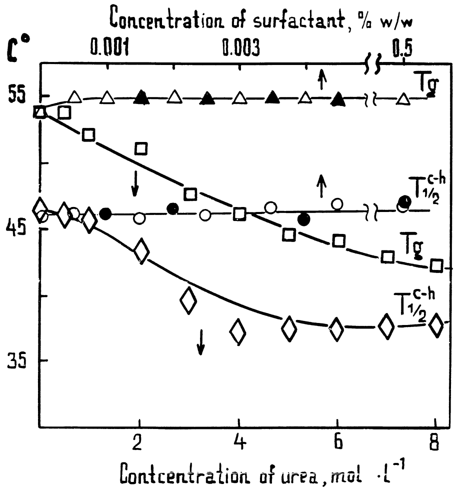

Fig. 12. Dependences of characteristics of 1.5% solution of K-form of κ-carrageenan in 0.11 M KCl on the concentration of an additive (Bzeudo et al., 1991). Rate of cooling—0.3 grad min^{-1}. $T_{1/2}^{c-h}$—the midpoint temperature of the coil-helix transition; T_g—temperature of gelation. Additive: □, and ◇, urea; ○, and △,Tween-80; ●, and ▲, Proxanol-305.

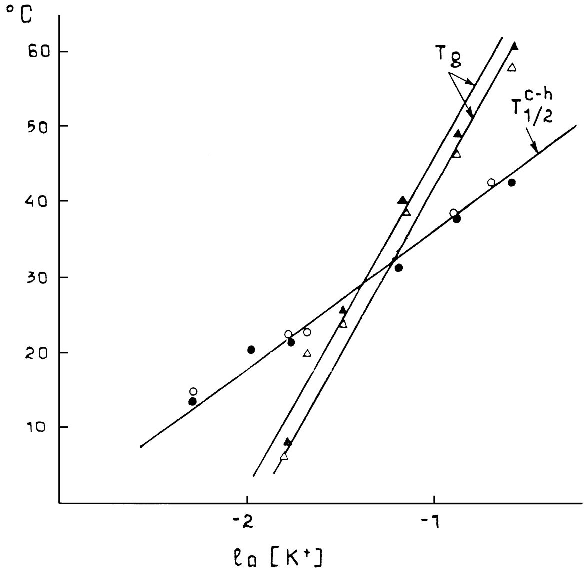

Fig. 13. Dependences of characteristics of Na-form of κ-carrageenan in KCl solutions on the concentration of K^+ ions (Plashchina et al., 1986a). Rate of cooling—0.3 grad min^{-1}. $T_{1/2}^{c-h}$—the midpoint temperature of the coil-helix transition; T_g-temperature of gelation. Concentration of polymer: ○, and △ 1.25%, and ●, and ▲, 2.5%.

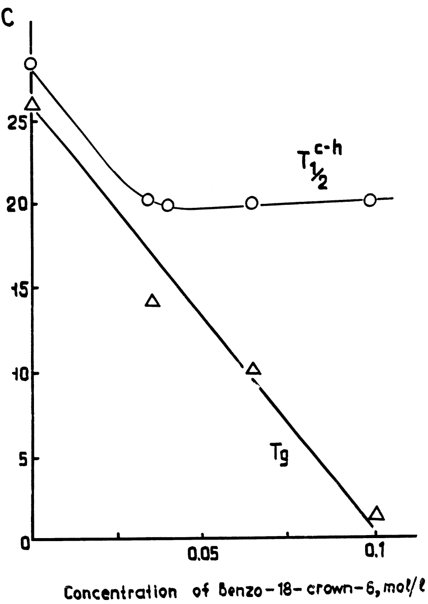

Fig. 14. Dependences of characteristics of aqueous solutions of K-form of κ-carrageenan on the concentration of a crown-ether (Bze-Udo et al., 1991). Rate of cooling—0.3 grad min^{-1}. $T_{1/2}^{c-h}$—the midpoint temperature of the coil-helix transition; T_g—temperature of gelation.

K^+ ions form also coordination, presumably ion-dipole, bonds with macromolecules of κ-carrageenan both in unordered and helical conformations. The density of coordination binding of K^+ ions does not exceed 1.2 ion per a disaccharide unit (Grinberg, Plashchina, Braudo, & Tolstaguzov, 1980; Plashchina, et al., 1986a; Yuryev, Blumenfield, Braudo, Tolstoguzov, 1991).

To reveal the structure-forming effect of coordination interactions between K^+ ions and κ-carrageenan, additions of crown-ethers were used. Crown-ethers saturate the coordination sphere of the cation, but preserve its charge. As is seen in Fig. 14, the addition of benzo-18-crown-6 results in the complete suppression of gelation of κ-carrageenan, whilst only a relatively slight decrease of the temperature of the conformational transition occurs. These data show that intermolecular coordination bonding of K^+ ions with κ-carrageenan provides the formation of its gel network.

The fact that the complex formation of K^+ ions with a crown-ether does not lead to the loss of their capacity to promote the helix-formation of κ-carrageenan proves that this effect originates from the charge shielding of sulfate groups by K^+ ions, both free and complexed with the crown-ether.

The peculiarities of the gelation of κ-carrageenan show that there is no distinct line between thermotropic and ionotropic gelation of charged polysaccharides.

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