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Thermodynamic considerations on polysaccharide functions. Polysaccharides came first

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Abstract

The molecular evolution of polysaccharide functions are considered from the perspectives of structure, thermodynamics and proposed biological values. The main ideas emerging from this thermodynamic approach are the following. First, processing food systems that typically contain denatured non-specifically interacting biopolymers, are a physical chemical model of the primordial soup. Second, polysaccharides were the first biopolymers. They were incompatible with one another and other proto-biopolymers. Third, cross-linking of dissimilar macromolecules would result in conjugates and could explain the parallel co-evolution of proto-biopolymers. Finally, self-reproducing conjugates would cause a phase separation within the primordial soup leading to a concentration of conjugates within dispersed phase particles whose properties could then have evolved into proto-cells. Polysaccharides, due to their incompatibility with proteins, had to be exported from the cytoplasm to form the cell-walls and exopolysaccharide protective capsules around primordial cells. The thermodynamic properties of polysaccharides and their effects on complex biopolymer mixtures became responsible for the ecological defense of cells from foreign macromolecules and their simultaneous nourishment by foreign molecules. This coexistence of protection and consumption of biomolecules by cells corresponds to the dependence of cells on the composition and structure of polysaccharides. The use of starch as a source of energy, and of pectin and cellulose as plant cell wall materials are a logical result of divergence of structure from a common ancestor based on the plagiarism of genetic systems for biopolymer biosynthesis.

Keywords: Biopolymer incompatibility; Conjugates; Non-specific immunity; Alimentary and protective polysaccharide capsules of the cell

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1. Introduction

One of the key scientific questions is why are three biopolymer species necessary? The most widely accepted hypothesis about the origins of life invokes a primordial world of nucleic acids (Gilbert, 1986; Nelson, Levy, & Miller, 2000; Nielsen, 1995; Orgel, 1998a,b). It was first formulated by Crick (1968) and Orgel (1968) and based on experimental discovery by the laboratories of Tom Cech (Kruger et al., 1982) and Sid Altman (Guerrier-Takada, Gardiner, Marsh, Pace, & Altman, 1983). According to this hypothesis, proto-nucleic acids fulfill both informative and catalytic functions to achieve self-reproduction. This hypothesis appears, however, doubtful on thermodynamic terms because of the incompatibility of macromolecules differing in composition and/or structure. The term 'proto-biopolymers' is used here to stress that the biopolymer ancestors would have been heterogeneous with unfolded structure, i.e. similar to modern synthetic polymers. A slight chemical and/or structural difference between macromolecules is, however, sufficient to render them immiscible at the molecular level in a common solvent (Flory, 1953; Tanford, 1961). Since RNA molecules must be probably folded to act as a catalyst but must be unfolded to act as a source of information (Green & Szostak, 1992), it is quite difficult to assume a molecular miscibility and biochemical co-operation of heterogeneous nucleic chains with one another and other macromolecules as co-solutes. The separation of different fractions of proto-nucleic acids and proto-nucleic acids with proto-proteins implies on principle that neither the RNA world, nor the protein world could exist separately or together with one another.

This paper considers the functional role of polysaccharides in the emergence of life and the evolution of their functions using the thermodynamic properties of modern native and denatured biopolymers (Tolstoguzov, 2002a,b, 2003a).

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2. Polysaccharide came the first

Many proto-biopolymer molecules would be necessary for the reproduction of each of them. It is almost impossible therefore to imagine how these molecules could meet each other and regularly co-operate biochemically in their random motion? How could protein molecules, RNA and DNA assemble a systematic biological collaboration? How could therefore evolution of the RNA world include proteins, polysaccharides and hybrid macromolecules? How could the fractionation of nucleic acids, proteins and their mixtures be minimised or inhibited?

Basic information concerning the phase behaviour of the main classes of modern proteins, polysaccharides and their mixtures has been obtained during last three decades in the field of food science (Antonov, Pletenko, & Tolstoguzov, 1987; Grinberg & Tolstoguzov, 1997; Polyakov, Grinberg, & Tolstoguzov, 1997; Tolstoguzov, 2000a,b). It was shown that incompatibility of modern biopolymers is the general rule rather than an exception. It was found experimentally that a difference in the conformation (e.g. folded and unfolded) of biopolymers could be sufficient for their limited co-solubility. Table 1 shows phase separation threshold values for several biopolymer mixtures (Antonov et al., 1987; Grinberg & Tolstoguzov, 1997; McDougall, Rigby, & Ring, 1997; Polyakov et al., 1997; Tolstoguzov, 2002a).

The first assumption, which can be made using the experience of food science in describing the phase behaviour of biopolymer mixtures is that an additional polymer would increase the co-solubility and minimize the fractionation of dissimilar nucleic acids and proteins. In other words, a third incompatible proto-biopolymer was necessary to force the co-solubility of the other two. This third biopolymer would stimulate self-association of other proto-biopolymers, give rise to phase separation and concentrate them in the disperse phase particles of the primordial soup. To this end, the third proto-biopolymer must be soluble in neutral and mild acid media and be chemically different from proto-proteins and proto-nucleic acids. A third biopolymer must be more hydrophilic and be sufficiently simple chemically to be produced in larger amounts than other proto-biopolymers. This third proto-biopolymer is obviously polysaccharide. Since both nucleic acids and polypeptides are polyelectrolytes, neutral polysaccharides have a higher chemical difference and could play a key role in the phase separation of the primordial soup.

Table 1
Phase diagram parameters for some biopolymer-1-biopolymer-2 solution mixtures

Biopolymer pair; Temperature (°C), pH, salt concentration	Critical point coordinates (% wt.)		Separation threshold (% wt.)
	Protein 1	Protein 2	
Casein + ovalbumin; 20 °C, pH 6.6.	6.5	13.9	19.7
Ovalbumin + soybean storage globulins; 20 °C, pH 6.6.	<10	>15	15 4
Bovin serum albumin + thermodenatured ovalbumin; 20 °C, pH 6.6–6.8	<10	>15	17.2
Ovalbumin + thermodenatured ovalbumin; 20 °C, pH 6.6–6.8	10.4	3.6	13.3
Caseinate (sodium) + amylopectin (MW. 38000 kD); 20 °C; 0.15 M NaOH; 25 °C, 0.15 M NaCl; pH 6.5	4.30	3.90	8.0
Caseinate (sodium) + dextran (MW. 2000; 484; 154 and 34.5 kD); 20–40 °C; pH 6.5; 0.15 M NaCl; 20 °C; 25 °C; 0.15 M NaOH; 0.0; 0.15; 0.30 and 0.5 M NaCl	4.50	3.65	7.8
Milk proteins (Micellar − casein + whey proteins + gum arabic (MW. 219 kD); 20 °C, pH 6.4.			6.7
Pectin (MW. 69 kD; esterification degree 62.7%) + arabic gum (MW. 219 kD); 20 °C, pH 5.0, 0.0–0.5 M NaCl; pH 2.5–7.0	0.26	4.10	3.10
Gelatin (MW 170 kD) + dextran (MW 2000 kD); 42.5 °C, pH 4.9. pH 4.6–5.4. 40 °C, pH 6.0, 0.2 M NaCl			1.5
Micellar − casein and whey proteins + apple pectin (MW. 69 kD, Esterification degree 62.7%); 20 °C, pH 6.4			0.9
Pectin (MW. 69 kD; esterification degree 62.7%) + locust bean gum; 20 °C, pH 5.0, 0.5 M NaCl	0.42	0.45	0.86
Pectin, esterified unbranched + pectin highly branched de-esterified Pectin, esterified unbranched + hemicellulose 20 °C, 0.5N KOH 0.5–4N KOH	0.25	0.2	0.4–3.2

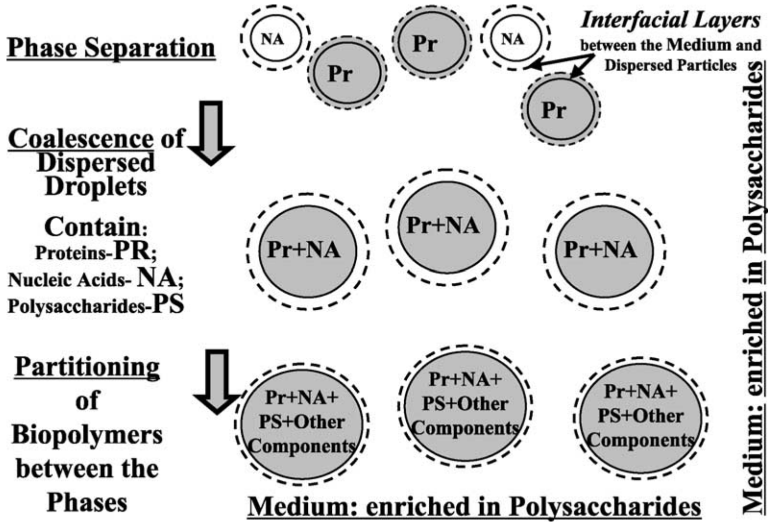

Fig. 1. Schematic presentation of the primordial soup as water-in-water emulsion with the continuous phase enriched in polysaccharides. Coalescence of dispersed particles exchange their components and increases the composition complexity of the dispersed phase.

Three phenomena could affect the composition of the primordial soup phases. The first is that co-existing phases act as two immiscible aqueous solvents where macromolecules are partitioned according to the general rule, ‘like dissolves in like’ (Tolstoguzov, 1997a, 2000b, 2002a). Proto-proteins ought therefore to be more concentrated within the disperse phase already enriched in proto-proteins than in the co-existing continuous phase enriched in polysaccharides. The same would also be true of nucleic acids. Fig. 1 shows this principle. The second phenomenon, shown in Fig. 2, is the easy deformation, breaking down and coalescence of aqueous dispersed particles in the bulk of the aqueous continuous medium. The coalescence (Figs. 1 and 2) mixes proto-biopolymers in the dispersed phase particles (Tolstoguzov, 1988, 1998).

The third phenomenon is cross-linking of macromolecules. Cross-linking would result in hybrid macromolecular particles, which in this approach are termed conjugates. Conjugates formed within the primordial soup conditions could conceivably contain a large number of proto-proteins, nucleic acids and polysaccharides. Cross-linking could be achieved by covalent bonds formed by the Maillard reaction (e.g. Babiker & Kato, 1998; Finot, 1982; Kato, Sasaki, Furuta, & Kobayashi, 1990; Nakamura & Kato, 2000; Nakamura, Kobayashi, & Kato, 1994) and/or non-covalent intermolecular interactions, such as hydrophobic interactions, coordination and H-bonds (Richter, Augistat, & Schierbaum, 1968; Tolstoguzov, 1999b). Covalent cross-linking would be enhanced on heating dry biopolymer mixtures

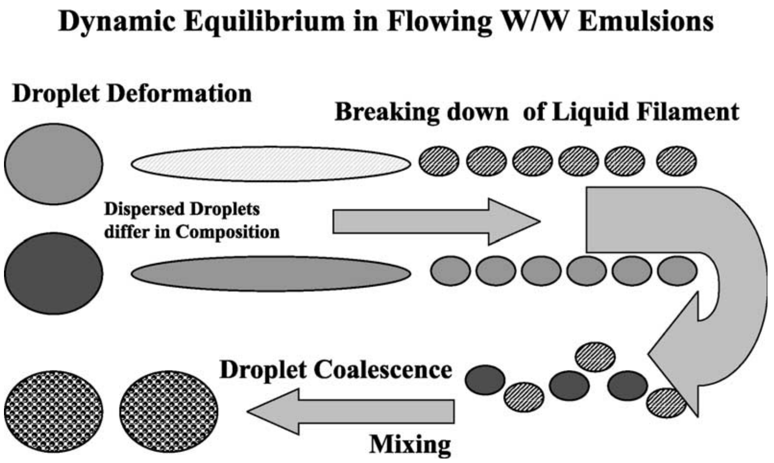

Fig. 2. General scheme of flow behaviour of W/W emulsions. The shear stresses are continuous through the interface and the liquid droplet result in the internal circulation inside the droplets, their deformation and breaking up long cylindrical droplets (liquid threads). Dynamic equilibrium: deformation—breaking down—coalescence of dispersed particles in a flowing W/W emulsion.

while non-covalent cross-linking is enhanced by the freezing of mixed biopolymer solutions. Neutral polysaccharides could play an important role in cross-linking other like-charged proto-biopolymers both by freezing (irreversible cryoconcentration) of biopolymer mixed suspensions and by the Millard reaction between amino acid monomer units and sugar monomer units of both polysaccharides and nucleic acids.

Thus, according to the proposed hypothesis, a third biopolymer, polysaccharides were necessary to overcome the immiscibility of proto-proteins with nucleic acids and to concentrate them within dispersed phase particles. Polysaccharides are in this approach proposed to have 'compatibilized' proto-biopolymers, forced cross-linking and provided a key precondition necessary to the subsequent joint molecular evolution of proto-biopolymers in the primordial soup.

3. Some other initial functions of polysaccharides

The primordial soup was most likely formed by cooling, consequently forming a saturated aqueous mixed salt solution. In such a medium, proto-biopolymers would tend to be salted out and electrostatic complexing according the Oparin's hypothesis (about complex coacervates as an initial form of life (Oparin, 1953) would be inhibited. In this perspective, the ability of polysaccharides to form insoluble coordination complexes with various metal-ions could be crucially important in decreasing the concentration of salts, especially of heavy metals in the primordial soup. An initial function of polysaccharides therefore would be to improve the primordial soup as a solvent for proto-biopolymers. This 'cleaning' activity of anionic and neutral polysaccharides could transform the primordial soup into a medium compatible with the emergence of life.

One more possible polysaccharide function could be catalytic activity. The complexes between polysaccharides and different heavy metal-cations could catalyse polymer synthesis in an entirely analogous fashion to that which has been supposed concerning clays by Cairns-Smith (Bujdak & Rode, 1997; Cairns-Smith, 1985; Zamaraev, Romannikov, Salganik, Wlassoff, & Khramtsov, 1997). It may be assumed that selection of enantiomer monomers for proto-biopolymers could be based on the adsorption mechanism similar to that of ligand-exchange chromatography (Davankov, 1991; Davankov, Navratil, & Walton, 1988). The high efficiency of this technique in separating enantiomers is based on the formation of metal-cation complexes with two mirror-image neutral (or charged) enantiomers. When the amino acid and/or sugar monomer-units associated with metal-cation (e.g. Cu) forms the chiral matrix, the mirror-image monomers can be preferably adsorbed from the solution of a racemic monomer mixture (Davankov, 1991). It is compelling that preferential binding of enantiomeric L-amino acid to metal-complex-D-sugar monomer units of anionic polysaccharide could underlie matrix synthesis of polypeptides.

Thus, polysaccharides are proposed to have been the first functional proto-biopolymers of the primordial soup that catalysed biosynthesis and improved the solubility and co-solubility of proto-biopolymers. Their next function could then have become the cross-linking of dissimilar macromolecules.

4. Conjugates

Without cross-linking of proto-biopolymers it is difficult to imagine how, under random thermal motion, nucleic acids and protein molecules could meet each other and systematically coordinate their biological functions.

Conjugates increase the co-solubility of proto-biopolymers and the stability of their single-phase mixed solutions (Tolstoguzov, 1994b, 2000b). The reason is that conjugates formed by cross-linking chemically different proto-biopolymer chains would have an affinity to non-cross-linked proto-biopolymer co-solutes. Due to the surface activity and high local concentration of polymer chains, conjugates typically stabilize of O/W emulsions and suspensions due to an increase in the viscosity, mechanical strength and like charge of the adsorption layers (Babiker & Kato, 1998; Kato et al., 1990; Nakamura & Kato, 2000; Nakamura et al., 1994; Tolstoguzov, 1993). Owing to the good dispersion-stabilizing properties of conjugates they could stabilize different colloidal particles, e.g. of clays. The encapsulation of clay particles by a polysaccharide as a protective colloid could result in catalytic chemical reactors with highly developed surface area. The same dispersion-stabilizing capacity of conjugates could than be used by cells as a macromolecular carrier (garbage-bin) to evacuate undesirable colloidal metabolites and parasites to protect cellular homeostasis. An evolutionary improvement of dispersion-stabilizing properties of conjugates could also result in exudative gums, e.g. such as Arabic gum (Tolstoguzov, 2003a).

According to the principle of conjugation during evolution, cross-linking increased the local concentration of chemically different proto-biopolymers, fixed their relative positions and made their interactions reproducible. The reversible attractive–repulsive interactions of conjugated chains of oppositely or like charged could change the conjugate conformation from the collapsed to the unfolded one. This association–dissociation of conjugated macromolecules could increase the extent of co-operativity and specificity of attractive interactions between them, increase chemical stability (against hydrolysis) of the conjugate. The improvement of topological chain complementation could contribute to the mutual catalysis, pairing of the monomer units and the joint evolution of proto-biopolymers. Some of the chains could act as matrices for adsorption of monomers, while some others could act as catalysts. The cross-links of chains assist by providing a reproducible starting point of recopying. A surprisingly high functional efficiency and specialization of modern biopolymers could presumably be a result of their competition within conjugates. In other words, it can be argued that all three proto-biopolymer species could initially be omnipotent. It could also be assumed that the use of pectin and cellulose for plant cell walls of all terrestrial plants could reflect the evolutionary choice of the most competitive organism, i.e. a last common ancestor.

5. Molecular symbiosis and mimicry in conjugates

In the proximity of cross-links, an increased local concentration of polymer chains could produce a phenomenon that can be called ‘molecular symbiosis’. This term means a mutual influence of dissimilar biopolymer macromolecules (symbionts) that favours the efficiency of at least one of them. Since each macromolecule present in a solution diminishes the volume (free volume) available for the other macromolecules, they mutually concentrate each other. The association–dissociation of long rigid chains can substantially and rapidly change the effective concentration of other biopolymers in a mixed solution. Molecular symbiosis is thus suggested to underlie the predominance of the two extreme macromolecular conformations typical of biopolymers: globular and rod-like (Tolstoguzov, 1999b, 2000b, 2002a).

Normally, the consequences of an increase in biopolymer concentration correspond to Le Chatelier’s principle, which states that a system in equilibrium, when subjected to a perturbation responds in a way that tends to minimize the effect of this perturbation. According to Le Chatelier’s principle, an increase in the concentration of macromolecules could stimulate evolution in the direction of a decrease in amount of moving particles and an increase in the density of their intra- and intermolecular structures. For instance, small additions of polysaccharides to a gelatin solution greatly accelerate formation and self-association of helical structures and increase the elastic modulus of the gel (Morris, 1990, 1998; Tolstoguzov, 1995, 1998). This means that an increase in local concentration of cross-linked macromolecules favours their compact helical and globular conformations and association. The evolutionary trend to more compact helical and globular conformations that has been termed ‘molecular mimicry’, could increase the similarity of macromolecular surfaces and their co-solubility (Tolstoguzov, 1999a,b, 2000a).

6. Helical conformations

Formation of helical macromolecules is one of the molecular strategies that produce molecular mimicry. The transition from a random coil to a helical conformation usually increases the chemical stability and biochemical efficiency of macromolecules. The latter is due to fixed surface topology and molecular dynamics. Intra- and intermolecular H-bonds and a reduced molecular surface area contacting with water (compared to that of random coil conformations) increase the chemical stability of molecular helices. The internal surface area of a nano-size molecular tube (formed by a helix, e.g. in starchy macromolecules) is inaccessible to water but accessible to hydrophobic compounds. The reason could be that three-dimensional networks of water molecules are more preferential energetically than single- or two-dimensional water structures. Helical conformations of chain segments also increases their packing density, e.g. in protein globules, starch granules and storage protein bodies (Tolstoguzov, 1999b, 2000a, 2002a). An increased chemical stability together with biochemical efficiency could be logical reasons for the evolutionary preference of helical biopolymer structures. It may be assumed that the development of helical structures has required for homochirality of proto-biopolymers and evolutionary selection of enantiomer monomers. The stability of helical conformations can only be achieved if the same enantiomers form a polymer chain. Thus, homochirality could be a key condition of molecular mimicry, chemical stability and biological efficiency of biopolymers.

7. Globular conformations

The globular structure typical of proteins and starch granules is another result of mimicry development (Tolstoguzov, 1999a,b, 2003a). The dense packing of chains decreases the surface area contacting with the aqueous medium. Most chemical information of globular proteins is hidden in the hydrophobic interior inaccessible for water. Hydrophilic side groups, mainly concentrated on the molecular surface, determine net charge, solubility of proteins and make them physically and chemically similar to each other. Compatibility of proteins and polysaccharides is additionally enhanced by their polyelectrolyte nature. Counter-ions increase the entropy of mixing biopolymers and their co-solubility. Starch lipids and starch proteins could control surface properties of the granules depending on the medium (Baldwin, 2001; Morrison, 1995; Tolstoguzov, 2003a; Warner, Eskins, Fanta, Nelsen, & Rocke, 2001).

Antifreezing and ice nucleating biopolymers appear to mimic hydrophobic particles and ice crystal surfaces, respectively. Their biosynthesis could be evidence of the conjugate-forming effect of freezing. The emergence and evolution of life could only have occurred if the negative effects of freezing on living structures were suppressed. Antifreezing and ice nucleating biopolymers are found in a wide range of modern organisms, including bacteria (e.g. soil bacteria), fungi, plants (e.g. carrot, cabbage, potato, etc.), invertebrates and fish (Feeney & Yeh, 1993; Griffith & Vanya Ewart, 1995; Lillford & Holt, 1994; Yeh & Feeney, 1996). Polysaccharides as the most ancient biopolymers must have been either resistant to freezing or actually express antifreezing properties due to rapid and co-operative adsorption onto growing ice crystals modifying their growing faces (Tolstoguzov, 2002a). The evolutionary development of molecular globular mimicry (of globular proteins) and supermolecular mimicry (e.g. starch granules and nucleic acid superhelices) resulted in dewatered structures. This formation of a dewatered core could probably reduce antifreezing biopolymer functions.

8. Proto-cells

The formation of proto-cells is proposed to have been a result of phase separation leading to the concentration of various conjugates in the dispersed phase particles of the primordial soup. Unlike molecular biopolymer solutions, colloidal dispersions are thermodynamically unstable because of an inherent excess surface free energy. Consequently, the destabilizing effect (depletion flocculation) induced by a polysaccharide added to a colloidal suspension of proteins (such as chloroplasts, casein, etc) is more pronounced than that of phase separation in mixed molecular solutions. Fig. 3 shows the difference between colloidal casein particles and globular milk whey proteins in their compatibility with a polysaccharide. Normally, phase separation of a protein–polysaccharide mixed solution takes place at a total biopolymer concentration exceeding 4%, whilst in a protein–polysaccharide colloidal suspension this corresponds to less than 1%. Polysaccharides were therefore applied to concentrate casein and precipitate chloplastes from a leaf protein solution (Antonov, Gringerg, Zhuravskaya, & Tolstoguzov, 1982; Antonov & Tolstoguzov, 1990; Zhuravskaya, Kiknadze, Antonov, & Tolstoguzov, 1986). Such behaviour must also be typical of phase separation of conjugates because of their colloidal dimension.

Self-reproduction of conjugates which increased their concentration had to lead to phase separation and an additional increase in concentration within the dispersed particles. The coalescence of liquid dispersed particles within the bulk of polysaccharide-rich media could result in the exchange of conjugates and macromolecules between them and involve the re-unification of their composition. The biochemical cooperation of conjugates could specialize their functions and make them mutually dependent within the cell. The coalescence, deformation and break down of these aqueous dispersed particles (Fig. 2) would result in an 'asexual proliferation' of proto-cells.

Dispersed droplets containing concentrated mixed solutions of conjugates and non-cross-linked macromolecules would be a good solvent for different organic compounds including monomers and oligomers. According to the mass action law, an increase in the concentration of monomers favours the formation of macromolecules. It has been shown that such monomers as sugars and amino acids can affect both the solubility and co-solubility of biopolymers (Tolstoguzov, 1994a,b).

It has been shown by Albertsson, Walter and Zaslavsky that the interfacial layer in two-phase systems formed by water-soluble polymer–polysaccharide mixtures can adsorb hydrophobic particles, cellular organelles and cells

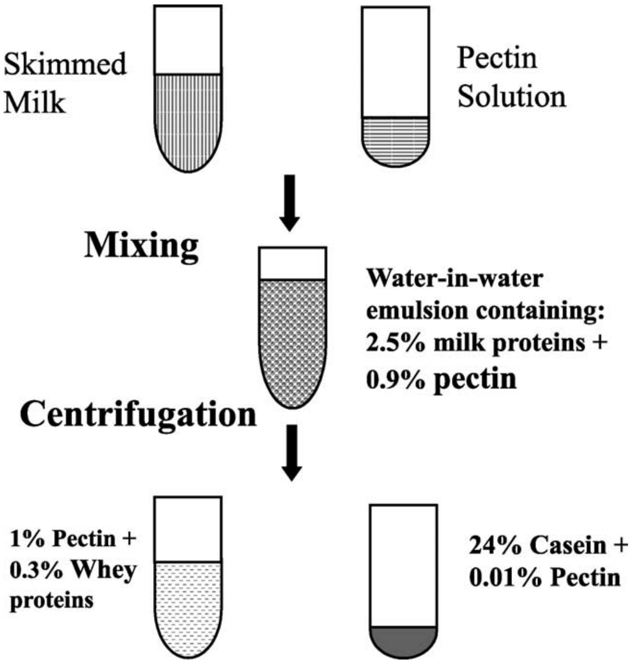

Fig. 3. A mixture of skimmed milk with 1% pectin breaks down into two liquid phases where the protein concentration in casein-rich phase exceeds 20% wt.

(Albertsson, 1972; Walter, Johansson, & Brooks, 1991; Zaslavsky, 1995). It is a logical assumption that the first membranes could have been formed by the adsorption of lipids within the interfacial layer around the dispersed particles, i.e. between the two aqueous phases of a W/W emulsion (Tolstoguzov, 2002a). The next membranes could be formed by adsorption of self-reproduced conjugates containing lipids and polysaccharides. These self-reproduced conjugates stabilized by hydrophobic interactions could be vehicles for lipids and polysaccharides to be transported into proto-cell together with all the tools necessary for their reproduction. It should be noted that the structure of multilayered cell walls appears to be similat to that of layered anisotropic gels of polysaccharides formed by diffusion of metal-cations in polysaccharide solutions (Thiele, 1967; Tolstoguzov, 1975).

9. Homeostasis

Since there are no sharp limits in nature, there was probably a continuous transformation process of the mineral world into the bioworld. This transformation of the chemical world into the biochemical world could be based on their common property. This common property could be the Le Chatelier's principle that describes typical behaviour of chemical systems in equilibrium. The system shifts its equilibrium, when subjected to any constraint, in the direction, which tends to nullify the effect of the constraint. This principle of maintaining equilibrium could also underlie the maintenance of dynamic biochemical equilibria in living systems, i.e. homeostasis. Using biochemical language, the stability of life, of any living body, any living community, their ability to survive means to maintain homeostasis. The ability to maintain a steady more-or-less constant chemical balance within a living system could be based on an increased efficiency of the Le Chatelier's principle due to multicomponent nature (or biodiversity) of living systems. Under conditions of periodic (day–night, seasonal) environmental changes, maintaining homeostasis makes a biological clock valuable if not necessary. The concept of homeostasis can be transferred from its molecular level to ecological and social contexts. In all cases, the more multicomponent metabolic networks the more stable its dynamic equilibrium, the more stable is homeostasis.

10. Nutrition and non-specific immunity of cells

Most bacterial species secrete exopolysaccharides and proteases to control their surroundings. The functions of exocellular polysaccharides include binding metals, cell-to-cell and cell-to-substrate adhesion, defense and nutrition of the cells. Fig. 4 shows this idea. It has been proposed that from the earliest evolutionary stages, both protection (non-specific immune defense) and nutrition could be achieved by the same process based on both the incompatibility of polysaccharides with foreign proteins and protein–polysaccharide complexing. Moreover, according to Le Chatelier's principle, the presence of foreign macromolecules could intensify self-association of polysaccharides and increase the density of the protective capsule. Consequently, an exopolysaccharide exocellular layer is impenetrable to foreign proteins, other macromolecules and viruses but penetrable for low molecular weight nutrients. This exopolysaccharide solution layer could, therefore, be regarded as both an 'alimentary' and 'protective' capsule of the cell (Tolstoguzov, 2000a, 2002a, 2003a).

If the exopolysaccharide solution layer around the cell acts as a phase that is incompatible with the biopolymers of the medium, it must be separated from the medium by an interfacial low viscosity layer. This interfacial layer surrounding the cell could organize rapid diffusion flow of nutrients around the cell and intensify the nutrition of

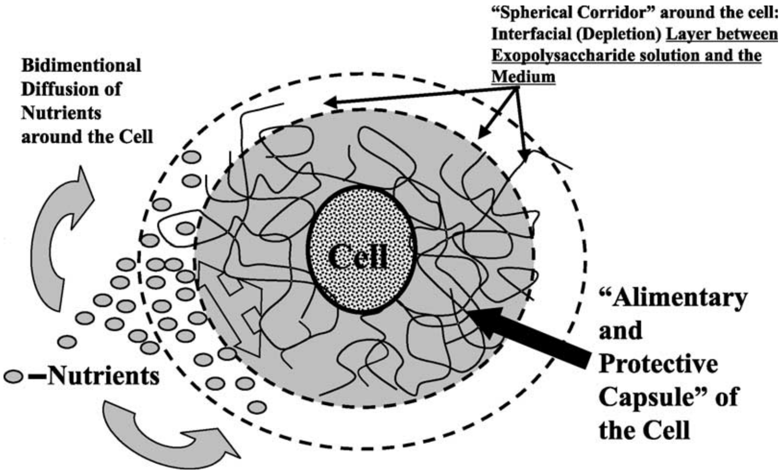

Fig. 4. Schematic illustration of alimentary and protective exopolysaccharide capsule covered the cell and the interfacial layer between the exopolysaccharide capsule and the medium.

the cell. Another contributory factor is that hydrophobic nutrients are concentrated within the interfacial layer between two aqueous phases surrounding the cell (Albertsson, 1972; Tolstoguzov, 2002a, 2003a,b; Walter et al., 1991; Zaslavsky, 1995). One more contributory factor enhancing cell nutrition could be called an 'octopus' effect. Certain polysaccharides could reversibly interact with monomer nutrients, form insoluble complexes precipitated on the surface of the cell. Reversible binding of sugars could correspond to the basic mechanism of ligand exchange chromatography (Davankov, 1991) while lipids could form insoluble inclusion complexes by adsorption within the helical core of end chain segments (Cramer, 1954; Morrison, 1995; Rutschmann & Solms, 1990). This hypothesis also means that primary structure of exopolysaccharide chains working like the arms of an octopus could contain information about the surroundings, antigens and nutrients typical of the cell. A more efficient fuel, lipids, when transported to the cell could preserve the exopolysaccharides as a nutritional reserve for the future. An increase in the concentration of the cells could provoke their competition for exopolysaccharides as the energy reserve concentrated outside the cells. This could have reduced the nutritional function of exopolysaccharides by their transformation into semicrystalline starch granules inside the cell (Tolstoguzov, 2003a).

11. Cell wall polysaccharides. Oligosaccharins

The multilayered cell wall of plants is a vital protective capsule. The attack of parasites involves an enzymatic and/or mechanical degradation of cell walls with the liberation of biologically active fragments, called oligosaccharins. The cell itself, if it is injured, also secretes an enzyme releasing the oligosaccharins from their own cell walls. Each oligosaccharin appears to regulate a particular plant function. For instance, oligosaccharins can initiate: (i) the death of the cell (to inhibit reproduction of a virus), (ii) the synthesis of protease inhibitors, (iii) the production of antibiotics, (iv) the control of growth, shape, morphogenesis and reproduction of the cell (Albersheim & Darvill, 1985; Albersheim et al., 1992; McDougall & Fry, 1991; Ozeretskovskaya & Romenskaya, 1996).

Since the main biological function of cell wall materials and exopolysaccharides is the defense against aggressive surroundings, various pathogens, toxic substances, etc., the composition and structure of these polysaccharides must be ecologically dependent. Unlike proteins, polysaccharides are not directly genetically determined and therefore are usually not monodispersed (Mohnen, 2002; Schols & Voragen, 2002; Voragen, Pilnik, & Challen, 1999). It seems likely that a relative similarity exists between the polysaccharide enriched surface layer of conjugates in the polysaccharide enriched medium and the exopolysaccharide capsule surrounding the cell in the medium that does not contain polysaccharides. The exopolysaccharide capsule could have evolved into the vegetable cell wall polysaccharides and into the mucopolysaccharide brush membrane lining the gut. Consequently, a relative compatibility between bacterial exopolysaccharides, the mucopolysaccharides of brush membrane and food fibers could be an important property dictating the competitive selection of the intestinal microflora (Tolstoguzov, 2000a, 2002a).

12. Nutrition

From the first emergence of life, protection from the surroundings and provision of nutrition were necessary for homeostasis and ultimately for reproduction. Nutrition and non-specific immunity as the key contributors to homeostasis, appear to be, therefore, highly conservative. Accordingly, food digestion conditions are, presumably, reminiscent of those on an ancient Earth. These conditions in the intestine, colon and other organs include the absence of O_2, a reductive atmosphere containing H_2, hydrocarbons, other gases and fatty acids produced by micro-organisms, and a limited amount of water. These conditions also include a large set of bacteria whose biodiversity (covering several hundred species in the colon and other organs) seems to be a key factor for the health of the microflora. The continuous chyme phase enriched in polysaccharides could correspond to that of the primordial soup. The composition of the continuous chyme phase could reflect the initial phase-forming, nutritional and protective functions of polysaccharides.

A later version of the most ancient biotechnology appears to be the fermentation of dietary fibre, i.e. cell-wall and exopolysaccharides, by the microflora bacteria in the colon. Since the composition and structure of dietary fibre are ecologically dependent and could provide information about aggressive surroundings, this ancient biotechnology could probably protect against local parasites and pathogens and be highly important for health of both the symbiontic microflora and the host. In other words, since cell-wall and exopolysaccharides could contain ecological information the traditional consumption of local fruits, vegetables, fermented vegetable and dairy foods could vaccinate microflora and improve immunity.

Thus, polysaccharides as the assumed first proto-biopolymer of the primordial soup are proposed to be the fundamental thermodynamic and biochemical determinant for the emergence and evolution of life. Polysaccharides are consequently the most abundant contemporary biopolymer and the main polymers on the planet.

13. Conclusion

Three main ideas underlie this paper. The first, polysaccharide enriched media in the primordial soup have favoured the joint evolution of proto-biopolymers by minimizing an effect of their incompatibility. A marked chemical difference between neutral and anionic polysaccharides and other biopolymers underlies phase separation of proto-biopolymer mixtures with concentration of the most macromolecular species in the dispersed phase particles.

The second, joint evolution of biopolymers has involved their cross-linking and formation of conjugates. In the bulk of these hybrid macromolecular assemblies, cross-links fix the relative positions of chains making reversible interchain interactions reproducible including mutual coding, catalytic and informative functioning. Concentration of biopolymers in conjugates could be close to those that are typical of biological systems and result in the joint evolution to proto-cellular organelles.

The third is phase separation of the primordial soup enriched in polysaccharides with the concentration of conjugates in the dispersed particles. The adsorption of self-reproducing, lipid containing conjugates between the aqueous phases, i.e. around the cell, could lead to membrane covered proto-cells. Polysaccharides have presumably preserved key biochemical (nutrition and non-specific immunity) functions and therefore retain their position as the most abundant polymers on the planet.

It should also be stressed that the considered features of polysaccharides and their interactions with other biopolymers, such as incompatibility, development of molecular mimicry and symbiosis, biodiversity, reproduction and homeostasis of macromolecular assemblies, etc. lead to the most general hypothesis that could be formulated as 'everything that an animal can do, biopolymer molecules can do'.

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