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FOODS AS DISPERSED SYSTEMS
Thermodynamic aspects of composition-property relationships in formulated food

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Abstract

Although most components contribute to structural and physical properties of food, the two main construction materials are proteins and polysaccharides in their molecular and colloidal dispersions. Native biopolymers in biological system interact specifically, whereas they are mainly denatured and interact non-specifically in formulated food. Most food components have limited miscibility on a molecular level and form multicomponent, heterophase and non-equilibrium dispersed systems. A thermodynamic approach is applicable for studying structure-property relationships in formulated foods since their structures are based on non-specific interactions between components. Thermodynamically-based operations, such as mixing of components, changing temperature and/or pH, underlie processing conditions.

To simplify considerations, attention will focus only on the effects of thermodynamic incompatibility of biopolymers on food dispersion functionality. The excluded volume effect of the macromolecules is the main reason for their immiscibility. Molecular mimicry of globular proteins causes their more-than-ten-fold-higher miscibility compared to classical polymers. Biopolymer incompatibility results in phase-separated liquid and gel-like aqueous systems. In highly volume-occupied systems aggregation, crystallisation and gelation of biopolymers and their adsorption at oil/water interfaces favour an increase in the free volume, accessible for macromolecules.

Keywords: dispersed systems, foods

Introduction

We do not know the dates of the greatest inventions, but manipulation of dispersed systems was certainly part of the history of the earliest civilizations. Civilization started with an agricultural revolution, when skills for grain milling and processing were acquired. Many biological and mineral raw materials were put through the same mill as grain, e.g. for bread and drinks, pottery, cosmetics, stone age paintings, ink, and other sophisticated products. The origins of the most ancient applications of dispersed systems remain intriguing.

The past thirty years has been a particularly fertile in the development of foods, the most complex of dispersed systems. The challenge facing us in foods is non-specific interactions of a great number of relatively independent components. Structural

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and kinetic approaches are mostly used in this field because of the thermodynamically unstable and non-equilibrium nature of foods [1, 2]. Our considerations are, however, devoted to a thermodynamic approach to composition-property relationships in food. To simplify attention will focus on formulated functional food. The reasons are an increasing significance of formulated food and the scientifically interesting problems: how can we change composition with predictable changes or without changing the properties of a food and how can labile nutrients and flavours be encapsulated in a food. To articulate basic concepts of understanding of food structures we will start with features of food dispersed systems.

1. The first feature of food dispersed systems is a huge diversity of physical properties. Both the dispersed phase and dispersion medium can exist in all three states of matter: solid, liquid and gaseous.

2. The second feature is morphological. Many foods are multiple dispersed systems. This means that each dispersed particle can itself be a dispersed system.

3. The third feature is that foods are mixed dispersed systems. This means that a dispersion medium can contain several types of dispersed particles. Foods can be a foam, an emulsion, a suspension and a gel at the same time.

4. The next feature is that foods are mainly aqueous non-equilibrium systems with structures based on biopolymers. The two main construction materials of foods are proteins and polysaccharides. They are multifunctional and simultaneously fulfil several structural functions.

5. One more feature is the structural hierarchy of foods. Since foods are normally molecular, colloidal, mixed, multiple and non-equilibrium dispersions simultaneously, elements of food structures greatly differ in size. Four levels of structural hierarchy in dispersed food systems can be distinguished: submolecular, molecular, supermolecular and macroscopic. Structural functions of a biopolymer depend upon its place in the structural hierarchy of the product [3].

We now focus on thermodynamic properties of biopolymer mixtures as a basis for the understanding of food structural hierarchy. The repulsive and attractive forces between different macromolecules underlie two opposite phenomena: biopolymer incompatibility and complexing [2–7]. Normally, when interbiopolymer attraction is inhibited, the excluded volume of macromolecules determines their phase behaviour.

Excluded volume

Figure 1 illustrates the idea of excluded volume. It shows two protein molecules. They are two adjacent spheres of the same radius R. One can easily deduce that the excluded volume (U) around each protein molecule which is not accessible to centers of other protein molecules, is eight-fold larger than the molecule itself. The excluded volume is still larger for non-spherical macromolecules. Excluded volume determines space occupancy in biopolymer solutions and competition for the space in mixed biopolymer solutions. Figure 2 shows the simplest model to illustrate competition between macromolecules for solution space. This may be the traffic on an overloaded motorway. Two opposite measures can make traffic more fluid: the collective

movement of vehicles by car-transporters and 'phase separation' of vehicles differing in size and interactions with the road between motorway lanes. The former model corresponds to biopolymer association and interbiopolymer complexing; the latter to phase separated systems [8].

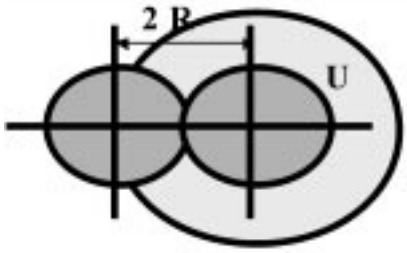

Fig. 1 Excluded volume *U* for the case of a globular protein. Because two protein molecules cannot occupy the same place in solution, the shortest distance between two molecules is equal to a diameter of each of them. This means that the excluded volume around protein molecule is a sphere with volume that is eightfold larger than that of the protein molecule because its radius is twofold longer than of this molecule

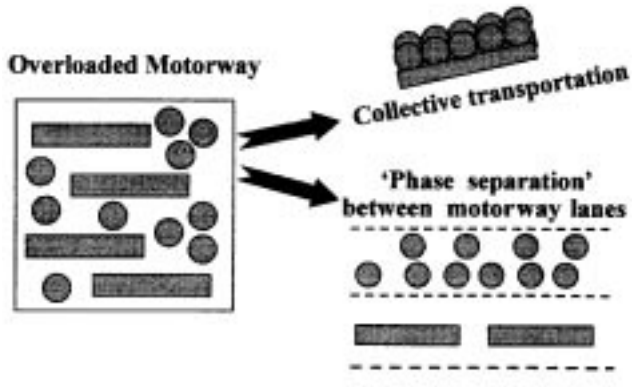

Fig. 2 Models for a decrease in excluded volume effects

The excluded volume determines the phase separation threshold. Its value usually exceeds 4% for protein-polysaccharide mixtures, and 12% for solution mixtures of various globular proteins [9–11]. Co-solubility of native globular proteins is surprisingly high, at least more-than-ten-fold-higher than that typical of classical polymers that tend to be completely separated between co-existing phases. High co-solubility is probably absolutely necessary for functioning enzymes and arises from molecular mimicry, i.e. the similarity of globular molecules [8, 9]. Formation of compact globules diminishes the excluded volume. Another result is hydrophilic chemically similar surfaces of protein molecules with the chemical information hidden in the globular interior. Due to molecular mimicry, globular proteins usually have quite similar physico-chemical properties, such as viscosity, surface activity, confor-

mational stability and gelation. Excluded volume effects do not influence the thermal denaturation of proteins, since thermal denaturation does not substantially increase the volume of molecules. On the contrary, denaturation greatly increases aggregation and incompatibility of proteins. Since formulated foods usually contain denatured proteins, incompatibility of biopolymers is one of the most common features of foods. The advantages of native proteins as food components are maximal co-solubility with other ingredients and a minimal contribution to the system viscosity.

Thermodynamic incompatibility of food macromolecules

Figure 3 shows the phase diagram typical of protein-polysaccharide mixed solutions [4–6, 10, 11]. The binodal curve separates the two regions of the single- and two-phase states of biopolymer mixtures. Compositions lying under the binodal curve correspond to single-phase solutions, where the biopolymers are completely miscible. The region lying above the binodal represents two-phase systems. The tie-lines connect the compositions of the co-existing phases. The binodal branches do not coincide with the phase diagram axes. This means that the biopolymers are limitedly co-soluble. When a protein solution, e.g. A, and a polysaccharide solution B are mixed, a mixture C breaks down spontaneously into two phases, D and E. One of which, D, is rich in protein and another E is rich in the polysaccharide. These two liquid phases form a water-in-water emulsion. The phase volume ratio corresponds to the ratio of the tie-line segments: EC/CD.

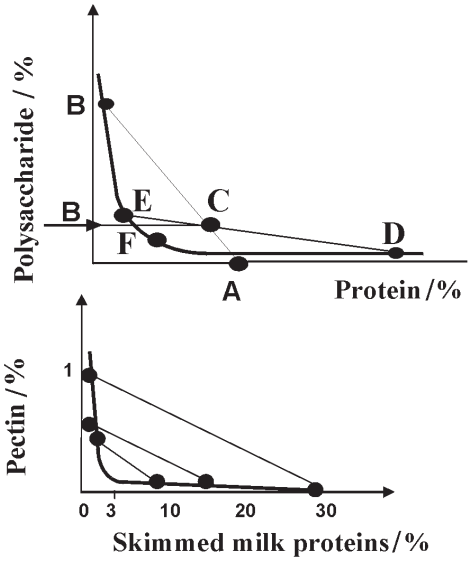

Fig. 3 Typical phase diagram for protein-polysaccharide-water systems and an example: the phase diagram for skimmed milk+high ester (65%) pectin mixed solutions

The phase diagram shows that a biopolymer B added to a food system, may perform its functional properties either within the bulk of a system in the concentration range below the binodal or within the volume of system phases in the range above the binodal. This illustrates the fact that the functionality of an added biopolymer will depend upon its place in the system structural hierarchy. We now turn to the question: how can biopolymer incompatibility govern the structure of food systems.

Water-in-water emulsions

Besides classical O/W and W/O emulsions a third type of water-in-water emulsions is typical of foods. Water-in-water (W/W) emulsions are phase separated liquid systems with equilibrium co-existing phases. Other features (Fig. 4) of W/W emulsions are: (i) low interfacial tension; (ii) low density and viscosity of the interfacial (or depletion) layer between the phases and (iii) high deformability of dispersed particles in flow. Low interfacial tension in W/W emulsions reflects similar compositions of co-existing phases, where water is the main component and biopolymers are partially co-soluble. The low density interfacial layer is due to a trend of incompatible biopolymers to have surroundings of the same type [3, 8]. The simplest model of excluded volume effects presented in Fig. 2 shows that there is always a low density layers between motorway lanes. These depletion layers are formed to diminish unfavourable interactions between vehicules differing in size.

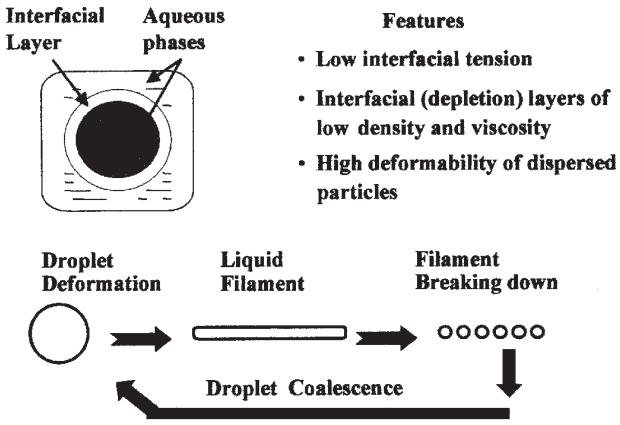

Fig. 4 Features of water-in-water emulsions

One more feature of W/W emulsions is a great difference in concentration between co-existing phases. This is due to the competition between the biopolymers for space in solution. The competition can be characterized (Fig. 3) by the angle made by the tie-line with one of the concentration axes. For instance (Fig. 3), the mixture of skimmed milk with 1% pectin breaks down into two liquid phases. The concentration of casein-rich phase increases from 3 in milk up to 30%. The pectin phase is diluted.

This process, called membraneless osmosis, governs water partition between the phases of foods [2, 14].

Oil-in-water emulsions

Figure 5 illustrates the stabilisation mechanism of O/W emulsions by protein-polysaccharide mixtures. Due to the excluded volume effect the addition of one biopolymer to a solution of another results in both biopolymers behaving as if they were in a more concentrated solution. For this reason (Fig. 5) addition of a polysaccharide re-

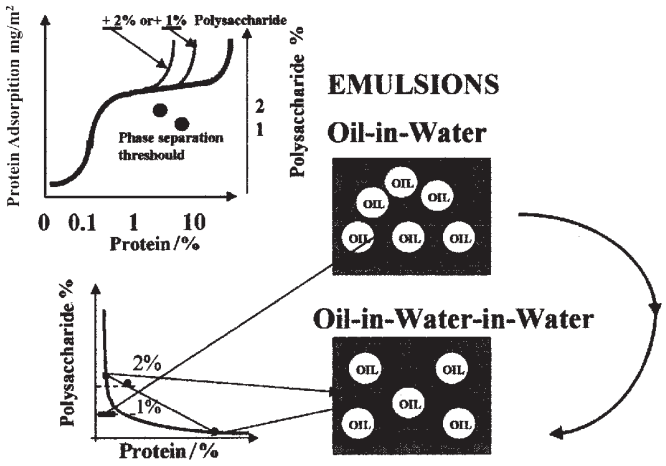

Fig. 5 Oil-in-water emulsions stabilised by protein-polysaccharide mixtures

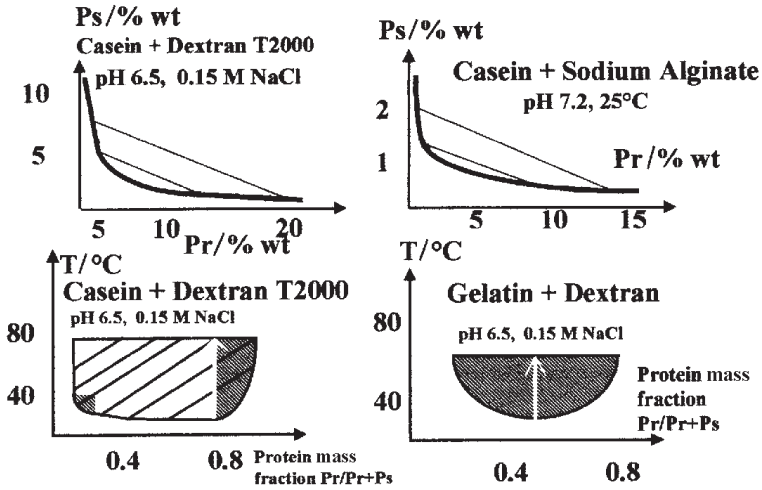

Fig. 6 Phase diagrams for protein of unfolded structure (casein, gelatin) – polysaccharide mixed solutions

duces the protein concentration required for its multilayer adsorption at the O/W interface. The comparison of the phase diagram with the protein adsorption isotherm shows that formation of protein multilayers is due to phase separation in the aqueous emulsion phase. Another factor affecting phase separation is a decrease in the protein hydrophilicity due to formation of protein-lipid complexes [1, 7]. Multilayer formation can be regarded as encapsulation of dispersed lipid particles and a transition from the single O/W emulsion to the double O/W/W emulsion, i.e. to the W/W emulsion with very low interfacial tension and an improved stability.

Figure 6 presents the phase diagrams of polysaccharides with proteins of unordered structure: casein and gelatin used in many technologies. A low co-solubility and its reduction with temperature are typical of such biopolymer mixtures. For instance, phase separation of an infant formula containing casein and maltodextrin, occurs upon sterilization and destabilizes the product [13, 14].

Water-in-oil emulsions

Figures 7 and 8 present lipid dispersed particles of multiple O/W emulsions. Multi emulsions are of importance since their composition can be varied without a remarkable change in properties. Filling a lipid phase by water droplets or gel particles reduces fat content. Filling with aqueous droplets and gas bubbles equalises the density of the phases. Filling with dry powders of proteins, amino acids or other nutrients control the composition and mask the flavour of foods. Figure 8 shows that an increase in the volume fraction of aqueous phase inside the oil droplets reduces the fat content. This corresponds to the transition from lipid droplets filled with water to water droplets covered by thin lipid layers. However, when concentration of dispersed particles increases, a lipid continuous phase can be formed due to phase inversion. This corresponds to the formation of a honeycomb-like structure of lipids, which can encapsulate up to 80% water [8, 14–17].

This type of low-fat spread is a composite formed by small spherical granules of aqueous gel bound together by a thin lipid film. For manufacturing the spread two features of dispersed systems are of importance. First, the interfacial layers of W/W emulsions can adsorb lipids. This provides a physical basis for the formation of a continuous lipid phase between the immiscible aqueous phases in W/W emulsions. Second is that surface properties of a gel depend on the medium in which gelation occurred. For instance, gelatin gels formed in an oil or air are not wetted with water, but are perfectly wetted with oil. For this reason a honeycomb-like structure is formed, upon mixing lipids and a surfactant stabilising W/O emulsions with two biopolymer solutions, e.g. of gelatin and maltodextrin. Gelation of the aqueous phases and crystallisation of the lipids can solidify this honeycomb-like construction. This gives butter replacers. Under shearing conditions low adhesion of granules to each other and lipids result in their rotation and a ‘ball-bearing’ effect. This lubricant effect, small size and hydrophobicity of the granules mimic fat globule size, surface and rheology. The ‘ball-bearing’ effect can be responsible for fluidity and fat mimetic characteristics of many foods and cosmetics. Honeycomb-like structures are involved in

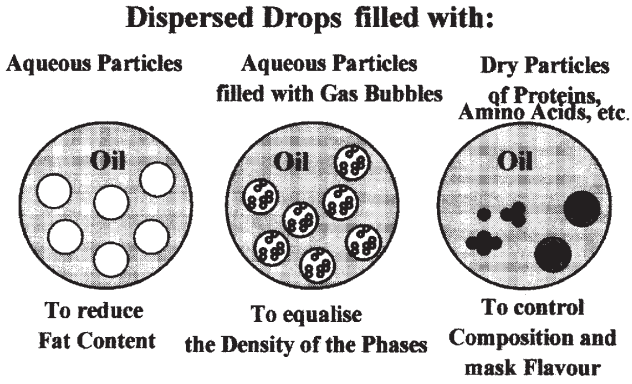

Fig. 7 Multiple oil-in-water emulsions

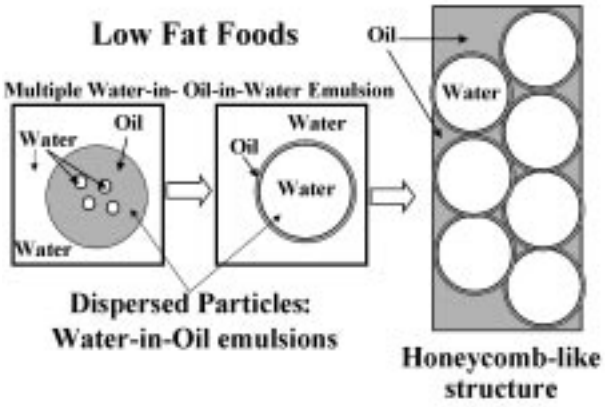

Fig. 8 Formation of honeycomb-like structure

the fat-like mouthfeel of microparticulated gels, fat substitutes based on polysaccharide additives, etc. [15, 16]. The next example is ice cream mixes [17].

Ice-cream mixes

Common features of ice cream stabilizers, i.e. polysaccharides and gelatin, are high excluded volume and hydrophilicity. These are probably of importance to minimize the growth of ice crystals. The concentration of stabilizers in ice cream mixes varies from 0.1 to 0.5% mass. Figure 3 shows, however that the addition of the same amount of apple pectin to skimmed milk results in phase separation of the mixture. This means that stabilizing agents induce phase separation of ice cream mixtures. Interfacial layers between aqueous immiscible phases may be partially filled by lipids and form honeycomb-like structures. Ice crystal growth may be stopped by highly developed surfaces of thin lipid layers, droplets, air bubbles and by an adsorption of stabi-

lizer macromolecules on surfaces of the growing ice crystals [17]. Freezing of water leads to an increase in the total concentration of aqueous phases and to their gelation.

Gels

Accordingly to Le Chateliers' principle, an increase in concentration of biopolymers favours intensification of structure forming processes: aggregation of biopolymers, their gelation and crystallization, i.e. processes (Fig. 2) decreasing the excluded volume [14–17]. For instance, crystallisation of amylopectin in gelatin gels was found by Doi [18]. Crystallisation of maltodextrin in gelatin solutions was found by Kasapis with coworkers [19]. Incompatibility of guar gum with starch [20] is probably the reason for an increase in the degree of crystallinity of starch and its decreased digestion rate in bread for diabetics [17]. Figure 9 shows the synergistic and antagonistic effects of blending biopolymers. These are: a decrease in the gel point of a single-phase mixed solution and an increase in the modulus of elastisity of the gel [21, 22]. This is due to excluded volume and mutual concentration of incompatible biopolymers. Since the elastic modulus of a gel is usually proportional to the square of its concentration the elastic modulus of a mixed gel can be several times higher than those of gels of its components. On the contrary, for two-phase mixed solutions the higher the volume fraction of dispersed particles, the lower the modulus of elasticity of the gels. This reflects a low adhesion between the filler and the matrix (similar to low-fat speads).

Figure 10 shows another example. These are thermomechanical properties of a gelatin gel, a Ca-alginate gel and a mixed Ca-alginate-gelatin gel. The mixed gel was prepared by cooling a gelatin-alginate mixed solution and immersing the gel in a calcium acetate solution. The mixed gel behaves like a gelatin gel below 30 and like a calcium alginate gel above 45°C. Within a range of temperatures from 30 to 45°C, the gel is anomalously highly deformable. The compliance maximum is reproducible upon cooling (curve 4) and re-heating (curve 5) of the gel. Its position (from 34 to 38°C) depends on the rates of heating and cooling of the gel.

The reason of this phenomena is that a thermomechanical study gives non-equilibrium values of gel compliance. It reflects changes in viscosity of dispersion medium of the Ca-alginate-gel during gelatin gelation and melting. Upon heating the gelatin network breaks down into macromolecular aggregates and then in macromolecules. Melting of aggregates results in an increase in viscosity due to an increase in concentration and flexibility of solute particles. This corresponds to a decrease in compliance on heating. Upon cooling, gelatin molecules are aggregated and reform the second network of the gel. Thus, the network of the Ca-alginate gel acts as a highly sensitive viscometer functioning at a small deformation without destruction of macromolecular aggregates. The surprisingly high deformability of the mixed gel at mouth temperature provides its tender consistency and stability on heating [21–23].

The reproducibility of the compliance maximum upon cooling and re-heating reflects an astonishing fact: incompatible biopolymers form interpenetrating networks. This is possible because gelation relates to the aggregation of macromolecules

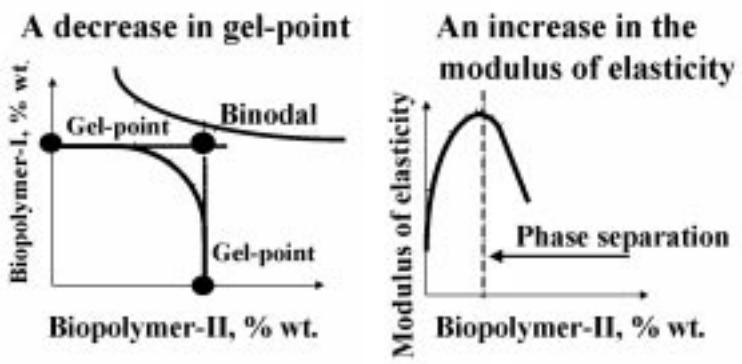

Fig. 9 Effects of excluded volume and phase separation on gelation of biopolymer mixtures

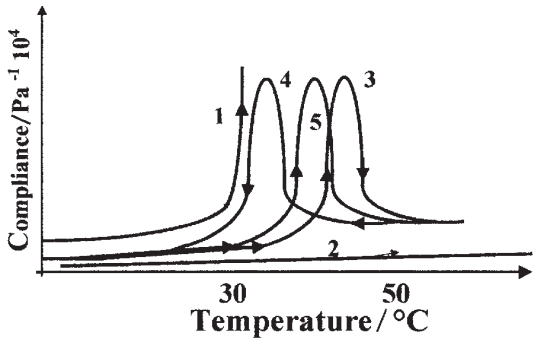

Fig. 10 Thermomechanical properties of mixed gelatin Ca-alginate gels. 1. 10% gelatin, 2. 0.5% Ca-alginate, 3. and 4. 10%gelatin+0.5% alginate (heating, cooling), 5. reheating the mixed gel

and leads to a decrease in their excluded volume (Fig. 2). Compared to the initial mixed solution the dispersion medium of a gel is always a better solvent for other biopolymers. Thus, formation of mixed gels is due to better mixibility of a biopolymer with a gel network of another one. This illustrates the difference in compatibility of biopolymers at supermolecular and molecular levels.

The several examples relate to biopolymer interactions with substances of low molecular mass. They illustrate flavour binding and release by globular and unfolded protein molecules and macromolecular aggregates [24–26]. Figure 11 presents the flavouring of gelatin gels. Amines used as fishy flavour components, were mixed with either a gelatin solution or a gel. A ball viscometer supplied with two electrodes and a water jacket was used for assessment of both the free amine concentration by conductivity and the gel melting temperature. Upon heating a sudden decrease in conductivity takes place during melting of macromolecular aggregates of gelatin. The conductivity value is not restored on cooling [24]. This reflects competitive bind-

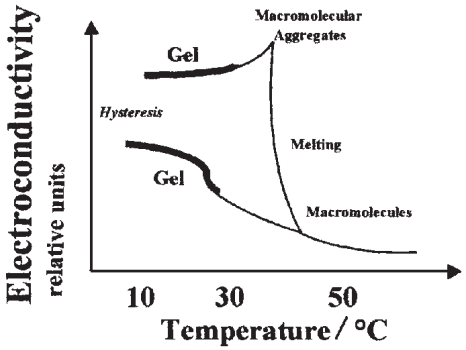

Fig. 11 Flavouring of gelatin gel

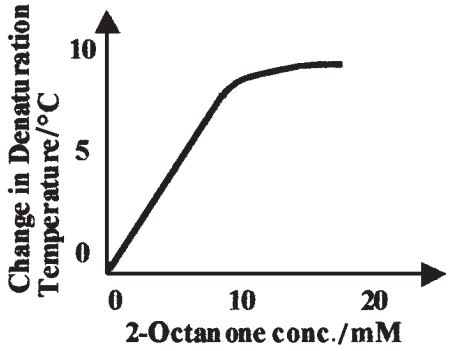

Fig. 12 Denaturation temperature of BSA-2-octanon complexes *vs.* the amount of bound 2-octanone

ing of low- and high-molecular ligands. Biopolymer binding sites are used either for gelatin aggregation and formation of network, or for binding amine molecules.

One more example is to illustrate the role of globular conformation in the molecular level of flavour adsorption. Many globular proteins can act as irreversible flavour adsorbents. An interesting problem is the reversibility and universality of binding. It was shown that a globular protein, serum albumin (BSA) can bind and release flavour in aqueous media [8, 25]. This main protein of the blood serum is presumably responsible for adsorption and transportation of low-molecular weight organic compounds. To improve BSA ability to bind and release flavours, its interbiopolymer complexes with pectin were used. Adsorption of 2-octanone from a neutral medium by the BSA molecules was changed by its desorption when the pH was moved to the acid region where the protein is unfolded on the pectin matrix. Figure 12 shows that adsorption of hydrophobic ligands by BSA is accompanied by an increase in the denaturation temperature, which is proportional to the amount of the compound bound

by the protein [25]. This effect of protein biometry makes use of BSA as a protein-sensor to detect low concentrations of flavours [8].

Conclusions

In conclusion, the efficiency of the thermodynamic approach to help understanding structural hierarchy in foods and the effects of food processing variables such as temperature, composition and concentrations upon evolution of a system should be stressed. My concern was to consider thermodynamical aspects of formation of food structures and to extrapolate this approach to some food processing problems. The examples discussed here demonstrate the importance of structural hierarchy in formulation of food dispersed systems. Mutual influence of different structural levels causes both unique structure-property integration in a food and a huge diversity of foods.

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