

CALORIMETRY, THERMAL ANALYSIS AND CHEMICAL THERMODYNAMICS IN FOOD SCIENCE. REPORT ON THE PANEL DISCUSSION *

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INTRODUCTION

Calorimetry and thermal analysis are of great interest in the characterisation of food materials inasmuch as they provide data relevant to the industrial processing of foodstuffs and shelf life, while chemical thermodynamics is of great assistance and practical importance in modelling the behaviour of several food systems.

A number of research topics in food science and technology could benefit from an experimental approach by means of calorimetry and/or thermal analyses, and thermodynamic interpretations. Examples include:

- the role of naturally occurring compounds in plants and foods
- the gelation of starch–water and protein–water systems
- protein denaturation
- drying
- enzymatic reactions
- triglyceride phase transitions
- heat capacity of foodstuffs, etc.
- selective preservation technologies
- “nutrient extraction and recombination”
- microwave heating
- fractionated crystallisation
- supercritical fluid extraction
- conditioning and storage in a modified atmosphere

Basic contributions from thermal analyses could support mathematical models for heat propagation in foods, the kinetics of degradative reactions (Maillard, lipid oxidation, enzymatic discolouration, etc.), spread-and-death of microorganisms and fermentation processes in homo- and heterogeneous phases.

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This list of topics indicates that information from and the experience of the investigation of other materials and chemical systems, such as polymers, proteins, solutions, etc., could be of great assistance in the study of food-stuffs and food processing because of the similarity of the research problems involved.

Nevertheless, calorimetry and thermal analysis have not yet received sufficient attention from agricultural chemists and food engineers, while researchers in laboratories devoted to calorimetric and thermal analysis investigations have not yet realized the great opportunities offered by their applications to food and agricultural science.

These reasons lay behind the panel discussion held by some of the scientists attending the 10th AICAT Meeting, namely G. Andrich, A. Braibanti, A. Cesaro, T.H. Lilley, P. Masi and M. Ollivon. The texts of their communications are summarised below. These reflect the requirements of modern food science and its expected developments, as reported by G. Andrich, and include examples of stimulating research lines that could be of interest for chemists, physical chemists and chemical engineers.

Andrich's general considerations are supported in the research works presented below, each of which can undoubtedly stimulate the interest of chemists and physical chemists in food science.

Those more inclined to molecular investigations will be interested in the studies by T.H. Lilley on the polyphenols, while classical thermodynamicists will find an important application of the well-known "thermodynamic activity" in the discussion by A. Braibanti on water in foodstuffs. Devisers of new multifunction instruments should be interested in the presentation by M. Ollivon on the coupling of DSC and microwave resonant cavity. Phenomena such as gelation and rheological changes due to modifications of the conformational order, familiar to those devoted to polymer science, are discussed by A. Cesaro in his presentation on carbohydrates. Finally, chemical engineers will find that the modelling of food processing is remarkably similar to that of other products, as shown in the communication by P. Masi.

All these contributions emphasize that food science and technology are multidisciplinary fields, because all foodstuffs require the adequate characterisation of a number of investigations and different approaches.

For example, Lilley's investigation began with a structural description of the molecules involved, while Braibanti found that a suitable rearrangement of the formal relationship between thermodynamic activity and the amount of water present a deeper insight into the water sorption, including a hypothesis concerning the extent of short-range cohesive forces among molecules.

GENERAL CONSIDERATIONS

G. Andrich, Institute of Agricultural Industries, University of Pisa, Italy

The development of food science in terms of both product innovation and optimisation of "know-how", involves two main areas of research that are very close to each other and are multidisciplinary:

(1) the analysis and quality control of raw materials, intermediates and final products; and

(2) the innovation and optimisation of production processes.

Production schedules involve materials with very complex structures and highly varied chemical compositions that undergo continuous physico-chemical transformations due to their interactions with the environment and the surrounding microflora. Further complexity arises from the fact that most foods are structured within biological tissues that often belong to living organisms.

In spite of a gradual inversion of the traditional trend, food analysis is still mainly "static", i.e. limited to the determination of the nature and amounts of single components. This approach cannot supply information concerning the evolution of the systems considered and is of little help in describing the behaviour of a food product during storage or technological processing.

Analysis as part of a thermodynamic approach, on the other hand, could provide a "dynamic" picture of such systems, since it would reflect the real position more closely and help plant engineers to identify suitable processing and preservation treatments and to optimise the working parameters involved.

Food production on an industrial scale could thus gradually become a science based on well established physical and biochemical laws allowing selection of appropriate processes and process conditions to maximise product quality and to minimise costs.

What is needed today is specific information on the physical properties of foodstuffs and their basic ingredients.

EXAMPLES OF RESEARCH LINES

T.H. Lilley, Department of Chemistry, University of Sheffield, Gt. Britain

It is undoubtedly true that many of the important problems in food and agricultural science are at present intractable. Part of the reason for this is that one is usually dealing with interactions occurring in multicomponent systems. In some situations, the molecules themselves are, from a chemical viewpoint, ill-defined and it is a truism to state that for a chemist the

starting-point of understanding any system must be an analytical structural description of the molecules involved.

A noteworthy example of chemical compounds of great interest in food science is represented by the naturally occurring polyphenols (*syn* vegetable tannins). These compounds have recently been studied [1] and form part of a large group of compounds (secondary metabolites) for which there seems to be no known defined biological function. Nonetheless, it is well-known that many Oriental folk-medicines derived from plants, as well as herbal remedies, such as those based on the raspberry (*Rubus idaeus*) leaf and hawthorn (*Crataegus* sp.), have polyphenolic substances as their active principle.

Another feature of the polyphenolic group is that they stimulate one of the taste sensations, namely astringency, and it is this aspect which we have recently been addressing.

The following principal objectives have been recently addressed:

(1) the nature of the interactions occurring between polyphenols of known structure and other naturally occurring compounds, such as proteins, polysaccharides and alkaloids; and

(2) the role of polyphenols in plants.

An intensive series of studies using a range of experimental techniques, including thermodynamic and spectroscopic procedures, has provided some partial answers [2]. The work done clearly shows that no single approach is sufficient to address such problems. The whole panoply of chemical weapons must be used. In other words, the tackling of significant problems in agricultural and food science demands that a multidisciplinary approach be adopted. Our experience is that the physical chemist has a pivotal part to play.

As a short comment to Lilley's conclusion, it can be observed that his position is in line with research on the role and properties of water in foodstuffs. The studies on water in foodstuffs presented below are typical examples of physico-chemical approaches.

The thermodynamic treatment of the sorption data presented by Braibanti permits recognition of the nature of the bond forces between water molecules and host substrates, and the evaluation of the Gibbs energy changes for sorption. The special equipment devised by Ollivon to record simultaneously DTA and dielectric dispersion traces is another example of applied physical chemistry.

A. Braibanti, Institute of Applied Physical Chemistry, University of Parma, Italy

The significance of water content in the preservation of food is well known; drying has been a common preservation method since ancient times. The general behaviour of yeasts, bacteria, moulds and enzymes can be reduced to a schematic view which predicts that at low water content they

lose their activity or viability, whereas at high water content they grow and develop their full potentiality. The same scheme applies to food deterioration.

It has been recognised that water activity, a_w , as expressed in solution thermodynamics, rather than total water content, is the parameter (along with pH and temperature) on which conservation and deterioration of food depend. Many properties of food systems, such as water sorption, swelling, voluminosity, water-holding capacity, dispersibility, wettability, solubility, viscosity, thickening, coagulation, etc., depend on or are related to a_w . This is measured by the equilibrium relative humidity (ERH), i.e. by the apparent equilibrium vapour pressure.

Many physico-chemical models have been proposed to describe the sorption process. Van der Berg and Bruin [3] report 77 models of sorption isotherms extracted from the literature. The acceptance of one model rather than another is based on its ability to reproduce the experimental data. Theories proposed for solutions of macromolecules, such as that by Flory [4], are sometimes employed to describe food systems with a large protein content [5,6].

The BET (Brunauer, Emmett and Teller [7]) model or its modified GAB (Guggenheim [8], Anderson [9] and de Boer [10]) version suggest the following expression for an isothermal multilayer sorption

$$\frac{W}{W_m} = \frac{CKa_w}{(1 - Ka_w)(1 - ka_w + CKa_w)} \quad (1)$$

where W is the weight of water per 100 g of dry solids, W_m is the weight of water for saturated monolayer per 100 g of dry solids, C is the Guggenheim constant, dependent on the sorption heats in the mono- and multilayer, K is the correction constant dependent on the properties of the water molecules in the multilayer with respect to pure water, and a_w is the ERH.

The GAB model has been widely adopted in the COST project [11]. As a result of the project, a computer program was arranged to reproduce the whole isothermal sorption curve from collected standard parameters for many kinds of foodstuffs.

According to this model, the shape of the W versus a_w isothermal trend can be divided into three regions.

Region I: at low water activity ($0 < a_w < 0.25$), moisture uptake is rapid. This kind of water is strongly bound to the hydrophilic, charged, polar groups of proteins and polysaccharides; its enthalpy of vaporisation is considerably higher than for pure water; it is mostly unfreezable and not available for chemical reactions or as a plasticiser. It is assumed that a monolayer of bound water is progressively formed in this region.

Region II: at higher a_w ($0.30 < a_w < 0.70$), moisture uptake becomes gradual and linear. Additional layers of water molecules gradually attain the

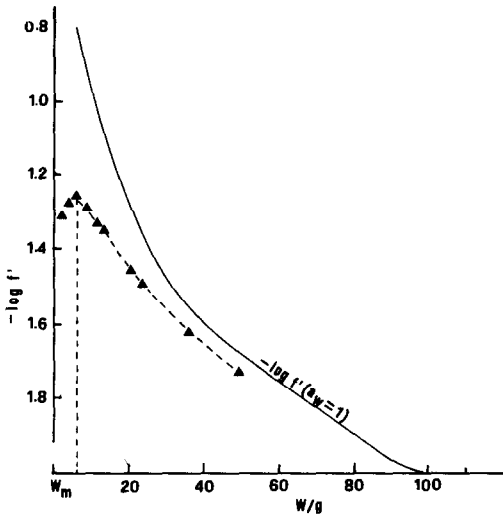


Fig. 1. Logarithm of the activity coefficient vs. the water content per 100 g of dry product. W_m is the water content for saturated monolayer. The continuous curve represents the limiting law for unit water activity.

structure and properties of normal water. The enthalpy of vaporisation is lower and the evaporation rate higher than in region I.

Region III: when a_w approaches unity ($0.75 < a_w < 1$), water behaves as in aqueous solutions. This also applies to water in voids, crevices, capillaries, and to water loosely associated with proteins.

It must be mentioned that the isothermal sorption curve is continuous, although encompassing biphasic (solid–vapour, regions I and II) and monophasic (region III) systems.

The physical discontinuity can be clarified if the W versus a_w relationship is rewritten in the form

$$a_w = f' W \quad (2)$$

where f' is a pseudo-activity coefficient which can be referred to as a specific efficiency factor normalised to 1 g of adsorbed water. Accordingly, the experimental (W , a_w) data can be represented in the plot of $\log f'$ versus W without additional assumptions or hypotheses.

Cod meat gives the trend reported in Fig. 1. The slope change on the left corresponds to the phase change from mono- to multilayer arrangement of the water molecules. The descending part of the diagram tends to the limiting trend

$$\log f'(a_w = 1) = -\log W \quad (3)$$

and indicates that water exceeding the monolayer shows a behaviour which progressively approaches that of pure water. The two curves coincide at $W = W_E$.

The area between the curves of $\log f'$ and $\log f'(a_w = 1)$ versus W is proportional to the incidence of the cohesive forces within the multilayered water around the substrate with respect to the cohesive forces within bulk water. Accordingly, the change of the average chemical potential accompanying the multilayer formation is given by

$$18 RT \int_{W_E}^{W_m} [\log f'(a_w = 1) - \log f'] dW \quad (4)$$

where 18 is the molecular mass of water.

Although the $\log f'$ versus W trend may not always allow a clear interpretation, it can nonetheless reveal the subtleties of the real behaviour of water.

Four general aspects should be considered for future research.

(1) New models or rationalisation and unification of the present ones.

(2) Development of novel inexpensive and reliable techniques for ERH measurements to improve those commonly employed [12].

(3) Determination of the properties of adsorbed water molecules by means of other physico-chemical methods in addition to the spectrophotometric ones employed today [13]. For example, those for interfaces and surfaces, conformational calculations [14] and empirical models [15–17].

(4) Study of the kinetics of water evaporation and of the processes that occur within the three regions of the GAB model to allow the possible application of irreversible thermodynamics to conservation, deterioration and processing of foods.

M. Ollivon, C.N.R.S./E.R. 286, Thiais, France

An improvement in the experimental investigation of water in foods has recently been proposed [18], namely a new thermoanalytical technique based on microwave heating which allows the measurement of complex permittivities as a function of temperature. This method is complementary to conventional DSC for the qualitative and quantitative determination of water in foods.

DSC measurements of ice fusion enthalpy permit easy determination of the amount of freezable water. This water is often referred to as “free”, although no special “freedom” has ever been evidenced but its ability to freeze. Its amount, determined by means of DSC, corresponds to water molecules both capable of freezing and accessible to nucleation under the experimental conditions. Although the evaluation and attribution of this enthalpy are still discussed, especially when the ice melting temperature deviates from 0°C, this determination is unquestionably useful in food research and biology.

During crystallisation, water molecules are prevented from freezing when their hydrogen-bond interactions with the substrate are strong (bound

water), as well as when they are inaccessible to nucleation, e.g. in water-in-oil emulsions, in porous or viscous matrices, such as glassy carbohydrate-water mixtures, etc.

Because no melting enthalpy is gathered from this kind of water molecule, it is particularly difficult to determine their presence and their interactions with the substrate by means of DSC. This becomes possible with measurements of complex dielectrical properties at very high frequencies which provide information concerning molecular motions in materials and, hence, the related molecular interactions.

The microwave domain is particularly suitable for the study of water-substrate interactions, since the main relaxation of bulk water at room temperature occurs at 17 GHz, and bound water or water-substrate relaxations are expected at lower frequencies. Due to the nature of these relaxations, which depend on the rotation of the water dipoles, they are spread over a broad frequency bandwidth. Nonetheless they are sensitive to the processes of molecular association in which the water is engaged.

A further advantage with respect to the enthalpimetric techniques is that dielectrical analysis reveals water properties at any water content. In thermal and dielectric analysis, complex permittivities of materials are recorded as a function of time, during microwave or conventional heating in a resonant cavity, while temperatures are measured with a special non-perturbing fluorimetric thermometer [18]. The details of the instrumental apparatus have been reported in the literature [19]. Water contents are determined by weighing.

Whatever the hydration level, from anhydrous to fully hydrated products, both the analysis of the heating curves and the variations of dielectric constant with time, as well as their comparison, give information on the energy transfer associated with the dielectric losses of the materials and the kinetics of the processes promoted by heating. The absence or presence of possible physical transformations, as well as of chemical reactions, can be demonstrated and quantified.

For simple relaxations, it can be shown that frequency and temperature relaxations are equivalent. One can thus work at constant frequency by varying the temperature, or at fixed temperature with varying frequency. These measurements provide an explanation of the complex heat- and mass-transfer mechanisms associated with microwave drying [19]. For example, comparison of the dielectrical constant variations recorded for foodstuffs containing different amounts of water and for the corresponding dry product allows evaluation of the dielectrical properties of each type of water encountered in association with the foodstuff. Water-substrate interactions are evaluated from both real and imaginary dielectric constant measurements and from computation of the slopes of their variations versus T , as well as from the determinations of the temperatures of the dielectric loss maxima. A typical study concerns the check of the water state in solid and molten polyols and sugars [19].

Ollivon's communication was found noteworthy by those interested in the study of carbohydrate solutions and carbohydrate polymers that form another important class of compounds entering many food materials: starches, alginates, pectins and various types of gums (agar, guar, arabic, etc.), largely diffused in natural tissues, have properties that are exploited in foods to control the rheology of the aqueous phase as thickeners, dispersing and/or gelling agents, as well as systems with intermediate properties. These are the reasons that lie behind the considerable scientific work devoted to these compounds, presented in this panel discussion by A. Cesaro.

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A knowledge of the structure of polysaccharides, including their three-dimensional molecular shape, and of their interaction with other food ingredients is essential for understanding, controlling and upgrading their function in food applications. The primary structure of polysaccharides (glycans in IUPAC notation) is complicated by the different kinds of linkages in the homopolymers (e.g. alpha and beta, 1-4, 1-3, 1-2 and 1-6, as in amylose, cellulose, scleroglucan, cyclic glucans and dextrans) and by the different monomeric units, giving rise to very many polymers.

Interactions affecting the secondary structure are the non-bonding ones due to rotation about the glycosidic linkages. Whenever ionic groups are present (e.g. carboxylate and sulphate), the ionic strength of the solvent can modulate the charge repulsion, or even fully shield the fixed charges through counter-ion condensation or specific site-binding. If all the monomeric units were in the same conformational minimum-energy state, the polysaccharide would assume a helical conformation with a geometry solely dependent on the type of glycosidic linkage.

From a practical point of view, the degree of conformational order determines the macroscopic features of interest (e.g. the rheology) and is easily monitored by the changes in optical properties. The structural parameters, which can vary because of thermal fluctuations ensuring conformational disorder and solubility, are almost exclusively the rotational angles. The structure may therefore be approached by statistical methods, e.g. Monte Carlo, giving some "snapshots" of more or less coiled chain trajectories. When charged groups are present, i.e. long-range interactions, the "average structure" of the system can be approached by a combination of thermodynamic and conformational treatments.

Native starch granules are partially crystalline. It is believed that such crystals belong to the amylopectin component, although high contents of either recognized crystal forms (A and B) have been obtained *in vitro* from low molecular weight amylose. The crystal regions are dispersed in an

amorphous phase. Starches show a non-equilibrium fusion, as well as typical properties (annealing, crystallisation and plastification by the solvent) of kinetically metastable polymers. Like these, starches show a glass transition.

Most polysaccharide systems form gels.

At room temperature, the native starch granules undergo a limited and reversible swelling in the presence of excess water. At higher temperatures (55–75°C, according to the starch stem), swelling becomes larger and irreversible. The starch structure undergoes changes which can be revealed by X-ray diffraction, birefringency and calorimetry. The mixture of swollen granules and aqueous solution of polysaccharides (mainly amylose) behaves like a viscoelastic gel, which can be described as a composite material.

By decreasing the temperature or by shielding fixed charges, one can facilitate the local ordering of linear polysaccharide chains with their consequent clustering, which appears to interact side-by-side via hydrogen bonds and/or salt bridges. The most striking fact is that gelation of the solution may occur at polymer concentrations as low as 1 g l^{-1} (the so-called “self-standing” gel).

Gel formation in the agar and carrageenan families is thermoreversible; large salt concentrations shift the sol–gel transition to higher temperatures. In all cases, a noticeable hysteresis is observed in heating-cooling cycles, such as for phase transitions under metastable conditions. In this case, nucleation, which kinetically controls the gelation, is due to the formation of locally ordered conformational structures.

Thermal analysis and high sensitivity DSC are extremely useful ways of studying non-equilibrium behaviour in retrogradation (reconstitution of a crystal phase in aged gels) and in gelation processes, and the role of water molecules as plastifying agents. Some relevant literature sources [20–27] are recommended for detailed information.

The conclusion of Cesaro's communication concerning non-equilibrium phenomena recalls that food processing very often implies control of such conditions. The extreme case of non-equilibrium processes is represented by heat- and mass-transfer phenomena, which may take place simultaneously during the production of food. These were dealt with by P. Masi.

P. Masi, Institute of Food Chemical Engineering, University of Salerno, Italy

Unfortunately, it must be recalled that although we are always able to draw models to describe heat and mass transfer, very little is known about the transport properties of foodstuffs, the thermal characterisation of which should also concern the biochemical and phase changes. These play an important role in determining the final character of the product, as in the case of thermal treatment of a mixture of ingredients to promote structuration or destructuration via protein denaturation.

In thermal analysis, thermomechanical investigations represent a powerful tool for the acquisition of information concerning the structural changes that take place during the heat treatment of foods. This technique basically consists of the dynamic analysis of a sample during a given thermal history.

The sample is subjected to dynamic mechanical deformation, e.g. sinusoidal shearing at a given amplitude and frequency, and the rheological response is recorded during a temperature scan at a given heating (cooling) rate. Foodstuffs display a viscoelastic rheological behaviour.

When heat is supplied to the sample, biochemical phenomena are activated and its structure changes. The corresponding variations in the elastic and viscous components of the rheological response will provide an insight into what is occurring at the molecular level.

For example, the thermomechanical analysis of a water–gluten mixture shows a decrease in its mechanical strength in the first heating steps (no structural changes are occurring); just above a critical temperature (about 60 °C), however, its behaviour reverses and its stiffness begins to increase. At the same time, $\tan \delta$ (a measure of the relative contributions of the viscous and elastic components of the rheological response) decreases. This means that it becomes more and more elastic.

If a small amount of albumin is added, this behaviour is enhanced, suggesting that at and above the critical temperature, S–H bonds are formed between protein molecules, and permanent and extended cross-links ensure the formation of a protein network with greater mechanical strength. Albumin addition would appear to favour this process by increasing the number of such cross links.

If starch is added, the thermomechanical behaviour is completely different; starch gelation is, in fact, accompanied by massive swelling which interferes with the macromolecular movements and, consequently, enhances the internal viscosity of the material.

CONCLUSIONS

The panel discussion focussed on some research that undoubtedly embraces both food science and technology, and includes chemistry and physical chemistry. Conventional and novel experimental approaches have been proposed along with data treatments based on classical thermodynamics. The opportunity for application of calorimetry and thermal analysis, as well as other physical methods, was made particularly clear.

The organizers hoped to stimulate the interest of chemists and physical chemists in food science and technology: the extent and complexity of the systems to be studied are indeed an exciting challenge.

Chemists and physical chemists can certainly enhance the evolution of food science by undertaking the inspection of phenomena and processes at the

molecular level: a goal that could also have significant consequences for industry.

REFERENCES

- 1 E. Haslam and T.H. Lilley, in C.F. Van Sumere and P.J. Lea (Eds.), *Ann. Proc. Phytochem. Soc. Eur.*, vol. 25, Clarendon, Oxford, 1985, p. 237.
- 2 E. Haslam and T.H. Lilley, *C.R.C. Critical Reviews in Food Science and Nutrition*, 27 (1988) 1.
- 3 C. van der Berg and S. Bruin, in L.B. Rockland and G.F. Stewart (Eds.), *Water Activity: Influences on Food Quality*, Academic Press, New York, 1981, p. 1.
- 4 P.J. Flory, *Principles of Polymer Chemistry*, Cornwell University Press, Ithaca, New York, 1953.
- 5 J.N. Kinsella and P.F. Fox, *C.R.C. Critical Reviews in Food Science and Nutrition*, 24 (1986) 91.
- 6 I.D. Kunz, Jr. and W. Kauzman, *Adv. Protein Chem.*, 28 (1974) 239.
- 7 S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 60 (1938) 309.
- 8 E.A. Guggenheim, *Applications of Statistical Mechanics*, Clarendon, Oxford, 1966.
- 9 R.B. Anderson, *J. Am. Chem. Soc.*, 68 (1946) 686.
- 10 J.H. de Boer, *The Dynamic Character of Adsorption*, Clarendon, Oxford, 1953.
- 11 R. Jowitt, F. Escher, M. Kent, B. McKenna and M. Roques (Eds.), *Physical Properties of Foods, Project COST-90, Part 1, 13-102*, Elsevier, London, 1983.
- 12 J.A. Troller and J.H.B. Christian, *Water Activity in Foods*, Academic Press, New York, 1979.
- 13 K. Hallega, in F. Franks and S. Mathias (Eds.), *Biophysics of Water*, Wiley, Chichester, 1982.
- 14 J.B. Matthew, *Ann. Rev. Biophys. Biophys. Chem.*, 16 (1986) 163.
- 15 K.D. Ross, *Food Technology*, 29 (1975) 26.
- 16 T.H. Lilley, *Int. J. Food Sci. Technol.*, 22 (1988) 563.
- 17 S.T. Soekarto and M.P. Steinberg, in L.B. Rochland and G.F. Stewart (Eds.), *Water Activity: Influences on Food Quality*, Academic Press, New York, 1981.
- 18 M. Ollivon, S. Quinquenet, M. Seras, M. Delmotte and C. More, *Thermochim. Acta*, 125 (1988) 141.
- 19 M. Seras, B. Courtois, S. Quinquenet and M. Ollivon, in R. Jowitt, F. Escher, M. Kent, B. McKenna and M. Roques (Eds.), *Physical Properties of Foods, Project COST-90 bis*, 17, Elsevier, London, 1987, p. 217.
- 20 I.C.M. Dea, in S. Paoletti and G. Blunden (Eds.), *Phytochemicals and Fine Chemicals, COST, EEC, Brussels*, 1988, p. 70.
- 21 E.R. Morris, in V. Crescenzi, I.C.M. Dea and S.S. Stivala (Eds.), *Recent Development of Industrial Polysaccharides*, Gordon and Breach, New York, 1987.
- 22 E.R. Morris, in M. Yalpani (Ed.), *Industrial Polysaccharides: Genetic Engineering, Structure/Properties Relations and Applications*, Elsevier, Amsterdam, 1987, p. 225.
- 23 D.A. Brant (Ed.), *Solution Properties of Polysaccharides*, ACS Symp. Ser. N. 150, Washington, 1981.
- 24 R.C. Jordan, D.A. Brant and A. Cesaro, *Biopolymers*, 17 (1978) 2617.
- 25 A. Cesaro, in H.J. Hinz (Ed.), *Thermodynamic Data for Biochemistry and Biotechnology*, Springer-Verlag, Berlin, 1986, p. 177.
- 26 F. Franks, *Pure Appl. Chem.*, 59 (1987) 1189.
- 27 L. Slade and H. Levine, in V. Crescenzi, I.C.M. Dea and S.S. Stivala (Eds.), *Recent Developments of Industrial Polysaccharides*, Gordon and Breach, 1987, p. 387.