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Thermal Gelation of Oat Globulin[1]

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The thermal gelation properties of oat globulin were studied under different conditions of temperature, protein concentration, pH, and ionic strength. Differential scanning calorimetry shows that oat globulin heated under conditions inducing gelation was not extensively denatured and exhibited highly cooperative transition characteristics. The chemical forces involved in gel formation were investigated by measuring the gel hardness under the influence of neutral salts, reducing agents, denaturants, and water-miscible solvent. Some fatty acid salts were effective in improving the gelling property of oat globulin near neutral pH.

Thermal coagulation and gelation are important functional properties of food proteins. Gels act as a medium for holding water, lipids, flavors, and other ingredients and impart unique rheological and textural qualities to food systems (Kinsella, 1979). As defined by Hermansson (1979), thermal coagulation is the random interaction of protein molecules to form aggregates, while gelation involves the formation of a three-dimensional network exhibiting a certain degree of order. Most heat-coagulable proteins are of animal origin, and the failure of most plant proteins to gel has been attributed to relatively high heat stability of the proteins (German et al., 1982).

Oat globulin, the major protein fraction in oats, has a quaternary structure very similar to that of soy 11S globulin (glycinin), a heat-coagulable protein. It is made up of six acidic and six basic polypeptides, and each acidic polypeptide is linked to a basic polypeptide by disulfide bonds to form a subunit. The six subunits are linked through noncovalent forces to form the hexamer (Derbyshire et al., 1976; Neilsen, 1985; Brinegar and Peterson, 1982). Our previous report (Ma and Harwalkar, 1987) shows that when a dilute oat globulin solution was heated at high ionic strength, both soluble and insoluble aggregates were formed, but the coagulation behavior was found to be significantly different from that of soy glycinin. While the heat-induced gelation of soy glycinin and the chemical forces involved have been extensively studied (Catsimpoolas and Meyer, 1970, 1971; Shimada and Matsushita, 1980; Mori et al., 1982, 1986; Babajimopoulos et al., 1983; Utsumi and Kinsella, 1985), little is known about the thermal gelation of oat globulin. The present work was conducted to study the gelling properties of oat globulin under various environmental conditions and to elucidate the mechanism and molecular forces involved in gel formation.

MATERIALS AND METHODS

Materials. Oats (variety Sentinel) were grown at the Central Experimental Farm, Ottawa, Canada. Dehulled groats were ground in an Alpine pin mill (Model 160 Z) and defatted by Soxhlet extraction with hexane.

Preparation of Oat Globulin. Globulin was extracted from defatted ground groats by the Osborne fractionation procedure (Osborne and Mendel, 1914). Groats were mixed with 1.0 M NaCl at a solvent to solid ratio of 10:1 and stirred at room temperature for 30 min. The slurry was centrifuged at 20000*g* for 30 min, and the residue was reextracted twice with 1.0 M NaCl. The combined supernatant was dialyzed exhaustively against distilled water at 4 °C, and the precipitated globulin was recovered by centrifugation and freeze-dried.

Heat Treatment. Dispersions of oat globulin were prepared at different protein concentrations with distilled water. Varying amounts of NaCl and other additives were added as solids, and the pH of the dispersions was then adjusted by the addition of 1 N HCl or NaOH. Mixing was by magnetic stirring in most cases, but for preparations containing reagents that are not readily dispersible in aqueous solution, e.g., fatty acid salts, mixing was by a Biosonik ultrasonic homogenizer (Bronwill Scientific, Rochester, NY) at low-energy output. The samples were then subjected to vacuum evacuation to remove dissolved air. Aliquots (4.0 mL) of samples were pipetted into 1.2 × 4 cm glass tubes. The tubes were covered with glass marbles and heated in a water bath at preset temperature. After heating, the tubes were immediately cooled by immersing in an ice bath.

Measurement of Gel Hardness. Hardness of the heated samples was measured with an Ottawa Texture

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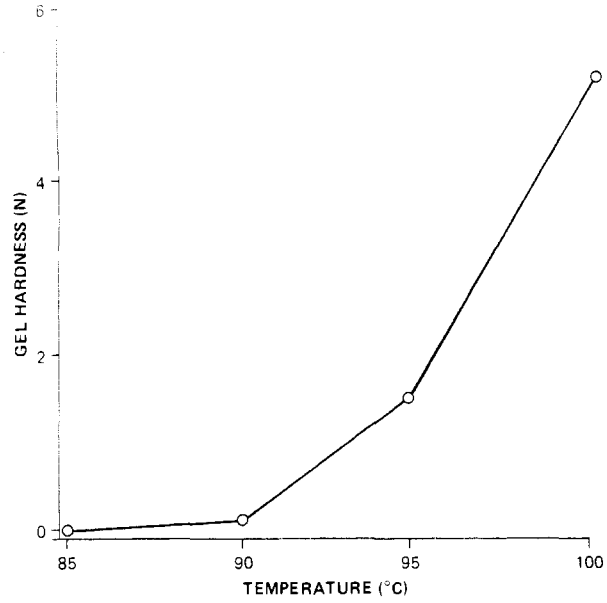

Figure 1. Effect of temperature on gel hardness.

Measuring System (OTMS) equipped with data acquisition system developed by the Engineering and Statistical Research Centre of Agriculture Canada. The back-extrusion method of Kramer and Hawbecker (1966) was used. A probe with diameter 1.0 mm less than the internal diameter of the glass tubes was lowered onto the sample at a crosshead speed of 5 cm/min to a depth of 2 cm, and the plateau force (in newtons) was recorded as gel hardness. Six replicates were measured for each treatment.

Differential Scanning Calorimetry (DSC). The thermal characteristics of native and heated oat globulin were examined by DSC using a Du Pont 1090 thermal analyzer equipped with a 910 DSC cell base and a high-pressure cell. Dispersions of oat globulin (10% w/v) were prepared by magnetic stirring or ultrasonic homogenization. After adjustment of pH and ionic strength, aliquots (10 μL) of the protein dispersion containing approximately 1 mg of globulin were pipetted onto polymer-coated aluminum pans and sealed with lids. A sealed empty pan was used as reference. To study the effect of heat treatment on DSC characteristics, oat globulin was heated in the sealed pan in an equilibrated water bath. After heating, the pan was cooled rapidly in an ice bath and reequilibrated to room temperature. The pan containing heat-treated protein was then heated in the calorimeter at a linear rate of 10 °C/min over the range of 30–140 °C. The onset temperature (T_m), peak or denaturation temperature (T_d), and heat of transition or enthalpy (ΔH) were computed from the thermograms by the 1090 analyzer. Width of peak at half-height ($\Delta T_{1/2}$) was also recorded for some samples.

RESULTS AND DISCUSSION

Due to the low solubility of oat globulin at acidic and neutral pH, an alkaline pH of 9.7 was used for most experiments, which gave a stable dispersion of globulin at 10% (w/v). Other conditions suitable for gelation were also established in preliminary experiments. Unless specified otherwise, oat protein gels were prepared at 10% protein, pH 9.7, 0.2 M NaCl, and heating at 100 °C for 20 min. Gels prepared under these conditions were opaque and off-white, had a smooth texture, and exhibited good water-holding capacity (no syneresis when subjected to centrifugation at 2000g for 15 min). The gels had a hardness reading of 5.2 N, which compared favorably with 7.0 N for 10% egg white gels prepared under identical conditions except at pH 7.0.

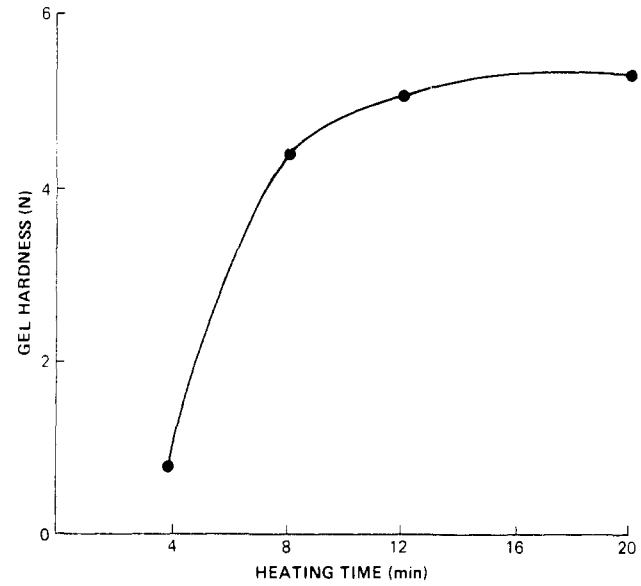

Figure 2. Effect of heating time on gel hardness.

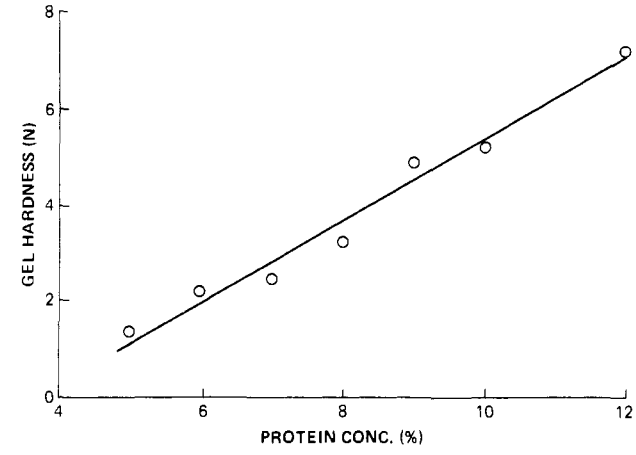

Figure 3. Effect of protein concentration on gel hardness.

Effects of Heating Temperature and Time. Figure 1 shows that oat globulin gelled at fairly high temperature. No gelation occurred below 90 °C although the dispersion became viscous. The gel hardness increased rapidly from 90 to 100 °C. The shape of the curve suggests that a harder gel can be obtained at temperature above 100 °C. The observation is consistent with the high heat stability of oat globulin with a denaturation temperature of about 110 °C (Harwalkar and Ma, 1987). Figure 2 shows that gel hardness increased progressively with an increase in heating time, leveling off at around 20 min.

Effect of Protein Concentration. Figure 3 shows that gel hardness is dependent on protein concentration. At concentration below 5%, no free-standing gel can be obtained. The gel hardness increased linearly with an increase in protein concentration from 5 to 12%.

Effect of Ionic Strength and pH. Figure 4 shows that ionic strength has a profound influence on gel-forming ability of oat globulin. At NaCl concentration below 0.05 M, no gels can be obtained. The gel hardness increased progressively with an increase in NaCl concentration to a maximum of 0.4 M. At higher ionic strength, gel hardness decreased and syneresis became significant at salt concentration above 0.8 M. Figure 5 shows that pH also has a significant effect on gelation. At acidic and neutral pH, very weak gels with poor water retention were obtained. The gel hardness increased rapidly from pH 8 to

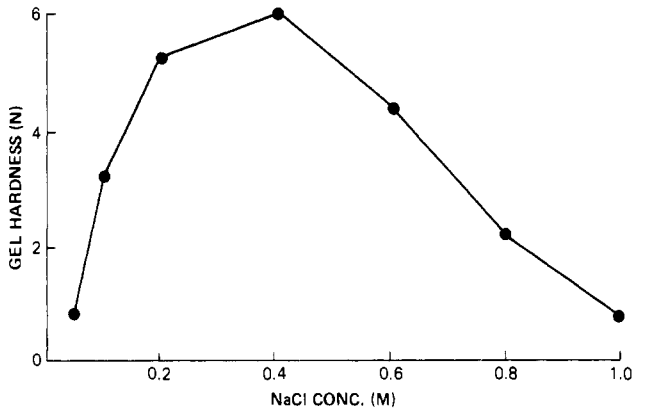

Figure 4. Effect of salt concentration on gel hardness.

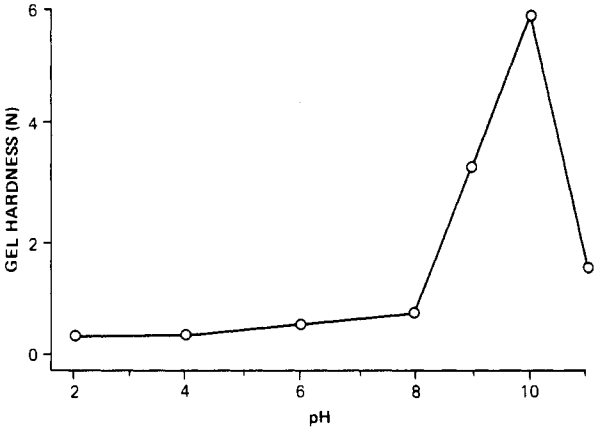

Figure 5. Effect of pH on gel hardness.

10 and then decreased markedly at higher pH.

Formation of gels is governed by the equilibrium between attractive (hydrogen bonding, hydrophobic interaction, disulfide linkage) and repulsive (electrostatic) forces among the thermally altered molecules (Ferry, 1948; Hermansson, 1979; Kinsella, 1982). The lack of gelation at very low salt concentrations may be attributed to the predominance of electrostatic forces at low ionic strength (Kinsella, 1982). NaCl and other salts have a charge-shielding effect (von Hippel and Schleich, 1969; Damodaran and Kinsella, 1982), and the suppression of ionic repulsion at higher NaCl concentration would enhance protein–protein interaction and the formation of a stable gel network. At NaCl concentration above 0.4 M, however, extensive cross-linking between oat globulin molecules may lead to compaction and collapse of the protein matrices with syneresis. The influence of pH on gelation may also be related to the charge effect. The basic polypeptide of oat globulin has an isoelectric point (pI) of around pH 9 (Brinegar and Peterson, 1982), and protein–protein interaction is generally optimal near pI where charge repulsion is balanced by charge attraction. The low gel hardness at acidic and neutral pH can be attributed to poor solubility of oat protein at this pH range (Ma and Harwalkar, 1984). In some preparations, protein precipitation was observed before the samples were heated, thus lowering the amount of dispersible protein and leading to poor gelation.

Thermal Transition Characteristics of Oat Globulin Gels. Figure 6 and Table I show the changes in DSC characteristics of oat globulin. When analyzed near neutral pH (no pH adjustment) in the presence of 0.2 M NaCl, oat globulin has a T_d of 111.0 °C and an enthalpy of 25.6 J/g. The thermogram shows a fairly sharp peak (Figure 6A)

Table I. Thermal Transition Characteristics of Oat Globulin[a]

treatment[b]	T_m, °C	T_d, °C	$\Delta T_{1/2}$, °C	ΔH, J/g
no pH adjustment	100.8 ± 0.5	111.0 ± 0.4	10.1 ± 0.1	25.6 ± 2.0
adjusted to pH 9.7	97.5 ± 0.4	109.6 ± 0.3	11.3 ± 0.1	18.3 ± 1.6
pH 9.7, preheated at 100 °C for 20 min	104.5 ± 0.5	111.1 ± 0.4	8.2 ± 0.1	14.7 ± 1.5

[a] Average of triplicate determinations ± SE. [b] Protein samples (10%) prepared in 0.2 M NaCl.

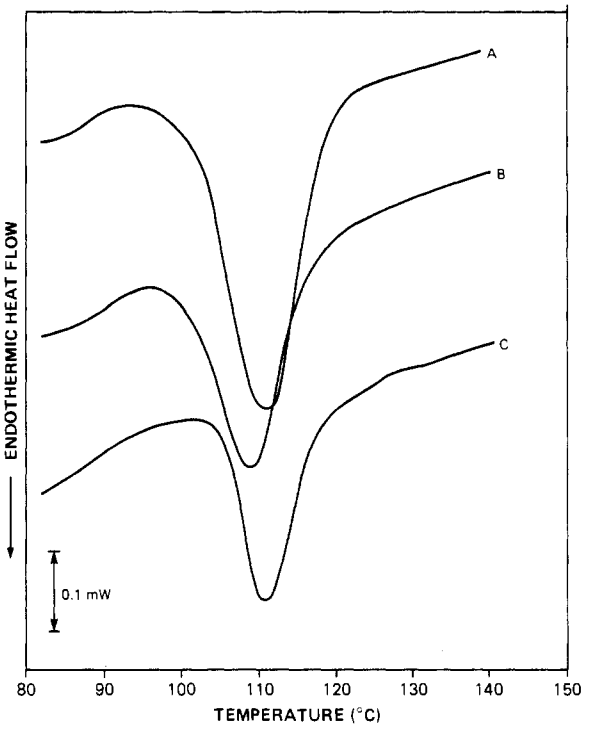

Figure 6. Differential scanning calorimetric thermograms of oat globulin; protein samples (10%) prepared in 0.2 M NaCl: (A) no pH adjustment; (B) pH adjusted to 9.7; (C) pH adjusted to 9.7 and preheated at 100 °C for 20 min.

with a $\Delta T_{1/2}$ value of 10.1 °C (Table I). When the medium was adjusted to pH 9.7, there was a broadening of the peak (Figure 6B) with a decrease in T_m and an increase in $\Delta T_{1/2}$ value, and both T_d and ΔH were lowered (Table I). When 10% globulin was preheated at 100 °C for 20 min, cooled, and reanalyzed by DSC, there was a further decrease in ΔH but T_d was increased to a value close to that of the native protein (Table I). The endothermic peak was considerably sharper than those of the native and alkaline-treated samples (Figure 6C), indicated also by a marked increase in T_m and decrease in $\Delta T_{1/2}$ value.

Marked decrease in heat stability and partial denaturation of oat globulin were observed at extreme acidic and alkaline pHs (Harwalkar and Ma, 1987) and was attributed to intramolecular charge repulsion. The fact that the protein was partially unfolded at alkaline pH prior to heating may play an important role in the thermal gelation process, probably by promoting more extensive protein interaction and aggregation. The present data show that when oat globulin was preheated under conditions leading to gelation (100 °C for 20 min at pH 9.7), there was a slight decrease in enthalpy (from 18 to 15 J/g), suggesting further denaturation. The decrease in enthalpy may also be due to protein aggregation (gelation), which is considered an exothermic reaction (Jackson and Brandts, 1970; Privalov and Khechinashvilli, 1974). The sharpness of an endothermic peak is an indication of the cooperative nature of the transition from native to denatured state (Wright et al., 1977). If denaturation occurred within a narrow range of temperature (low $\Delta T_{1/2}$ value), the transition is con-

Table II. Effect of Some Protein Structure Modifying Agents on Gel Hardness[a]

reagent	concn	gel hardness (N)
control (no additive)		5.20 ± 0.35[b]
dithiothreitol	10 mM	1.81 ± 0.08
N-ethylmaleimide	10 mM	3.71 ± 0.25
sodium dodecyl sulfate	0.5%	4.05 ± 0.34
sodium dodecyl sulfate	1.0%	2.13 ± 0.20
urea	3 M	3.86 ± 0.22
urea	6 M	1.39 ± 0.06

[a] All samples (10% protein) prepared in 0.2 M NaCl, pH 9.7. [b] Average of six determinations ± SE.

sidered highly cooperative. The sharpening of the peak and lowering of $\Delta T_{1/2}$ value in the heated sample therefore suggests increased cooperativity. This may be due to the fact that protein in a gel matrix has a more compact and ordered structure than protein in dispersion, would have higher heat stability (higher T_d), and would denature in a highly cooperative manner. The marked decrease in $\Delta T_{1/2}$ and increase in T_m could also be attributed to the existence of multiple domains with differing thermostabilities (Privalov, 1982). The endotherm shown in Figure 6C may represent the more heat-stable domains while the less stable ones were denatured by heat treatment.

Effects of Protein Structure Modifying Reagents. The effects of some protein structure perturbants on heat gelation were studied, and the results are presented in Table II. Dithiothreitol (DTT), a reducing agent, greatly reduced the gel hardness. DTT caused the dissociation of oat globulin into acidic and basic polypeptides by breaking disulfide linkages, promoting interactions of the dissociated monomers to form aggregates (Ma and Harwalkar, 1987). However, precipitation of the monomers would prevent the formation of a strong gel matrix. Addition of reductant also promoted aggregation (Wolf and Tamura, 1969) and reduced gel-forming ability of glycinin (Utsumi and Kinsella, 1985).

The addition of 10 mM N-ethylmaleimide (NEM), a SH-blocking agent, also decreased gel hardness (Table II). NEM may hinder gelation by blocking the free SH groups and preventing thiol disulfide exchange reaction. Heat aggregation of oat globulin near neutral pH in high ionic strength was not significantly affected by NEM (Ma and Harwalkar, 1987), suggesting that thiol–disulfide interchange was limited. The reactivity of SH groups is higher at alkaline pH than at neutral pH (Sawyer, 1968; Ananthanarayanan et al., 1977). Hence, thiol–disulfide interchange may play an important role in thermal gelation of oat globulin at pH 9.7. NEM was found to inhibit aggregation and gelation of glycinin at 100 °C in high ionic strength (Wolf and Tamura, 1969; Mori et al., 1982). When it was heated at 80 °C in low ionic strength, NEM did not prohibit gelation of glycinin but the gel formed was fragile (Utsumi and Kinsella, 1985).

The gel hardness was markedly reduced by the addition of 0.5 and 1% sodium dodecyl sulfate (SDS), an anionic detergent (Table II). SDS binds to proteins by noncovalent forces and causes denaturation (Steinhardt, 1975). Increases in net charge on protein molecules could increase ionic repulsion and hinder protein–protein interaction and thermal coagulation. Suppression of heat aggregation by SDS has been reported in egg white proteins (Hegg et al., 1978), arachin (Kella and Rao, 1985), and oat globulin (Ma and Harwalkar, 1987). The addition of another denaturant, urea at 3 and 6 M concentrations, also decreased the gel-forming ability of oat globulin (Table II). Urea destabilizes both hydrogen-bonding and hydrophobic interactions (Kinsella, 1982), and the data suggest that these secondary forces are involved in the gelation process.

Table III. Effect of Anions on Gel Hardness and T_d[a]

anion	gel hardness (N)	T_d, °C
Cl^-	5.20 ± 0.35[b]	110.3 ± 0.8[c]
Br^-	5.62 ± 0.30	108.7 ± 0.7
I^-	6.00 ± 0.42	107.4 ± 0.6
SCN^-	6.88 ± 0.44	106.1 ± 0.7

[a] All samples (10% protein) prepared in 0.2 M sodium salt with pH adjusted to pH 9.7. [b] Means of six determinations ± SE. [c] Average of three determinations ± SE.

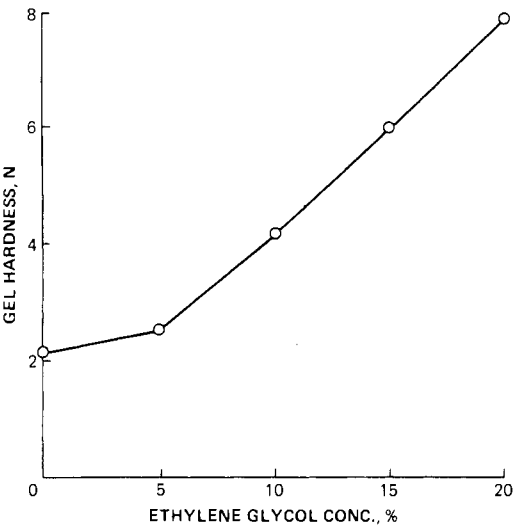

Figure 7. Effect of ethylene glycol concentration on gel hardness. Protein samples (10%) prepared in 0.2 M NaCl, pH 8.5.

When the anion in the buffer was changed from Cl^- to Br^-, I^-, and SCN^-, the gel hardness was increased, while T_d was decreased progressively from 110.3 to 106.1 °C (Table III). These anions follow the lyotropic series of salts (Hatefi and Hanstein, 1969), with increasing protein structure perturbing effect (von Hippel and Wong, 1964; Damodaran and Kinsella, 1982). Previous work (Ma and Harwalkar, 1987) indicates that the relative effectiveness of these anions in lowering heat stability and promoting thermal aggregation follows this lyotropic series. Although the heating temperature was below T_d, a decrease in thermal stability may enhance the disruption of the oat globulin quaternary structure, leading to more extensive aggregation and gelation. Anions higher in the lyotropic series also have greater water structure breaking activity and protein solubility (Damodaran and Kinsella, 1982) and may increase the concentration of soluble protein in the medium, leading to the formation of harder gel upon heating.

Figure 7 shows that gel hardness was markedly increased with an increase in the concentration of ethylene glycol (EG) in the medium. The buffer was adjusted to pH 8.5, and the gel hardness of the control sample (2.1 N) was considerably lower than that (5.2 N) at pH 9.7. EG, a water-miscible solvent, lowers the dielectric constant of the medium and enhances hydrogen-bonding and electrostatic interactions (Tanford, 1962; Damodaran and Kinsella, 1982). The data again suggest the involvement of such chemical forces in gelation of oat globulin. Thermal stability of oat globulin was also decreased markedly by EG (Harwalkar and Ma, 1987), which again may promote gelation.

Effects of Fatty Acid Salts. Since optimal gel formation of oat globulin required alkaline pH, which is not suitable for most food applications, attempts were made to lower the gelation pH and to retain good gelling prop-

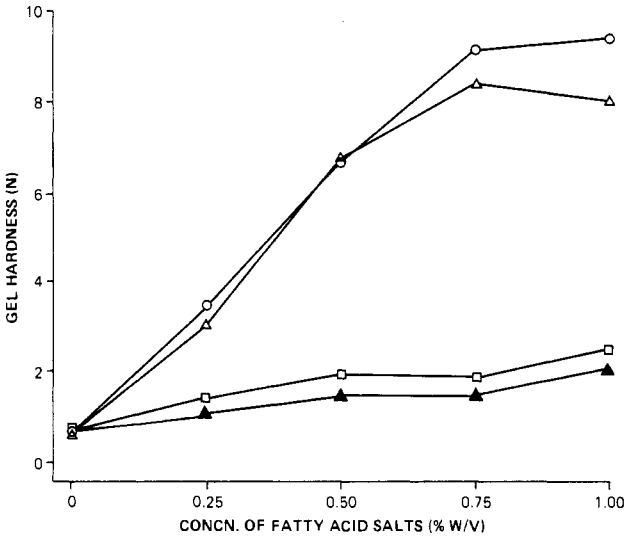

Figure 8. Effect of fatty acid salts on gel hardness; protein samples (10%) prepared in 0.2 M NaCl, pH 8.0: (△) sodium undecanoate; (○) sodium laurate; (□) sodium heptadecanoate; (▲) sodium stearate.

erties by the use of some fatty acid salts including sodium stearate, a food-grade additive.

Figure 8 shows that addition of some fatty acid salts has a profound effect on the gel-forming ability of oat globulin at pH 8.0. A very weak gel showing extensive syneresis (upon standing or centrifuging at low speed) was formed in the absence of fatty acid salts. Addition of either sodium undecanoate (C_{11}) or sodium laurate (C_{12}) led to a dramatic increase in gel hardness, leveling off at a concentration of 0.75% (w/v) of the salts in the medium. The gel hardness at salt concentration above 0.5% was actually higher than that (5.2 N) of the control gel formed at pH 9.7. Sodium heptadecanoate (C_{17}) and stearate (C_{18}) also promoted gelation although the increase in gel hardness was much less dramatic compared with the other two salts (Figure 8). The gels formed in the presence of any of the four fatty acid salts had excellent water-holding capacity. When the gel samples were centrifuged at 2000*g* for 15 min, the percentage syneresis was decreased from over 50% for the control (no additive) to less than 10% in the presence of 0.5% fatty acid salt. It was also noted that fatty acid salts improved gelling properties of oat globulin even without added NaCl, and gels can be formed at considerably lower temperatures (<90 °C).

These fatty acid salts also affect the thermal stability of oat globulin. Figure 9 shows that T_d was markedly reduced by either sodium laurate and undecanoate, while sodium heptadecanoate and stearate only led to a slight decrease in T_d. The enthalpy was not significantly affected by fatty acid salts (data not shown).

Fatty acid salts have been found to improve gel-forming ability and reduce thermal stability of myosin (Egelandsdal et al., 1965). Fatty acid salts with higher aliphatic chain length produced greater changes in myosin, whereas our data show that salts with lower chain length were more effective. It was suggested that the increase in gel strength was due to binding of these amphiphiles to protein, causing repulsion between protein chains and a more ordered aggregation (gelation) upon heat treatment (Egelandsdal et al., 1965). Reduction in heat stability may also promote gelation.

GENERAL DISCUSSION

Our data show that, under appropriate conditions of pH, ionic strength, and protein concentration, oat globulin can form a fairly firm gel with a smooth texture and good

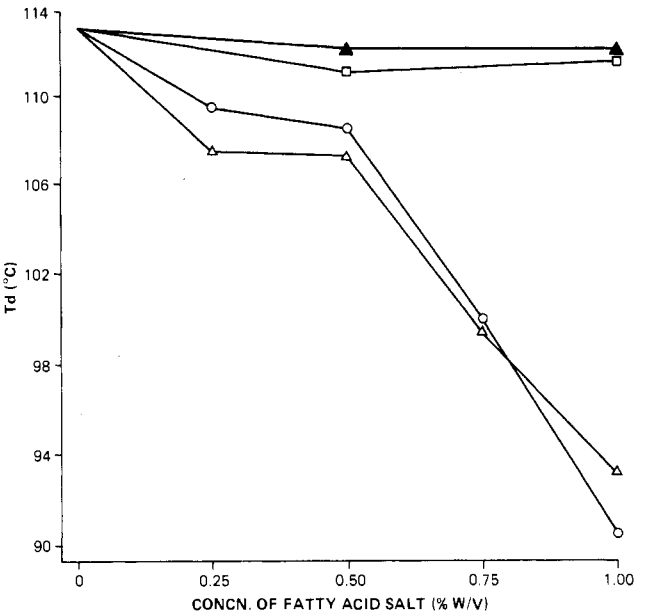

Figure 9. Effect of fatty acid salts on thermal transition temperature (T_d) of oat globulin; protein samples (10%) prepared in 0.2 M NaCl, pH 8.0: (△) sodium undecanoate; (○) sodium laurate; (□) sodium heptadecanoate; (▲) sodium stearate.

water-holding property. This is unique considering the exceptionally high thermal stability of the protein. Gelation can occur at temperatures (90–100 °C) well below the denaturation temperature (≈110 °C), and DSC data show that the heat-induced gels retained considerable native structure when compared to the unheated control, suggesting that gelation did not require extensive protein denaturation. This seems to contradict the generally accepted view that coagulation (and gelation) is preceded by denaturation, following the scheme $N \rightleftharpoons D \rightarrow A$, where N denotes native protein, D denatured molecule, and A the aggregate (or gel) (Ferry, 1948). However, it has been suggested that, for oligomeric proteins with complex quaternary structures such as glycinin, heat may cause association/dissociation of the oligomer to induce aggregation and disruption of the quaternary structure alone can lead to coagulation/gelation (German et al., 1982).

Although gelation of oat globulin occurred at temperatures below its T_d, gel hardness was greatly influenced by the amount of heat (temperature/time) applied, and a lowering in T_d by various treatments (e.g., addition of specific anions, ethylene glycol, and fatty acid salts) improved the gel-forming ability. Mori et al. (1986) showed that 10% glycinin gels prepared by heating at 100 °C for 20 min were 4 times harder than those heated for 1 min, and electron microscopic examination concluded that increased gel hardness by prolonged heating was attributed to stabilization of the initial network structure by various molecular forces. When they are subjected to identical heat treatment, the protein with lower thermal stability would be able to form the initial gel network more readily than the protein with higher heat stability, and the network can therefore be stabilized to a greater extent. A decrease in thermal stability may also enhance disruption of the quaternary structure of oat globulin by heat, promoting aggregation and gelation.

Reagents such as neutral salts, reductant, SH-blocking agents, denaturants, and water-miscible solvents perturb the tertiary and quaternary structures of proteins by stabilizing or destabilizing covalent and noncovalent chemical forces. These reagents affected oat globulin gelation to varying extents, and the data suggest that formation of a

gel network depends on the balance between attractive (hydrogen-bonding and hydrophobic interactions) and repulsive (electrostatic) forces. Disulfide linkage and thiol–disulfide exchange reaction may also play a role in the gelation process, although their involvement in thermal aggregation of oat globulin (at low protein concentrations) was limited (Ma and Harwalkar, 1987).

Like other plant proteins such as glycinin, oat globulin has limited use as a heat-coagulable protein in food formulations due to its high heat stability and low dispersibility near neutral pH. The alkaline pH for optimal oat globulin gelation is also not normally encountered in foods. The effectiveness of additives such as some fatty acid salts in lowering heat stability and promoting gel formation at pH near neutrality may enhance the use of oat protein in food applications requiring gelation at lower temperature and pH, e.g., comminuted meat products.

ACKNOWLEDGMENT

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Registry No. Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; SCN^-, 302-04-5; NaCl, 7647-14-5; dithiothreitol, 3483-12-3; *N*-ethylmaleimide, 128-53-0; Na dodecyl sulfate, 151-21-3; urea, 57-13-6; ethylene glycol, 107-21-1; Na undecanoate, 17265-30-4; Na laurate, 629-25-4; Na heptadecanoate, 1002-82-0; Na stearate, 822-16-2.

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