



The presence of alkylcyclopentanes and alkylcyclohexanes in the pyrolysis of oils with high oleic acid content indicates that ring formation may occur with the assistance of the double bond through a mechanism similar to that proposed in Figure 1.

The high potential of one of these palms as renewable resource of energy is illustrated in Chart I, which is an overview of the major products obtained from babassu nut; this palm tree grows wild throughout more than 35 million acres in the Brazilian northeastern states.

Registry No. 1-Hexene, 592-41-6; n-hexane, 110-54-3; 1heptane, 592-76-7; n-heptane, 142-82-5; 1-octene, 111-66-0; noctane, 111-65-9; 1-nonene, 124-11-8; n-nonane, 111-84-2; 1-decene, 872-05-9; n-decane, 124-18-5; 1-undecene, 821-95-4; n-undecane, 1120-21-4; 1-dodecene, 112-41-4; n-dodecane, 112-40-3; 1-tridecene, 2437-56-1; n-tridecane, 629-50-5; 1-tetradecene, 1120-36-1; ntetradecane, 629-59-4; 1-pentadecene, 13360-61-7; n-pentadecane, 629-62-9; n-hexadecane, 544-76-3; n-heptadecane, 629-78-7; noctadecane, 593-45-3; methylcyclohexane, 108-87-2; ethylcyclopentene, 2146-38-5; methylcyclohexene, 1335-86-0; ethylcyclohexane, 1678-91-7; ethylcyclohexene, 27138-39-2; n-propylcyclohexane, 1678-92-8; n-propylcyclohexene, 31620-24-3; n-butylcyclopentene, 50984-85-5; n-butylcyclohexane, 1678-93-9; namylcyclopentane, 3741-00-2; n-amylcyclopentene, 29031-90-1; n-butylcyclohexene, 31620-25-4; n-amylcyclohexane, 4292-92-6; n-amylcyclohexene, 31620-32-3; n-hexylcyclopentane, 4457-00-5; n-hexylcyclopentene, 87156-78-3; n-hexylcyclohexane, 4292-75-5; n-heptylcyclopentene, 87156-79-4; n-hexylcyclohexene, 31620-26-5; n-octylcyclopentane, 1795-20-6; n-octylcyclohexane, 1795-15-9; n-nonylcyclohexane, 2883-02-5; oleic acid, 112-80-1.

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Effects of Various Anions on the Rheological and Gelling Behavior of Soy Proteins: Thermodynamic Observations

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The effects of neutral salts on the gelation of soy protein isolate and the 7S and 11S protein fractions were studied. The relative effects of salts on the viscosities of progel and gel followed the lyotropic series for anions, i.e., $SO_4^{2-} < Cl^- < Br^- < SCN^-$. NaSCN, which is a protein structure destabilizer, profoundly increased the melting temperature as well as viscosity of the gel, whereas NaCl, which is a protein structure stabilizer, decreased the gel viscosity but increased the melting temperature. However, the ΔH° of gelation was unaffected by the type of the salts used and exhibited a value of about 1 kcal/mol. On the basis of the results, we invoke that the major forces involved in the gelation of soy protein is hydrogen bonding and van der Waals interactions; the contribution of hydrophobic and electrostatic interaction is negligible.

The possession of a range of functional properties has considerably extended the potential use of soy proteins in food applications. Properties such as water binding, emulsifying, whipping, thickening, flavor binding, and the ability to form films and gels have been successfully realized in many food formulations and in new product development in recent years (Kinsella, 1979). The ability of gels to act as a matrix for holding water, lipids, sugars, flavors, and other ingredients is important in comminuted

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sausage products and is the basis of many oriental foods such as tofu (Kinsella, 1976). Previous studies have shown that heat-induced gelation of the aqueous dispersion of soy globulin depends on protein concentration and time and temperature of heating (Catsimpoolas and Meyer, 1970; Circle et al., 1964; Furukawa et al., 1979). The effects of salts, thiols, sulfite, and lipids have been studied to understand the mechanism and the molecular forces involved in the gelation process (Aoki, 1965; Catsimpoolos and Meyer, 1970, 1971; Circle et al., 1964; Furukawa et al., 1979; Ishino and Kudo, 1977). The results led to the suggestion that the three-dimensional network of gel structures may be formed via hydrogen bonding, hydrophobic associations, and ionic interactions and possibly through disulfide linkages of unfolded polypetides. The major forces involved in stabilizing the gel network have not been characterized.

Since 7S and 11S constitute the major fractions of soy proteins, knowledge of their behavior to environmental perturbants such as temperature, pH, ionic strength, and solvent composition is basic to the understanding of gelation phenomena. Determination of conformational responses to the changes in the external environment in terms of measurable rheological parameters of progel and thermodynamic evaluation of phase-transition characteristics of progel-gel systems should aid in establishing some pattern of experimental behavior and interpretation of the interactions involved.

The present study was undertaken to elucidate the effects of specific anions on the rheological properties of soy protein dispersions during heating and cooling regimes and relate these to changes in terms of the conformational and bulk properties of the system. Based on thermodynamic calculations and observations of the effects of different salts in stabilizing the network, an estimation of enthalpy changes during reversible progel-phase transitions was made.

MATERIALS AND METHODS

Preparation of Whole Soy Protein Isolate (SI), 7S, and 11S Components. Soy protein isolate, 7S, and 11S components were prepared from defatted soybean flour according to the method of Thanh and Shibasaki (1976). In all experiments, freshly prepared dispersions were used. Dispersions of the proteins in distilled water were made up on a weight percentage basis. Mixing was accomplished with a magnetic stirrer. Air was removed by low-speed centrifugation.

When salts were added to the dispersions, salt was first dissolved in half of the final amount of water and then mixed with the protein dispersed in the remaining water. This was done to enhance solubilization of the proteins. The pH of the dispersions was adjusted by using 1 N HCl or NaOH.

Viscosity. Viscosity was measured with a Haake Rotovisco RV-1 viscometer by using an NV spindle with a double-gap beaker mounted in a double-walled temperature control assembly. The temperature of the sample was maintained by circulating water from a constant-temperature bath through the jacket of the assembly.

The volume of the sample used was 9 mL. Measurements were taken at 5-min intervals for the specified total heating time. The zero time represents a 2-min lapse from the addition of sample to the first reading. This was the time required for the sample to reach the required jacket temperature. Subsequent to attainment of the heating temperature, samples were cooled down to 5 °C by circulating cold water. During cooling of the samples, viscosity was measured at each 10 °C temperature drop.



Figure 1. (A) Viscosity of soy isolate (SI), 7S, and 11S proteins as a function of time upon heating at 80 °C. (B) Viscosity changes during progel to gel transition upon cooling from 80 to 5 °C. Protein concentration was 11% in water, pH 8.0. The shear rate was 523.3 s^{-1} .

Melting Point. The melting point of the gel was determined by a modification of the method described by Bello et al. (1962). Protein dispersions (5 mL) were placed in test tubes (10×76 mm) that were stoppered and heated at 80 or 90 °C for 30 min. The tubes were then cooled in an ice bath and stored at 4 °C for 24 h. Steel ball bearings (2.67 g and approximately 8 mm in diameter) were placed just under the surface of the gel, and the tube was heated by immersion in a water bath. The temperature of the gel was monitored by using a thermocouple, which was inserted in a tube identical with the sample tube. The melting point was taken as the temperature at which the ball reached the bottom of the tube.

Expansion and Contraction of Gels. Cylindrical glass micropipets (100 μ L) were filled to the mark with the protein dispersions. The micropipets were stoppered at both ends with a rubber band. The tubes were immersed in a constant-temperature water bath, and the samples were heated at the indicated temperature for 30 min. At the end of the heating time, the change in length was measured with a magnifier (divisions 0.005 in.), and then the micropipets were immersed in an ice bath for 1 h. The change in length of the gel due to contraction was measured. The coefficient of expansion or contraction, defined as the ratio of change in volume (ΔV) to initial volume (V), was computed as $\Delta V/V = (\Delta L/L) \times 100$.

RESULTS AND DISCUSSION

The heat-induced viscosity changes in soy protein isolate and the two major protein fractions, i.e., 7S and 11S, are shown in Figure 1A. Heating of the protein solution irreversibly converts the sol state to progel state, which is reflected in increase in the viscosity (Catsimpoolas and Meyer, 1970). The progel viscosity of the 7S fraction was significantly higher than that of the 11S component. This may be due to differences in their molecular structures as well as their differential response to thermal treatment. The 11S protein contains 21 disulfide linkages (Badley et al., 1975). The extensive inter- and intramolecular disulfide linkages within the oligomeric structure of 11S



Figure 2. Effect of temperature of heating and protein concentration on the apparent (A) expansion and (B) contraction of soy isolate gel at pH 8.0.

renders it more resistant to thermal dissociation and unfolding of the subunits (German et al., 1982). Furthermore, since the thermal transition temperature of 11S at zero ionic strength is about 80 °C (Hermansson, 1978), the lower progel viscosity of 11S at 80 °C may be due to incomplete unfolding of the protein. On the other hand, the absence of disulfide linkages and the lower thermal transition temperature, i.e., 67 °C (Hermansson, 1978) of 7S may facilitate ready thermal dissociation and subsequent unfolding of the 7S protein. The net increase in the hydrodynamic volume as well as increase in the intermolecular interactions upon unfolding may increase the frictional resistance to flow, which is reflected in the higher progel viscosity (Figure 1A). This is in agreement with some of the other reports in the literature (Rha and Lee, 1977; Saio et al., 1969). However, the rate of increase in the progel viscosity of soy protein isolate was higher than that of the individual protein fractions (Figure 1A). This may reflect interactions between the subunits of the constituent 7S and 11S protein fractions during heating. Recently, it has been shown that upon heating both 7S and 11S undergo dissociation and denaturation and the dissociated basic subunits of 11S interact electrostatically with the subunits of 7S, forming soluble complexes (Damodaran and Kinsella, 1982). The hydrodynamic flow behavior of such complexes may be different from that of the individual components. This may be the reason for the observed higher progel viscosity of heated soy protein isolate. The gel viscosity of soy protein isolate was also significantly higher than that of the combined 7S and 11S protein fractions (Figure 1B). This indicates that the complexes formed between the subunits of 7S and 11S upon heating



Figure 3. Effects of various neutral salts on the apparent viscosity of soy isolate progels formed after heating 10% protein dispersions at 80 °C for 40 min. pH was 8.0. The shear rate was 348.9 s⁻¹.

form a better and stronger three-dimensional network upon cooling than the 7S or 11S fraction alone. The heat-induced unfolding and the subsequent increase in the hydrodynamic volume are reflected in the positive changes in the coefficient of expansion of the progel as well as the coefficient of contraction upon cooling of soy isolate gels (Figure 2).

The major forces involved in the formation of a threedimensional network in thermally reversible gels are noncovalent in nature such as hydrogen bonding and hydrophobic and electrostatic interactions. In order to understand the magnitude of contribution of each force in the formation of gel structure, the effects of various neutral salts on gelation were studied. The rationale for this approach was based on the assumptions that at low concentrations neutral salts affect electrostatic interaction between protein molecules via charge neutralization by the counter ions, while at sufficiently higher concentrations, in addition to charge neutralization effects, neutral salts have specific effects on protein conformation and affect hydrophobic interactions between the nonpolar residues (von Hippel and Schleich, 1969; Damodaran and Kinsella, 1981). In this respect, NaCl and Na_2SO_4 act as structure stabilizers whereas NaSCN acts as a structure destabilizer. If either electrostatic interactions or hydrophobic interactions are involved in the formation of protein gel structure, then it is reasonable to assume that in the presence of neutral salts the selective weakening of these forces on the strength of the gel may reveal the relative magnitude of these forces in the formation and maintenance of the gel matrix.

The effects of NaCl, Na₂SO₄, NaBr, and NaSCN on the viscosity of progel at various concentrations are shown in Figure 3. The viscosity of the progel decreased with salt concentration in the case of Na₂SO₄, NaCl, and NaBr, indicating that the protein molecules are protected from thermal unfolding at higher concentrations of these salts. While the NaCl-, NaBr-, and NaSCN-treated gels were translucent in appearance, the Na₂SO₄-treated gels were opaque. This could be due to insolubilization and precipitation of the protein by Na₂SO₄. In the presence of NaSCN the progel viscosity increased with salt concentration, indicating that the protein was progressively unfolded. Similar results were also obtained for the viscosity of the gel after cooling at 5 °C (Figure 4).

The rate of change in the viscosity of soy protein dispersion (10%) at 80 °C in the presence of 0.75 M NaCl,



Figure 4. Effects of various neutral salts on the apparent viscosity of 10% soy isolate dispersion cooled at 5 °C after being heated at 80 °C for 40 min at pH 8.0. The shear rate was 348.9 s⁻¹.



Figure 5. (A) Effects of various salts on the rate of change of apparent viscosity of 10% soy protein isolate in water heated at 80 °C, pH 8.0. (B) Apparent viscosities of soy protein isolate at different temperatures during the cooling cycle. The shear rate was 348.9 s⁻¹.

NaBr, Na₂SO₄, and NaSCN is shown in Figure 5. The rate of change as well as the maximum viscosity of the progel after 40 min of heating was considerably higher in the presence of 0.75 M NaSCN and lower in the presence of NaCl, NaBr, and Na₂SO₄ compared to the control. A similar pattern was obtained for the viscosity of the gels after cooling at 5 °C. The relative effects of the salts on the viscosities of progel and gel followed the lyotropic series (von Hippel and Schleich, 1969)

$$\mathrm{SO}_4^{2-} < \mathrm{Cl}^- < \mathrm{Br}^- < \mathrm{SCN}^-$$

Both NaCl and Na_2SO_4 are known to stabilize protein structure by stabilizing hydrophobic interactions, whereas NaSCN destabilizes the protein structure via weakening of the hydrophobic interactions within the protein (von Hippel and Schleich, 1969). The observed lower progel viscosity as well as the gel viscosity in the presence of NaCl and Na_2SO_4 may be due to stabilization of the protein



Figure 6. Log concentration vs. reciprocal melting temperature plots for soy isolate gels in the presence of 0.5 M NaCl and NaSCN. The gels were formed by heating the aqueous protein dispersions at 90 °C, pH 8.0, for 30 min and then aging at 4 °C for 24 h.

structure against thermal denaturation. Similar observations were made by Catsimpoolas and Meyer (1970). In the presence of NaSCN, which is known as a structure destabilizer, heating of soy protein at 80 °C may result in complete unfolding of the protein. Such extensive unfolding increases the effective hydrodynamic volume of the protein, which is reflected in the higher progel viscosity.

It is interesting to note that the viscosity of the soy gel was higher in the presence of NaSCN and lower in the presence of NaCl, NaBr, and Na₂SO₄ (Figures 4 and 5). If the hydrophobic interactions play an important role in the formation of gel structure, then in the presence of NaSCN, which is known to destabilize hydrophobic interactions, one would expect a decrease in the strength of the gel. Similarly, in the presence of NaCl and Na_2SO_4 , which are known to stabilize hydrophobic interactions, one would expect an increase in the gel strength. However, the formation of a stronger gel in the presence of NaSCN and weaker gels in the presence of NaCl and Na_2SO_4 suggests that the contribution of hydrophobic interactions to the formation of a three-dimensional gel structure is marginal. The observed higher gel viscosity in the presence of NaSCN could be due to extensive unfolding of the protein. The unfolding of the protein would expose large numbers of functional groups from the interior of the protein to the aqueous environment, which facilitates formation of an intricate three-dimensional network of unfolded polypeptides with numerous hydrogen bonds. On the other hand, the stabilizing effect of NaCl and Na_2SO_4 on protein structure by minimizing unfolding may reduce the effective number of contact points for hydrogen bonding and thus decrease the gel viscosity.

In order to understand the thermodynamics of soy protein gels, the effect of protein concentration on the melting point of the gel was studied. The data were analyzed according to the relationship (Eldridge and Ferry, 1954)

$$\log C = \frac{\Delta H^{\circ}}{2.303 R T_{\rm m}} + \text{constant}$$

where C is the protein concentration in g/L, $T_{\rm m}$ is the melting point of the gel in absolute temperature, R is the gas constant, and ΔH° is the enthalpy of gelation. According to the above equation a plot of log C vs. $1/T_{\rm m}$ should give a straight line, with a slope of $\Delta H^{\circ}/(2.303R)$.

The effect of soy protein isolate concentration on the melting point of the gel in the presence of 0.5 M NaCl and 0.5 M NaSCN is shown in Figure 6. These two salts were



Figure 7. Log concentration vs. reciprocal temperature plots for soy 7S protein gels in the presence of 0.5 M NaCl and NaSCN. The gels were formed by heating the aqueous protein dispersions, pH 8.0, at 90 °C for 30 min and then aging at 4 °C for 24 h.

chosen for the study to represent two classes of affectors on hydrophobic interactions as well as on the stability of protein structure. It may be noted that the concentration of soy protein isolate required for the formation of gel structure with a particular melting temperature differed considerably with type of salt used (Figure 6). Since the melting temperature is dependent on the number of cross-links formed (Eldridge and Ferry, 1954), for the formation of the same number of bonds in the gel structure the concentration of protein required in the presence of NaSCN is less than in the absence of NaSCN or in the presence of NaCl. Similar results were also obtained for soy 7S protein (Figure 7). This is probably because of extensive unfolding of the protein in the presence of NaSCN, which may increase the number of functional groups available for the formation of noncovalent bonds in the gel structure.

It may be pointed out that the addition of 0.5 M NaCl affects both soy isolate and soy 7S gels alike by increasing the melting temperature by 11 °C, whereas addition of 0.5 M NaSCN increases the melting point of soy isolate gel by 17 °C and that of soy 7S by about 19 °C (Figures 6 and 7).

The plots of log C vs. $1/T_{\rm m}$ were linear in the presence of both NaSCN and NaCl, as well as the control (Figure 6). The enthalpies of bond formation during gelation, calculated from the slopes of the curves in Figure 5, are given in table I. It may be noted that the presence of NaCl or NaSCN did not have any influence on the enthalpy of gelation and exhibited a value of about -1 kcal/mol of cross-linking. This implicitly suggests that the type of bonds involved in the formation of the three-dimensional network was not affected by the type of salt used.

The major types of noncovalent forces involved in the formation of reversible gel structure are Van der Waals interactions, hydrogen bonds, electrostatic bonds, and hydrophobic interactions. It may be assumed that the observed net enthalpy of gelation is the sum of the enthalpies of all the above forces involved. That is

$$\Delta H^{\circ}_{gel} = \Delta H^{\circ}_{hydrophobic} + \Delta H^{\circ}_{electrostatic} + \Delta H^{\circ}_{H \text{ bonding}} + \Delta H^{\circ}_{dispersion}$$

Should all forces be involved, it is reasonable to expect that elimination of one or more of these without affecting the

Table I. Heat of Reaction (ΔH°) for the Formation of Cross-Links of Gels Made from Soybean Proteins under Different Treatments

sample ^a	ΔH , kcal/mol
soy protein isolate (SI) SI plus 0.5 M NaCl SI plus 0.5 M NaSCN 7S fraction 7S plus 0.5 M NaCl 7S plus 0.5 M NaSCN 11S fraction	$\begin{array}{r} -0.951 \\ -1.006 \\ -1.088 \\ -1.166 \\ -1.262 \\ -1.436 \\ -0.850 \end{array}$

 a Gels were prepared by heating at 90 °C for 30 min and aged for 24 h at 4 °C. The pH of protein dispersions was 8.0.

others will influence the observed enthalpy of gelation. It is also reasonable to expect that the electrostatic interactions will be minimized or eliminated at 0.5 M ionic strength of either NaCl or NaSCN. Logically this should have an effect on the observed ΔH° of gelation. But, the observed results (Table I), which show relatively little effect of either NaCl or NaSCN on the enthalpy of gelation of soy protein isolate, suggest that the electrostatic interactions between positively charged amino groups and negatively charged carboxylate groups play only a minor role in the maintenance of gel structure. NaSCN has been known to destabilize hydrophobic interactions (von Hippel and Schleich, 1969; Damodaran and Kinsella, 1981). Hence, in the presence of 0.5 M NaSCN both the electrostatic and hydrophobic interactions will be expected to be minimized, which should greatly affect the ΔH° of gelation. But since the observed ΔH° of gelation is the same in the presence or absence of 0.5 M NaSCN, the contribution of both the electrostatic and hydrophobic interactions to the stability of gel structure is very negligible. These results apparently suggest that the major forces involved in the formation of soy gel structure may be hydrogen bonding and Van der Waals interactions.

Catsimpoolas and Meyer (1970) reported that treatment of the progel with 6 M urea inhibited gelation of soy upon cooling. This phenomenon is usually interpreted as due to destabilization of hydrophobic interactions which are presumed to be necessary for gelation. But, it is known that urea affects both hydrophobic and hydrogen-bonding interactions. Hence, the effect of 6 M urea on the gelation of soy may also be attributed to prevention of intermolecular hydrogen bonding during gelation. Such an interpretation is consistent with the results presented here and also our suggestion that the hydrogen bonding is the most important noncovalent interaction involved in the gelation of soy proteins.

The log C vs. $1/T_{\rm m}$ plots for soy protein isolate, soy 7S, and soy 11S protein fractions are shown in Figure 8. The ΔH° values calculated from the slopes of these lines did not show appreciable differences. On the basis of the observed ΔH° values, 7S protein exhibited a higher gel strength than either soy protein isolate or 11S protein (Table I). However, the concentration of these proteins required to form a gel with the same melting temperature followed the order soy protein isolate < 7S protein < 11Sprotein (Figure 8). In other words, although the ΔH° of gelation of soy protein isolate was less than that of the 7S protein, in order to form the same number of cross-linkages in the gel, a lower concentration of soy protein isolate was required compared to the 7S or 11S protein. This is in agreement with the data shown in Figure 1 in which soy protein isolate exhibited a higher progel and gel viscosity than either 7S or 11S protein at the same protein concentration.



Figure 8. Log concentration vs. reciprocal temperature for soy isolate, soy 7S, and soy 11S at pH 8.0. The gels were formed by heating aqueous protein dispersions, pH 8.0, at 90 °C for 30 min and then aging at 4 °C for 24 h.

It is interesting to note that while the gel viscosity of soy isolate decreased in the presence of NaCl (Figures 4 and 5b), the gel exhibited higher melting temperature in the presence of NaCl (Figure 6). This suggests that apparently there is no correlation between the melting point and the flow behavior of the gel. In other words, while the presence of NaCl in the medium increased the number of bonds formed during gelation, it reduced the drag force against flow. This may be because of stabilization of the protein into a compact globular structure in the presence of NaCl. Such stabilization may reduce the effective hydrodynamic volume of the protein. Neutralization of charges at 0.5 M NaCl may further decrease the hydration potential of the protein and hence decrease the hydrodynamic volume. Both these effects may decrease the gel viscosity as shown in Figure 5. However, the suppression of the electrostatic repulsive interaction between protein molecules at 0.5 M ionic strength may allow association and formation of a greater number of hydrogen bonding and other interactions on the surfaces of these compact protein molecules. Since unfolding is inhibited by NaCl, the formation of bonds may be only between the immediate neighbors and thus a three-dimensional network may not be formed. However, the net increase in the number of interactions in the presence of 0.5 M NaCl is reflected in the higher melting temperature of soy isolate gels (Figure 6).

In spite of the differences in their physicochemical characteristics, soy isolate, soy 11S, and soy 7S exhibited almost identical changes in the enthalpy of gel formation, i.e., about 1 kcal/mol (Table I). According to classical thermodynamics, the thermodynamic state of the system at the melting temperature can be expressed as $\Delta G^{\circ} =$ $\Delta H^{\circ} - T_{\rm m} \Delta S^{\circ}$, where ΔG° is the free energy change for gelation, ΔS° is the entropy change, and $T_{\rm m}$ is the melting temperature of the gel. Since the enthalpy change, ΔH° , for the gelation of soy isolate, soy 7S, and soy 11S is the same, it can be treated as a constant. Then, the free energy change, ΔG° , for gelation of these proteins at $T_{\rm m}$ is a function of ΔS° . For the ΔG° to be more negative, i.e., for greater degree of gelation, the entropy change ΔS° at $T_{\rm m}$ should be more positive. If we assume that the entropy production, ΔS° , of the system is related to the ease with which the protein molecule can dissociate and unfold, then the free energy change for gelation of soy isolate, soy 7S, and soy 11S is solely a function of the extent of their unfolding at the gelation temperature. The observed differences in the protein concentrations required for the formation of gels of soy isolate, soy 7S, and soy 11S having the same melting temperature (Figure 8) is the direct thermodynamic manifestation of the differences in their ability to unfold (greater ΔS°). In this regard, the unfolding ability of these proteins follows the order soy isolate > soy 7S > soy 11S. This is in agreement with the qualitative interpretation of the observations on changes in the progel and gel viscosities.

Registry No. SO₄²⁻, 14808-79-8; Cl⁻, 16887-00-6; Br⁻, 24959-67-9; SCN⁻, 302-04-5.

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