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# Rheology of Sea Buckthorn (*Hippophae rhamnoides* L.) Juice†

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Juice extracted from sea buckthorn fruits was subjected to dynamic rheological measurements in a controlled stress rheometer. Sea buckthorn juice exhibited wide variations in flow behavior from pseudoplastic to dilitant with increasing temperature. The power law model suitably ($r \geq 0.975$, $P \leq 0.001$) described the shear-stress versus shear-rate data of the juice. Changes in apparent viscosity of the juice with increasing temperature obeyed the Arrhenius law at shear stress above 1 Pa but deviated from it at low shear stress of 0.1 Pa. The rheological behavior of sea buckthorn serum obtained after centrifugation of the juice was similar to those of the juice and sucrose solution at high shear rate but differed from them at low shear rate. Addition of ethanol insoluble substances up to 7% (w/v) to the juice changed its rheological behavior to resemble that of a sea buckthorn juice concentrate at 48 °Brix, although frequency dependence was unaffected above 1 Hz. Sea buckthorn juice was found to be thermostable within the temperature range from 25 to 70 °C, although critical changes occurred in juice components above 70 °C.

**Keywords:** *Sea buckthorn juice; rheology; ethanol insoluble substance; concentrate; viscosity; flow behavior; Hippophae rhamnoides*

## INTRODUCTION

Sea buckthorn (*Hippophae rhamnoides* L.), a hardy, deciduous shrub with yellow or orange berries, is attracting considerable attention mainly for its medicinal value and great economic potential (Li and Schroeder, 1996). The value of sea buckthorn is often based on the nutritional value of its fruit. Sea buckthorn products based on fruit pulp or juices are rich in vitamin C, provitamin A, other vitamins, especially of the B group, and phytochemicals and are therefore considered to have therapeutic and chemopreventive activities (Li and Wang, 1998; Li and Liu, 1991). Sea buckthorn juice is known to block the endogenous formation of *N*-nitroso compounds more effectively than ascorbic acid and thereby prevent tumor production (Li and Liu, 1991). Peizhen et al. (1989) reported that concentrated sea buckthorn juice significantly inhibits the growth of sarcoma, lymphocytic leukemia, and human gastric cancer cells when injected intraperitonally in mice and suggested that it has antitumor effects.

Processing of juice from small fruit is a complex operation with many variables that influence final product quality. A good knowledge of the flow behavior of the juice is essential to understand and improve the technologies for different kinds of juices, that is, clear, cloudy, or nectar. In this regard, rheology has implications on processing equipment design, product development, and storage and transportation of juices. Most common fruit juices exhibit complex and variable rheological behavior, that is, time dependence, shear stress dependence, and viscoelasticity (Chen, 1992; Rao, 1995). In addition, factors such as temperature, concentration, and fruit composition influence rheological properties of juices from even lesser known fruits such as loquot and sloe (Ibarz et al., 1996a,b). The rheological behavior of sea buckthorn juice has not been reported.

Clear sea buckthorn juice can be obtained according to a patented cold process (Heilscher and Lorber, 1996) in which the berries are crushed and strained on sieves and the juice is separated using ultrafiltration or centrifugation after the pulpy mass has been heated at 50−55 °C. Cold pressed juice, according to this patent, constitutes an emulsion consisting of an oil phase, a liquid phase, and particles of the fruit flesh. High local shear and pressure loads exerted during mechanical treatments or high-pressure homogenization can destroy the emulsion, resulting in an unstable juice (Kleinschmidt et al., 1996). To overcome the problems associated with juice processing, stability, and storage, our investigation focused on the rheological behavior of sea buckthorn juice. Such information is critical in determining power requirements for engineering operations such as pumping and mixing of juices, in quality control of finished products, and in improving fruit quality.

## MATERIALS AND METHODS

Fruits of sea buckthorn cv. Indian Summer were obtained at maturity from shrubs grown as shelter belts in Saskatchewan, Canada. After sizing through screen (1.7 mm), the fruits were pressed in a vertical hydraulic press (5-A, Hein-Werner) under a maximum pressure of 172 bar. The presscake was repressed under pressure (221 bar), and juices from both pressings were combined. To obtain ethanol insoluble substances (EIS), press cake, stored frozen and subsequently thawed, was stirred overnight at 10 °C with distilled water (1:3, w/v). The water soluble extract was filtered (Whatman No. 4), freeze-dried, and then extracted with ethanol (95%; 1:5,

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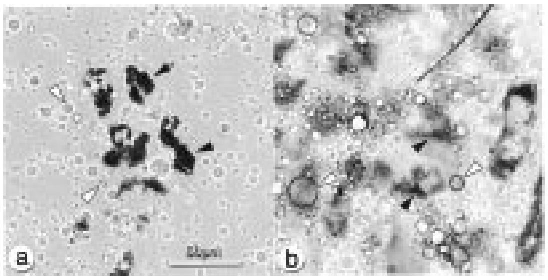

**Figure 1.** Photomicrographs of sea buckthorn juice in transmitted light: (a) fresh, unheated juice; (b) heated juice, 90 °C, 3 min. White and black arrows indicate oil droplets and condensed granular material, respectively.

w/v) by stirring for 1 h at 20 °C. The EIS was recovered by filtration (Whatman No. 4). Serum was obtained from juice by centrifugation (IEC HN-S II centrifuge, International Equipment Co., Needham Heights, MA) at 2800 rpm for 20 min. The serum constituted ~83.5% (w/w) of the juice and had a soluble solid content of 11.4 °Brix. Concentration of the juice was performed initially at 25 °C and then at 43 °C in a Savant SC 110 Speed Vac concentrator (Savant Instruments, Inc., Farmingdale, NY). Soluble solid content of the concentrate was 47.6 °Brix. A digital refractometer (Abbe Mark II, Reichert Scientific Instruments, Buffalo, NY) was used to measure soluble solids content at 20 °C.

Dynamic rheological studies were performed on a Bohlin controlled stress rheometer (CVO, Bohlin Instruments Ltd., Gloucestershire, U.K.), using a cone-plate geometry (cone angle = 2°, diameter = 60 mm) with a gap size set at 70 $\mu$m. This rheometer includes software (Bohlin Software Package Windows 95, v 5.4) that permits data analysis and systematic recordings of time, temperature, frequency, phase angle, complex modulus, elastic modulus ($G'$), viscous modulus ($G''$), complex viscosity, shear stress, and strain. Applied torque is converted to strain through rotational movement. Samples were loaded on the plate of the rheometer and covered with a thin layer of food grade silicone oil to prevent evaporation. A solvent trap with low-viscosity silicone oil (4.3 cP, Brookfield viscosity standard, Stoughton, MA) enclosed and insulated the sample from heat loss. Temperature ramps were implemented from 25 to 85 °C at the rate of 1 °C/min and a constant frequency of 0.5 Hz, and the shearing was performed under a constant stress of 0.5 Pa. Single measurements were recorded for temperature ramps for all samples except juice, which was replicated three times, obtaining highly reproducible data (relative standard deviation $<\pm 5\%$). Frequency sweeps over four decades (from $10^{-1}$ to $10^{2}$ Hz) and initial stress of 0.1 Pa were performed at 25 °C. The amplitude of oscillation was kept sufficiently low and controlled by the manufacturer's software to ensure linear behavior. Viscosity responses were monitored by subjecting the sample to a shear stress of 0.1−4 Pa at temperatures of 5, 10, 25, 40, and 55 °C. Frequency sweeps and viscosity responses were performed in triplicates, and the experimental variation about the mean value was always $<\pm 2\%$.

Light microscopy was performed on fresh and heated juice. Sea buckthorn juice was heated rapidly in a steam kettle to 90 °C, held for 3 min, and cooled rapidly to 40 °C by passing cold water through the steam jacket. One to two drops of well-mixed juice was placed on a slide and covered with a cover slip. The juice preparation was viewed using a Zeiss Axiophot microscope and photographed using transmitted light.

## RESULTS AND DISCUSSION

Sea buckthorn juice is a complex system consisting of several types of particles including translucent and granular particles of diverse sizes (Figure 1). The round or spherical particles are oil droplets; they stain deep orange by Oil O Red. Sea buckthorn juice is a three-phase system containing up to 1.4% (w/w) oil (Beveridge et al., 1999). The spherical droplets (white arrows) are slightly to distinctly orange, probably because of the high carotenoid content of sea buckthorn berries and juice. Many large aggregates of cellular material are yellow to dark orange in the original juice and are clearly visible in Figure 1a (black arrows). Heating to 90 °C for 3 min causes an obvious increase in the juice consistency experienced sensorily in the fingers and visually by tipping tubes of heated juice. These changes are reflected in the microscopic morphology of the juice particulate. Some oil droplets increase considerably in size as expected because coalescence of oil droplets is enhanced by increased temperature. Large droplets grow at the expense of smaller droplets, resulting in a lower total interfacial surface energy in the system and a wider range of droplet sizes between the larger and smaller droplets. Also, the granular particulate (Figure 1a) changes through either aggregation of the condensed particles or disruption of the compact structures to porous, more open structures (or both). In apple mash heated to 90 °C for ~30 s (McKenzie and Beveridge, 1988), clear evidence for mash particle disruption was obtained by electron microscopy, but the complicating factor of an oil phase was not present. The yellow-orange pigment noted in Figure 1a as localized primarily in the granular particulate has been dispersed throughout the juice in Figure 1b, supporting a contention that the particulate has been dispersed or solubilized at least to some extent by the heating procedure.

Rheologically, one would expect non-Newtonian behavior from particulate-containing samples, especially following thermal treatments causing thickening and gelation. The increased particle interaction in heated juice is clear from the micrographs.

Sea buckthorn juice exhibited wide variation in flow behavior from pseudoplastic to dilatant with increasing temperature (Figure 2). The power law model

$$\tau = k(\gamma)n \tag{1}$$

where $\tau$ is the shear stress, $k$, the consistency index, $\gamma$, the shear rate, and $n$, the flow behavior index, fitted ($r \geq 0.975$, $P \leq 0.001$) the shear rate/shear stress data well, and it was used to calculate the different rheological parameters ($n$ and $k$) of sea buckthorn juice. The flow behavior index ($n$) was 0.85 for sea buckthorn juice at 5 °C, which was therefore considered a pseudoplastic fluid by definition (Chen, 1992). This non-Newtonian behavior has been attributed to the presence of high molecular weight substances in solution and/or to the dispersed solids in a fluid phase (Rao, 1977). At 10 °C, the flow curve of the juice approximated Newtonian behavior, because $n$ was 1. At temperatures >10 °C, sea buckthorn juice behaved like a dilatant fluid, because $n$ was >1. The pseudoplasticity of the juice decreased (i.e., $n$ values increased) while the consistency index ($k$) decreased with increasing juice temperature. The shear rate evolution of the apparent viscosity (Figure 2) of the juice decreased with increase in temperature. At temperatures <10 °C, the juice was shear-thinning, that is, apparent viscosity decreased with increasing shear rate. Above 10 °C, sea buckthorn juice was a dilatant fluid, that is, apparent viscosity increased with increasing shear rate. The reversible breakdown of the viscous structure at elevated temperatures may be due to the recovery of a polymer network. A gradual formation of structure was observed at 55 °C, especially at high shear

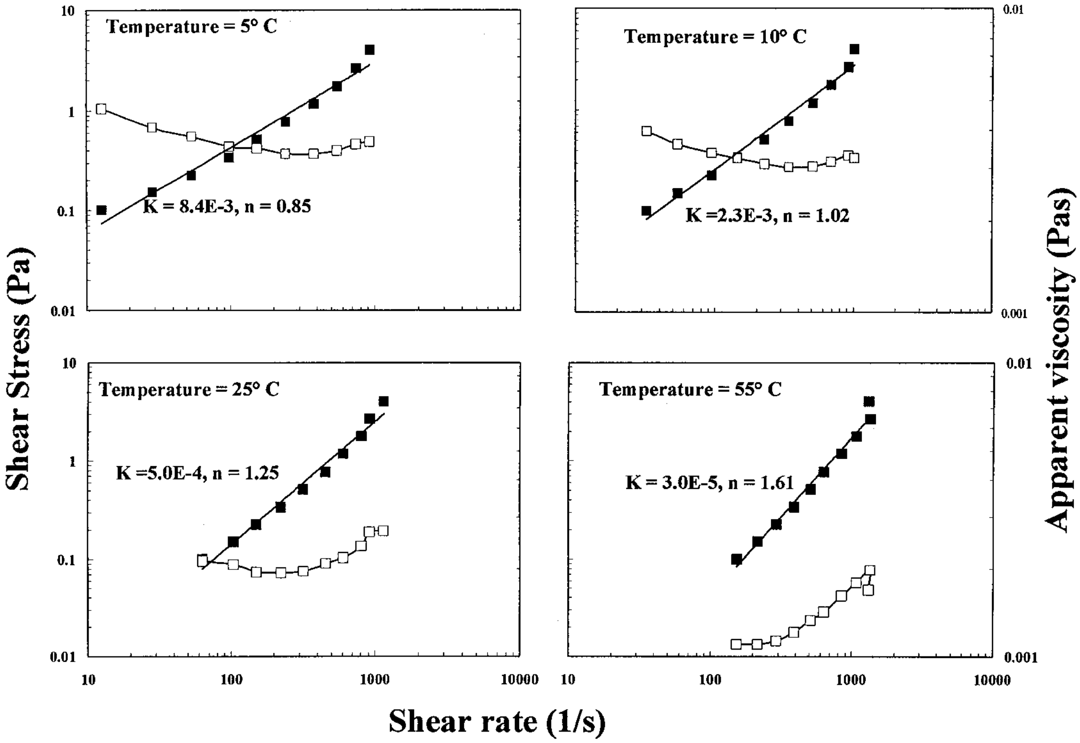

**Figure 2.** Flow behavior of sea buckthorn juice at various temperatures. Shear stress and apparent viscosity are denoted by solid and open symbols, respectively. Shear stress sweep is from 0.1 to 4.0 Pa.

rate probably due to a gradual thickening occurring at 55 °C that exceeds the breakdown rate due to shear thinning. Thus, sea buckthorn juice provides natural thickening at high temperature and high shear rate. This information is useful in the production of fruit products such as jams and jellies. The power law relation between apparent viscosity and shear rate of the juice was poor ($0.502 < r < 0.601$) up to 25 °C and it produced a good ($r = 0.921$, $P \leq 0.001$) fit at 55 °C. This could probably be due to the reduced viscosity resulting from an increase in free volume of the juice at temperatures >25 °C.

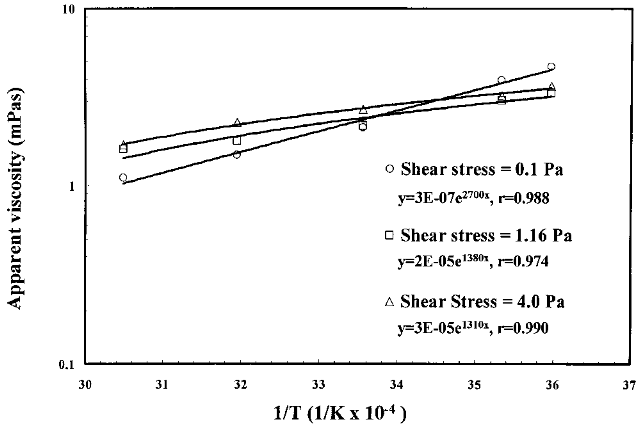

**Figure 3.** Arrhenius plot for sea buckthorn juice for three shear stress levels between 5 and 55 °C, corresponding to 36 and 30 $1/k \times 10^{-4}$, respectively.

The influence of temperature on apparent viscosity of fluids can be described according to an Arrhenius type equation (Chen, 1992)

$$\log \eta = E_a/(2.3RT) + \eta_\infty \qquad (2)$$

where $\eta$ is the apparent viscosity, $\eta_\infty$, an empirical viscosity constant, $E_a$, the activation energy of flow, $R$, the ideal gas constant, and T, the absolute temperature. Semilog plots of apparent viscosity versus inverse of absolute temperature gave significant correlation ($r \geq 0.974$, $P \leq 0.01$) when plotted using the linear regression method (Figure 3). Changes in apparent viscosity with temperature showed Arrhenius behavior of sea buckthorn juice, particularly at shear stress >1 Pa. Deviations from Arrhenius behavior were observed at low stress (0.1 Pa), especially at mid temperature range (25 °C or 33.5 $1/T$) leading to higher activation energy ($E_a = 51.7$ kJ/g·mol), indicating low particle–particle interaction. Apparent viscosity showed the least dependence on temperature at stress >1 Pa, thereby reflecting similar activation energies (26.31 and 25.06 kJ/g·mol) at shear stresses of 1.16 and 4 Pa, respectively, between 5 and 55 °C (i.e., 36 and 30 $1/T$). The similar activation energies at shear stress >1 Pa may partly be due to the disintegration of large particles into smaller symmetrical fractions that reduce resistance to flow, implying shear thinning at large shear stress. The activation energy values for sea buckthorn juice were comparable to those of depectinized apple juice and cloudy apple juice (Chen, 1992). The apparent viscosity of sea buckthorn juice, from $2 \times 10^{-5}$ to $3 \times 10^{-7}$ Pa, was within the same order of magnitude as those of clarified juices (Ibarz et al., 1992). Shear stress >1 Pa was effective in reducing the apparent viscosity of sea buckthorn juice, suggesting that minimal flow rate (stress >1 Pa) may be enough to prevent fouling of heat exchangers when concentrating or pasteurizing the juice.

The rheological behavior of sea buckthorn juice was similar to that of a sucrose solution of the same soluble solids content (11 °Brix) and comparable to that of serum, but only at high shear rate (Figure 4). The flow behavior of the serum at low shear rate deviated from that of the juice and sucrose solution, suggesting the presence of soluble polymers and/or suspended solids, which are considered to be responsible for strong

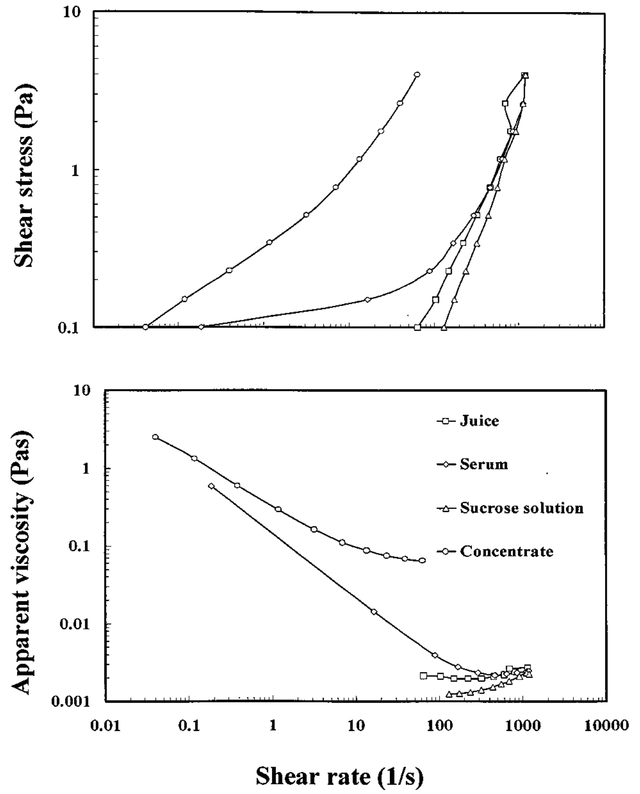

**Figure 4.** Rheological behavior of sea buckthorn juice and its components. Shear stress sweep is from 0.1 to 4.0 Pa.

particle–serum interactions. Concentration of the juice (48 °Brix) by increasing the suspended solids resulted in increased apparent viscosity and imparted a pronounced non-Newtonian behavior with finite yield stress of 0.067 Pa. A similar increase in apparent viscosity was obtained in the presence of ethanol insoluble substances (EIS) extracted from sea buckthorn cake. Addition of 5 and 7% EIS (w/v) altered the flow behavior of the juice such that it behaved similarly to that of the concentrate (Figures 4 and 5). Hence, the EIS, which according to Dongowski (1996) makes up 4.7% of fresh berry weight and consist of 9% pectin, may be used in beverages to boost viscosity.

In oscillation tests, sea buckthorn juice exhibited rheological characteristics indicative of a typical viscoelastic liquid—a substantial increase in $G'$ and $G''$ with increasing frequency by 9 orders of magnitude and the predominance of the viscous component ($G'' > G'$) at low frequency (Figure 6). At frequency $>1$ Hz, a restabilization process occurred which imparted to the juice similar viscous and elastic components ($G' \sim G''$), indicating an entangled polymer flow state. Addition of EIS induced significant changes in the rheology of sea buckthorn juice: the storage and loss moduli increased systematically, and the crossover of $G'$ and $G''$ curves moved to higher frequencies indicative of a weak gel formation. Values of $G'$ and $G''$, when plotted with frequency (0.01–1 Hz) on a log–log scale, gave straight lines ($r = 0.791$, $P \leq 0.001$) with slopes of 60.0, 58.5, and 59.0 and 38.9, 37.3, and 38.2 for juice, juice with 5% (w/v) EIS, and juice with 7% (w/v) EIS, respectively. The similar slope of log $G'$ vs log frequency ($\leq 1$ Hz) curves for juice and juice with EIS suggests limited changes to the nature of the bonds in the juice system due to the presence of EIS. Values of $G'$ and $G''$ at frequency of oscillation $>1$ Hz continued to show frequency dependence and were largely unaffected by the presence of EIS, possibly due to increased cross-linking. The rheology of sea buckthorn juice, with and without EIS, shared some features common with the Zimm molecular model in which the moduli become equal and increase together with a slope of $^{1}/_{2}$ (Barbosa-Cánovas et al., 1996).

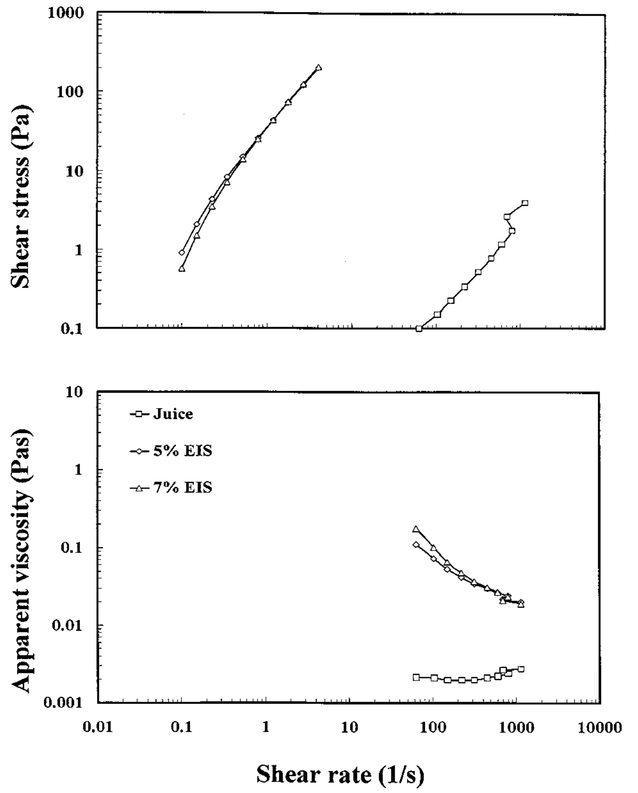

**Figure 5.** Effect of EIS on the rheology of sea buckthorn juice.

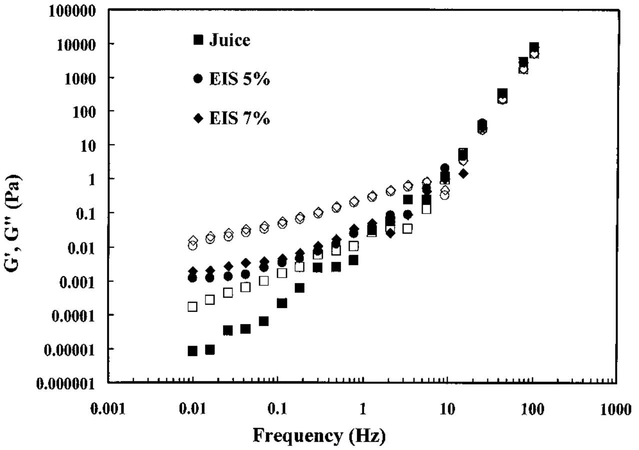

**Figure 6.** Dynamic rheological spectra of sea buckthorn juice. Elastic ($G'$) and viscous ($G''$) moduli are denoted by solid and open symbols, respectively. Applied stress = 0.1 Pa.

The thermal evaluation of the juice in the 25–85 °C temperature range was performed to observe the viscoelastic changes that may occur due to aggregation and/or gelation. Semilogarithmic plots of $G'$ and $G''$ against temperature at 0.5 Hz (Figure 7) revealed that the viscoelastic response of sea buckthorn juice was almost unaffected by temperature (i.e., it was thermally stable) and similar to that of sucrose to 50 °C. Value of $G'$ was similar in magnitude to $G''$ at 25 °C for juice and sucrose, but thereafter an increase in $G''$ occurred. This increase in the viscous component ($G''$) can be attributed to heat-induced reactions. Temperature stimu-

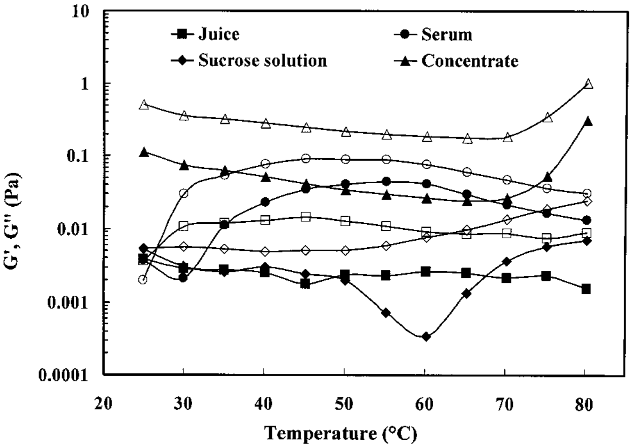

**Figure 7.** Temperature dependence of the rheology of sea buckthorn juice and its components. Elastic (*G*′) and viscous (*G*″) moduli are denoted by solid and open symbols, respectively. The rheological parameters were measured at constant frequency = 0.5 Hz, shear stress = 0.5 Pa, and heating rate = 1 °C/min.

lated the rheological transformation of serum. Thus, a structure formation (deviation of *G*′ from baseline) occurred at 30 °C for the serum, followed by temperature-dependent moduli from positive (30−60 °C) to negative (60−80 °C). Components in the juice other than sucrose, such as soluble pectin, seem to contribute predominantly to the change in temperature dependence of the moduli. The high *G*′ of the serum in contrast to that of sucrose solution is in accordance with the reports of Vitali and Rao (1984) and may be due to the presence of residual pectin in the serum. The *G*′ and *G*″ values of the concentrate were 2 orders of magnitude greater than those of the juice at 25 °C. Increase in temperature up to 70 °C resulted in a decrease of the viscoelastic response of the concentrate, indicating degradation of molecular structure and inhibition of molecular hydration. The parallel increase and decrease of *G*′ and *G*″ from 30 to 70 °C for serum and concentrate, respectively, suggest absence of a network formation. Concentration of the juice led to the development of a gel network at elevated temperature as monitored by the sharp rise in *G*′ over a narrow temperature range (70−80 °C). The starting point of the gel network development for the concentrate and sucrose was similar at ≈70 °C, indicating that sucrose may be responsible for or contributing to the increased network formation of the concentrate as the temperature increased. Viscosity characteristics, *G*″, of the concentrate were also altered at 70 °C with rapid increase in *G*′, probably a result of heat-induced aggregation, which may play an important role in determining the flow characteristics of the concentrate.

The various constituents of sea buckthorn juice seem to affect its rheological behavior under different conditions. Hence, processing of the juice to obtain products such as clarified juice, pasteurized juice, concentrated juice, juice drinks, and nectars may lead to the rheological changes observed in this study. The transition points where changes in rheological properties occur in the juice can be used as critical parameters to control its flow behavior when protocols for processing, storage, and handling of sea buckthorn juice and juice products are established.

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