ABSTRACT

We have determined the density, rheological behavior and surface tension of whey protein concentrate (WPC) solutions.

Densities ($\rho$) were measured at concentrations of 0.05–0.40 w/w at temperatures of 20–35°C. The results were expressed as a function of temperature and mass fraction ($w$). This function fit the data with deviations of less than ±0.4%.

Apparent viscosities ($\eta_a$) for WPC solutions with mass fractions $w \leq 0.20$ at temperatures of 10–40°C and high shear rates, 50–1,200/s, were found to be independent of shear rates, implying that the rheological behavior of WPC solutions is Newtonian. Dynamic viscosity ($\eta$) data were fitted to an empirical function of the WPC mass fraction and temperature with a mean deviation of ±4.7%.

Surface tensions ($\sigma$) were determined for mass fractions between 0.01 and 0.30 at 25°C. At this temperature and $w = 0.05$, there was a critical surface tension, $\sigma_c = 42.5$ mN/m. When $w \geq 0.10$, the arithmetic mean of $\sigma$ at 25°C was 46.3 mN/m. The surface tension values were similar to those published for skimmed milk at 25°C. In addition, for $w = 0.05$ and $w = 0.20$, we found that at temperatures between 20 and 40°C, the surface tension decreased linearly with temperature. These linear equations fit our experimental data with an average deviation lower than ±0.4%.
PRACTICAL APPLICATIONS

Density, rheological behavior and surface tension are required to design and control processes with momentum, heat and mass transfer. The process of producing protein concentrates from milk or whey by ultrafiltration uses spiral-wound membranes. The cross-flow pressure drop and permeate mass flow are a function of fluid density and viscosity, which in turn depend on concentration and temperature. The ultrafiltration process used to concentrate solutions with mass fractions of about 0.10–0.20 w/w must then be treated to avoid physicochemical or microbiological alterations. Spray drying is usually used as the preservation technique. In the spray-drying design, these physical properties are necessary to calculate the mean droplet diameter and droplet size distribution.

INTRODUCTION

Whey protein concentrate (WPC) is a high-quality protein source with many applications in the food industry. Milk proteins in soluble and dispersed form are widely valued as food ingredients, having excellent surface-active and colloid-stabilizing characteristics (Singh and Dalgleish 1998; Dickinson 2001). WPC enzymatic hydrolysates are used mainly as a nitrogen source in the formulation of baby foods and enteral nutrition (González-Tello et al. 1994a). They are also used in the production of functional and medical foods (Schlimme and Meisel 1995; FitzGerald and Meisel 2003).

The rheological behavior of WPC solutions has been studied by Tang et al. (1993) at a shear rate of 10–290/s at different temperatures and pH values. Tang et al. (1993) found Newtonian behavior for WPC solutions with \( w \leq 0.10 \). Hermansson (1975) and Herceg et al. (2002) also reported Newtonian behavior for diluted WPC solutions, up to about 0.10 w/w. Tang et al. (1993), for \( 0.15 \leq w \leq 0.20 \), 22C and \( \mathrm{pH} = 6 \), found that apparent viscosities decreased slightly with the shear rate, \( \dot{\gamma} \), at low shear rates (lower than 50/s). At shear rates higher than 50/s, the apparent viscosities were not a function of shear rates. Morison and Mackay (2001), considering how changing lactose concentrations affected the rheological behavior of WPC solutions, reported that the non-Newtonian power-law index \( (n) \) for WPC solutions from 23.2 to 17.5% w/w protein concentration is independent of the lactose concentration and has values of \( n \geq 0.94 \). For example, for 17.5% of protein at 20C, \( n = 0.98 \), and therefore shear rates will have little influence on apparent viscosities. Alizadehfard and Wiley (1996) found pseudoplastic behavior for WPC solutions for 40–50% w/w. In short, data published for the rheological behavior of WPC solutions indicate that for concentrations lower than 10–12% w/w, the
solutions show a Newtonian behavior. If the WPC solutions are concentrated, with a mass fraction of $0.10 \leq w \leq 0.20$, and a low shear rate ($\dot{\gamma} \leq 50/s$), the behavior is pseudoplastic. However, for these same concentrations ($0.10 \leq w \leq 0.20$) at high shear rates ($\dot{\gamma} \geq 50/s$), the apparent viscosities are practically independent of the shear rate and consequently the rheological behavior of WPC solutions is Newtonian. For $w \geq 0.30$ the rheological behavior is pseudoplastic (Tang et al. 1993; Alizadehfard and Wiley 1996).

None of the aforementioned studies consider the effect that changes in WPC concentration and temperature exert on dynamic viscosities. Density and surface tension data of WPC solutions are not available in the literature.

The objective of this work was to determine the densities, dynamic viscosities and surface tensions of WPC solutions, establishing correlations for these physical properties as functions of the temperature and the WPC concentration. Density, rheological behavior, and surface tension are required to design and control processes with momentum, heat and mass transfer. These correlations will serve as a basis to calculate the aforementioned properties for the design, control and optimization of whey ultrafiltration and whey spray-dryer design.

**MATERIALS AND METHODS**

**Materials**

WPC (lactoalbumin 75L) was supplied by Milei (Leutkirch, Germany). The mean protein content (77.6%) was determined by the Kjeldahl procedure. The molecular weight profiles, determined by size-exclusion high-performance liquid chromatography (González-Tello et al. 1994b), are shown in Table 1. The moisture, 4.7%, was determined by infrared moisture balance AD-4714A with an accuracy of ±0.01 g. The remaining composition, analyzed by Abbott Laboratories (Granada, Spain) was lactose 3.73%, carbohydrates 7.32%, fat 3.9%, ash 2.75% and different oligoelements ($\text{Na}^+: 192 \text{ mg/100 g}$; $\text{K}^+: 624 \text{ mg/100 g}$; $\text{Ca}^{2+}: 424 \text{ mg/100 g}$; $\text{P}: 300 \text{ mg/100 g}$; $\text{Cl}^-: 68 \text{ mg/100 g}$).

<table>
<thead>
<tr>
<th>Component</th>
<th>MW (kDa)</th>
<th>Chromatographic area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seroalbumin</td>
<td>69</td>
<td>15.0</td>
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<tr>
<td>$\beta$-lactoalbumin</td>
<td>18.2</td>
<td>43.9</td>
</tr>
<tr>
<td>$\alpha$-lactoalbumin</td>
<td>14.2</td>
<td>24.4</td>
</tr>
<tr>
<td>Peptides</td>
<td>&lt;1</td>
<td>16.7</td>
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Preparation of Samples

The WPC solutions were prepared by adding WPC powder in Milli-Q water (Millipore, Billerica, MA) preheated to 45°C and stirring until dissolved. The temperature was kept constant during the preparation of the solutions. If any foam appeared, the solution was sonicated for 30 min or until the foam disappeared. The solutions were prepared by weight, using an analytical balance with an accuracy of ±10^-4 g and stored at 4°C for use within 48 h, during which time they remained unaltered. The pH of the solutions was around 6.5 and, although that value varied slightly with the concentration of WPC solutions, this change was negligible within our concentration range.

Density Measurement

The density of the WPC solutions was measured with an Anton Paar vibrating-tube densimeter (model DMA 38, Anton Paar, Graz, Austria) with an accuracy of ±0.1 g/L. The measurements were repeated five times, the tube being washed after each measurement (first with Milli-Q-quality water, and afterward with acetone), and then air-dried. The values reported are the arithmetic means of five experiments.

Viscosity Measurement

The apparent viscosity of the WPC solutions was measured using a dynamic shear viscometer with a concentric cylinder-measurement cell, Haake RV550 viscometer (Karlsruhe, Germany), with an NV sensor assembly, for a viscosity range of 2–2,000 mPa·s and shear rate of 27–27,000/s. The system, checked using the Cannon Standard Viscosity Oil S6 and S60, was found to be accurate to ±0.001 mPa·s or ±3% of reading, whichever was greater. The Haake RV550 viscometer was used to determine the apparent viscosity, shear stress, and shear rate of the WPC solutions as a function of the mass fraction and temperature. The temperature control had an accuracy of ±0.1°C and was calibrated to an accuracy of better than 0.5°C. The mass fraction and temperature dependence were measured between 0.10 and 0.20 w/w, and 10 and 40°C, respectively, where the shear rate varied from 50 to 1,200/s. Duplicate experiments showed good repeatability of apparent viscosity (±1%). The water viscosities were taken from the tables of the CRC Handbook of Chemistry and Physics (Lide 2001).

Surface Tension Measurement

The surface tension of the WPC solutions was measured with a Krüss tensiometer (model K-8, Krüss Gmbh, Hamburg, Germany), which uses the Du Nouy ring method. The ring dimensions were R = 9.545 mm and R/r = 51.6,
and the accuracy of this tensiometer was ±0.1 mN/m. The temperature was kept constant to an accuracy of ±0.1°C. The tensiometer was calibrated with Milli-Q quality water before each measurement and the platinum ring cleaned with acetone, air-dried and flamed between each sample trial. The measurements were repeated five times and the arithmetic mean taken as the most probable value. The SD of the surface tension determination was lower than ±0.2 mN/m. The water surface tension was taken from the tables of the CRC Handbook of Chemistry and Physics (Lide 2001).

RESULTS AND DISCUSSION

Density

The densities of the WPC solutions (Table 2) were fitted to the following equation:

$$\frac{\rho}{\rho_w} = 1 + 0.313w$$

(1)

where $\rho$ is the density of the WPC solutions, $\rho_w$ is the density of water at the same temperature, and $w$ is the mass fraction of WPC solutions (see Fig. 1). This equation shows the variation in the density of the WPC solutions with the mass fraction of WPC and temperature; $\rho_w$ is an available datum (Lide 2001). Also, the water density can be calculated with an error of less than 0.1 kg/m$^3$ using the following relation:

$$\rho_w = 999.84 + 0.053(T - 273.15) - 7.315 \times 10^{-3} (T - 273.15)^2 + 3.03 \times 10^{-5} (T - 273.15)^3$$

(2)

<table>
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<tr>
<th>$w$</th>
<th>$\rho \pm \text{SD, kg/m}^3$</th>
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<tbody>
<tr>
<td></td>
<td>20°C</td>
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<tr>
<td>0.00</td>
<td>998.2*</td>
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<tr>
<td>0.05</td>
<td>1,012.9 ± 0.1</td>
</tr>
<tr>
<td>0.10</td>
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</tr>
<tr>
<td>0.20</td>
<td>1,059.6 ± 0.1</td>
</tr>
<tr>
<td>0.30</td>
<td>1,092.1 ± 0.3</td>
</tr>
<tr>
<td>0.40</td>
<td>1,126.9 ± 0.2</td>
</tr>
</tbody>
</table>

* Water data (Lide 2001).
where \( T \) is the temperature in K. Equation 1 fits the experimental results with a deviation of less than \( \pm 0.4\% \).

**Rheological Behavior at High Shear Rates**

Apparent viscosities of the WPC solutions measured at 10 and 20°C, as a function of shear rate, 50–1,200/s, are shown in Fig. 2. This plot reveals that for \( \dot{\gamma} \leq 50/s \), apparent viscosities were independent of shear rate. Morison and Mackay (2001) found that high shear rates have little influence on viscosities. Similar results were found for our data. Therefore, given high shear rates, \( \dot{\gamma} \geq 50/s \), apparent viscosities are not a function of shear rates, so that the rheological behavior of WPC solutions is Newtonian. The rheological properties of protein solution are governed by composition, molecular mass, protein size and shape, degree of hydration, and intermolecular interaction. The intermolecular interaction between protein molecules may be especially important with respect to rheological properties. The breaking up of protein aggregates because of shearing at shear rates higher...
than normal for formation of aggregates as a result of Brownian motion could explain the nondependence of apparent viscosities with respect to the shear rate (Tang et al. 1993; Alizadehfard and Wiley 1996).

Table 3 presents the values of dynamic viscosity at high shear rates as a function of the WPC concentration and temperature. For each mass fraction, an Arrhenius equation, Eq. (3), was proposed to fit dynamic viscosities:

\[ \eta = \exp \left( A + \frac{E_A}{RT} \right) \]

where \( T \) is the temperature in K, \( A \) is the Arrhenius constant, \( R \) is the gas constant, and \( E_A \) the activation energy. Figure 3 shows that at constant mass fraction, the dynamic-viscosity data were fitted by Eq. (3). The activation energy is constant and its value is 19.92 kJ/mol. This was consistent with an activation energy of 20.1 kJ/mol at 20% of total solids reported by Tang et al. (1993) and 20.2 kJ/mol reported by Morison and Mackay (2001). The Arrhenius constant \( (A) \) is a linear function of WPC concentration (Fig. 4). Therefore, Eq. (3) is transformed into
where $\alpha$ and $\beta$ are fitting parameters. For the calculation of the best values of $\alpha$, $\beta$ and $E_A$, a program was written to optimize these parameters under the condition of minimum average absolute deviation, defined by Eq. (5):

$$AAD = \frac{1}{N} \sum_{i=1}^{N} \frac{abs(\eta_{\text{exp}} - \eta_{\text{cal}})}{\eta_{\text{exp}}}$$

The optimum values found for $\alpha$, $\beta$ and $E_A$ are $\alpha = -8.171$, $\beta = 11.789$, $E_A = 19.92$ kJ/mol. Equation (4) reproduces our experimental data with a deviation lower than $\pm 10\%$, while the mean average deviation was $\pm 3.5\%$.

**Surface Tension**

Surface tension ($\sigma$) values at 25C and WPC mass fraction from 0.01 to 0.30 w/w are shown in Fig. 5, together with those of water at the same
temperature. In this figure, it was found that the values of $\sigma$ decrease with the concentration until $w = 0.05$. At this point, there was a critical concentration of proteins that minimized the value of the surface tension, $\sigma_c = 42.5$ mN/m. From this concentration, the $\sigma$ values slightly augmented and remained constant for $w \geq 0.20$. WPC is a well-known surface-active material and is required to achieve maximum surface activity. Any excess of surfactant (in this case whey protein) in the solution will be shielded by the air–water interface and consequently will not contribute to the surfactant effect (Waltra and Jenness 1984; Roehl and Jelen 1988; Adhikari et al. 2007). The arithmetic mean value of $\sigma$ at 25°C for the WPC solutions was 46.3 mN/m for $w \geq 0.10$. This value was similar to the data published by Roehl and Jelen (1988) at 25°C for pasteurized skimmed milk (45.2 mN/m) and untreated skimmed milk (46.5 mN/m), but was slightly higher than those reported by the same authors for whole-whey solutions ($41.7 \pm 1.2$ mN/m).

Figure 6 shows the variation of the surface tension with temperature for $w = 0.05$ and $w = 0.20$, in which we found a linear decrease in the surface tension with temperature, in a way similar to that of the surface tension of pure
water for this temperature range. The surface tension data were fitted to the following equations:

\[ \sigma = -101.2 - 0.197 \cdot T \quad \text{for } w = 0.05 \]  

\[ \sigma = 79.8 - 0.110 \cdot T \quad \text{for } w = 0.20 \]

Equations (6) and (7) fit our experimental data with an average deviation of lower than ±0.4%.

**CONCLUSIONS**

We have measured densities, dynamic viscosities, and surface tensions of WPC solutions at different concentrations and temperatures. Density and dynamic viscosity were fitted to an empirical equation that is a function of
temperature and WPC mass fraction. The surface tension values for the WPC solutions at 25°C decreased with the concentration, having a critical surface tension equal to $\sigma_c = 42.5$ mN/m when $w = 0.05$, whereas for $w \geq 0.10$, $\sigma$ values remained roughly constant. This behavior is typical of surfactant materials. Within the range of our experiments, surface tensions decreased linearly with temperature. The algorithms proposed enable the prediction of the dynamic viscosity, density, and surface tension of the WPC solutions over a wide range of concentrations and temperatures.

**NOMENCLATURE**

- $A$: Arrhenius constant, Eq. (3)
- $E_A$: activation energy, J/mol
- $n$: non-Newtonian index
- $R$: gas constant, J/mol/K
- $T$: temperature, K
- $w$: mass fraction

**FIG. 5. SURFACE TENSION OF WHEY PROTEIN CONCENTRATE SOLUTIONS**

$T = 25$C. Error bars represent the SD of the mean (SD $\leq 0.2$ mN/m).
ACKNOWLEDGMENT

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Greek Letters

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\beta$</td>
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<tr>
<td>$\sigma$</td>
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REFERENCES


