

Viscosity of Whey Protein Solutions*

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Received: 11 June 1994; accepted 15 October 1994

ABSTRACT

The apparent viscosity of whey protein solutions is studied as a function of shear rate, temperature and shearing time (at pH 6.5), using a coaxial cylinder and cone & plate viscometer (Haake VT500).

Aqueous solutions containing up to 54 wt% whey are subjected to shear rates between 10 and 3200 sec^{-1} . For concentration up to 25 wt% the viscosity is independent of the shear rate and time. For whey concentrations of 30 wt% and above, the viscosity decrease asymptotically with an increasing shear rate. The power law index is approximately constant over the range 30-40 wt% whey. The viscosity of 30-35 wt% solutions is independent of time of shearing, but is dependent on time for solutions of 40 wt% and greater. A thixotropic hysteresis effect (for $T < 50^\circ\text{C}$) and a rheopectic hysteresis effect (for $T = 52^\circ\text{C}$) are observed for solutions of 40 wt% and greater.

Key Words

viscosity, whey protein solutions, shear rate, shear stress

INTRODUCTION

Whey protein plays an important role in controlling the texture of food products [1]. Whey protein solutions are also of commercial interest because of their high nutritional value and excellent functionality in food applications [2]. In this regard, physical and flow properties of proteins can provide information necessary for the optimal design of unit processes and quality control of the manufacturing process and final products [3].

In general, the viscosity of protein solutions are expected to be dependent on the concentration, shape [4], size [5,6] molecular weight, flexibility,

intermolecular interactions [7,8], degree of hydration and charge of the proteins [9-18]. The viscosity can also be influenced by external factors such as temperature, pH and ionic strength [3,19-21].

Some viscometric studies have already been completed by other researchers on whey and its constituent proteins. However, knowledge of the effects of concentration, temperature and pH on viscosity is not complete. This paper reports the effect of shear rate and time on whey protein solutions. The changes in the apparent viscosity is characterised in terms of the aggregation and denaturation of the protein molecules.

* Presented in the First International Seminar of Polymer Science and Technology, 2-4 May 1994, Shiraz, Iran.

MATERIALS AND METHODS

Preparation of Samples

Whey protein concentrate (Alacen 152) was supplied by the New Zealand Dairy Research Institute. The composition of the powder is 79.4% protein, 9.3% lactose, 4.5% fat and 3.7% moisture. Whey protein solutions were prepared by placing a preweighed protein sample into a flask containing milli-Q-Water, mixing with a magnetic stirrer until dissolution was complete, diluting to the desired concentration, and then storing at 4°C prior to testing. Samples of 40 wt% and greater were stored at 4°C for approximately 10-15 hours to ensure that solution structure was in the fully recovered state. The normal pH of whey solution was 6.5 for all experiments.

Viscometric Measurements

The Haake VT500 viscometer with a built-in microprocessor was used to determine the apparent viscosity, shear rate and shear stress of the whey solutions as a function of temperature

and shearing time. Two coaxial cylinder (NV and MV1) and one cone & plate (pK1-1.0°) sensor systems were used in a temperature controlled jacket connected to a thermostated water bath. The range of viscosities and shear rates for which the three sensors are suitable is shown in Figure 1. The NV sensor was used for concentrations up to 35 wt% while the MV1 sensor was used for solutions of 40 wt% and greater. The cone and plate sensor was used to determine the time-dependent behaviour of the solutions.

The temperature-dependence of the apparent viscosity was measured between 20 °C and 40 °C for solutions up to 54 wt%. The viscosity of 40-45 wt% solutions was also measured at 50-60 °C. The producibility of the results was $\pm 1\%$.

RESULTS AND DISCUSSION

Effect of Concentration on Apparent Viscosity

The average viscosity of solutions was determined for shear rate of 500 s⁻¹. The values of the average

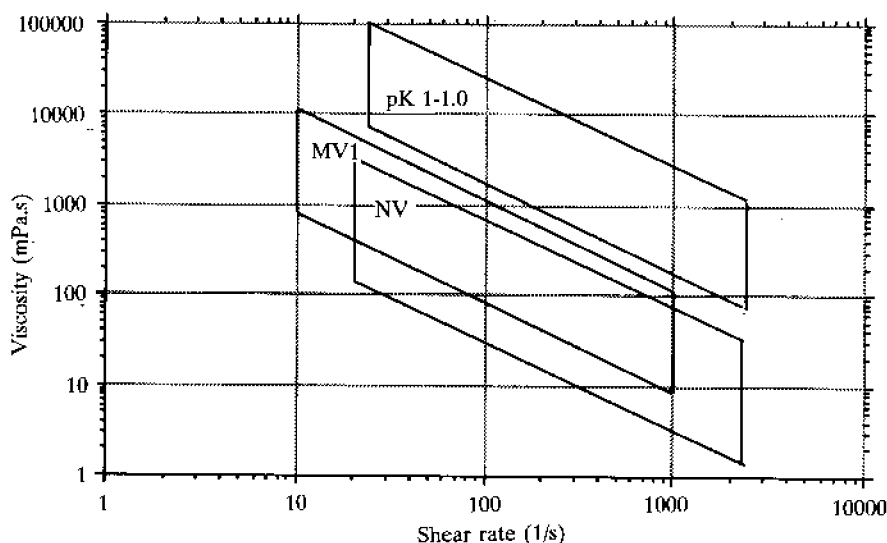


Fig. 1. The capabilities of the different Haake sensor systems.

viscosity for various temperatures and concentrations are given in Table 1. Solutions with concentrations of less than 10% wt obeyed a form of Einstein's viscosity equation. This relationship at 20 °C and pH 6.5 was found to be:

$$\mu = \mu_w (1 + 0.146 C) \quad (1)$$

Where:

μ_w = Viscosity of water = 1 mPa.s at 20 °C

μ = Viscosity of whey protein solution (mPa.s)

C = Concentration of whey protein solution (wt% whey).

For solutions with concentrations between 10 wt% and 35 wt%, the relationship between the average viscosity and concentration became non-linear. The data at 20 °C and pH 6.5 were accurately described by the equation: ($r^2=0.99$)

$$\mu = 0.83 \exp (0.133 C) \quad (2)$$

All results for solutions from 0-54 wt% at 20 °C and pH 6.5 could be slightly less well described

($r^2 > 0.98$) by a similar equation:

$$\mu = 0.94 \exp (0.135 C) \quad (3)$$

The effect of protein concentration on the average viscosity is shown in Figure 2.

Effect of Shear Rate on Apparent Viscosity

Aqueous solutions containing up to 54 wt% protein were subjected to shear rates between 10 and 3200 sec^{-1} . The viscosity of solutions below 25 wt% was independent of the shear rate or the time of shearing. For the range 25 wt% < C < 40 wt%, the viscosity was dependent on the shear rate, the solutions displaying pseudoplastic behaviour.

For protein concentrations of 30 wt% or higher, the viscosity decreased asymptotically with increasing shear rate. The effect of shear rate on the apparent viscosity is shown in Figure 3. The power law index (n) for all solutions is shown in Table 1. When the index is close to one, the viscosity is independent of the shear rate. From the table, it can be seen that whey protein

Table 1. Viscosity and power law exponent index (n) of whey protein (pH=6.5 & $\dot{\gamma} = 500$ 1/s).

Temperature Concentration (wt%)	20 °C		25 °C		30 °C		35 °C		40 °C	
	μ (cp)	n	μ (cp)	n	μ (cp)	n	μ (cp)	n	μ (cp)	n
2.5	1.4	1.02	1.3	1.05	1.2	1.04	1.1	1.02	1	1.04
5	1.8	1.03	1.7	1.04	1.7	1.03	1.6	1.02	1.4	1.03
10	2.5	1.05	2	1.06	1.8	1.04	1.7	1.08	1.6	1.05
20	10	1.07	7	1.07	5.8	1.07	5.2	1.07	4.7	1.07
25	22	1.04	11	1.04	10	1.07	8.8	1.08	7.7	1.08
30	52	0.82	50	0.86	43	0.83	36	0.83	32	0.83
35	88	0.87	74	0.85	62	0.81	53	0.89	46	0.90
36	110	0.83	102	0.82	87	0.81	73	0.82	60	0.84
40	235	0.81	216	0.82	145	0.81	112	0.83	79	0.81
46	610	0.73	530	0.72	470	0.73	420	0.72	392	0.71
53	1530	0.67	1403	0.68	1320	0.69	1280	0.69	1215	0.66

solutions become non-Newtonian somewhere above 25 wt%. The power law index decreases slowly for 25-40 wt% and then rapidly above 40 wt%.

Effect of Shearing Time on Apparent Viscosity

The viscosity of all solutions up to 35 wt% is independent of time. A thixotropic hysteresis effect was observed for solutions in the range from 40-54 wt% as can be seen in Figure 4. At 52 °C, rheopectic behaviour was observed for solutions of 40 wt% and greater as shown in Figure 5.

Effect of Temperature on Apparent Viscosity

Figure 6 shows the effect of temperatures between 20 °C and 40 °C on the viscosity of solutions at different concentrations. Temperature-dependent results could be fitted by straight lines by plotting $\log(\mu)$ vs. $1/T$ which is followed the Arrhenius equation:

$$\mu = A \exp(E/RT)$$

Where μ is the apparent viscosity (mPa.s), E

the activation energy of flow (kJ/mol), R the universal gas constant, T the absolute temperature (°K) and A a constant (mPa.s). Values of E and A are given in Table 2.

CONCLUSION

The concentration dependence of the apparent viscosity on the shear rate observed by other researchers [3,13,20-22) was confirmed by this study for whey protein solutions. The effect of concentration may be divided into three separate regions.

In the first region, the solutions obey Einstein's equation [9,10], that is, the viscosity is linearly related to the concentration. The first region applies to dilute concentrations up to 10 wt% and for shear rates between 10 and 3200 s⁻¹. The region is characterized by low molecular interactions between whey protein molecules.

In the second region, which applies to semi-dilute concentrations between 10 and 35 wt%, deviation from Einstein's equation was

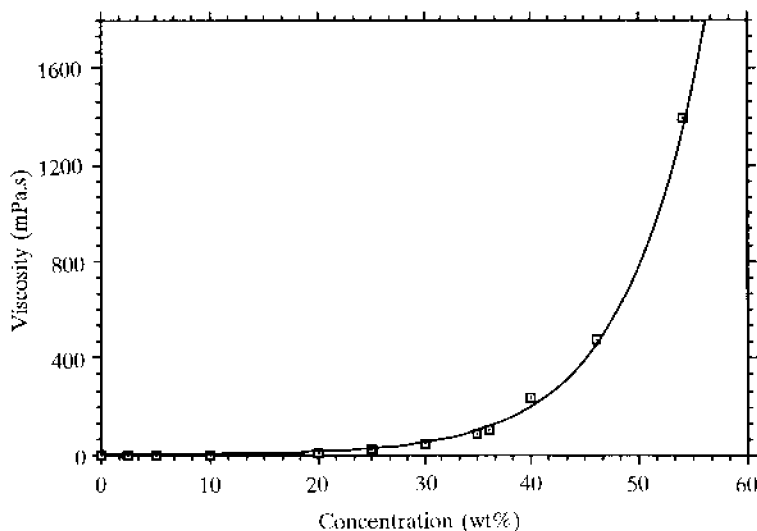


Fig. 2. The effect of protein concentration on average viscosity (T=20 °C, $\dot{\gamma} = 500$ 1/s & pH=6.5).

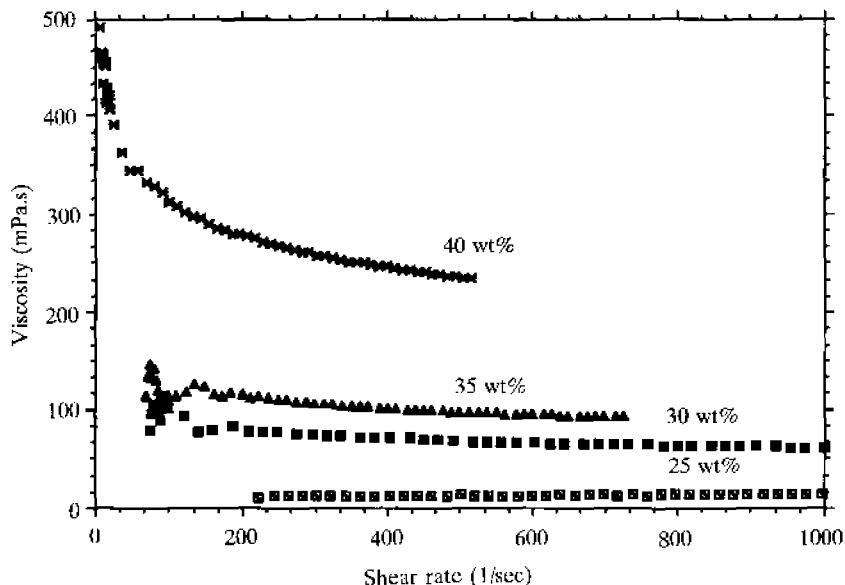


Fig. 3. The effect of shear rate on apparent viscosity ($T=20\text{ }^{\circ}\text{C}$, & $\text{pH}=6.5$).

exhibited by non-linear concentration dependence of the viscosity because of the increasing effects of both hydrodynamic and molecular interactions [1,20,21].

In the third region for concentrated solutions greater than 35 wt%, the hydrodynamic and molecular interactions between protein molecules reaches a maximum. The pseudoplastic behavior observed for this region, may be explained by the disaggregation of molecules due to shearing occurring at a higher rate than the normal formation of aggregates as a result of Brownian motion [21] which results in deformation or removal of the protein hydration sphere and rupture of weak bonds such as ionic and hydrogen bonds and in dissociation of protein aggregates [16,23]. The time-dependent thixotropic behavior of whey protein solutions for highly concentrated solutions ($C \geq 40\text{ wt}\%$, $T < 50\text{ }^{\circ}\text{C}$) can also be caused by the aggregates breaking [24]. The rheopectic behavior ($C \geq 40\text{ wt}\%$ and $T = 52\text{ }^{\circ}\text{C}$) could be caused by unfolding or uncoiling of

protein molecules. In this way, the shape and size of proteins can be changed and increased, thus causing increases in the apparent viscosity of the

Table 2. Values of activation energy (E) and (A) a constant in the Arrhenius equation for whey protein solutions ($\text{pH}=6.5$ & $\dot{\gamma}=500\text{ 1/s}$)

Concentration (wt%)	A ($\mu\text{ Pa.s}$)	E(kJ/mol)
10	4.7	15.2
20	4.1	18.3
25	2.11	21.4
30	2.72	24.4
35	2.96	25.1
40	0.38	33.3

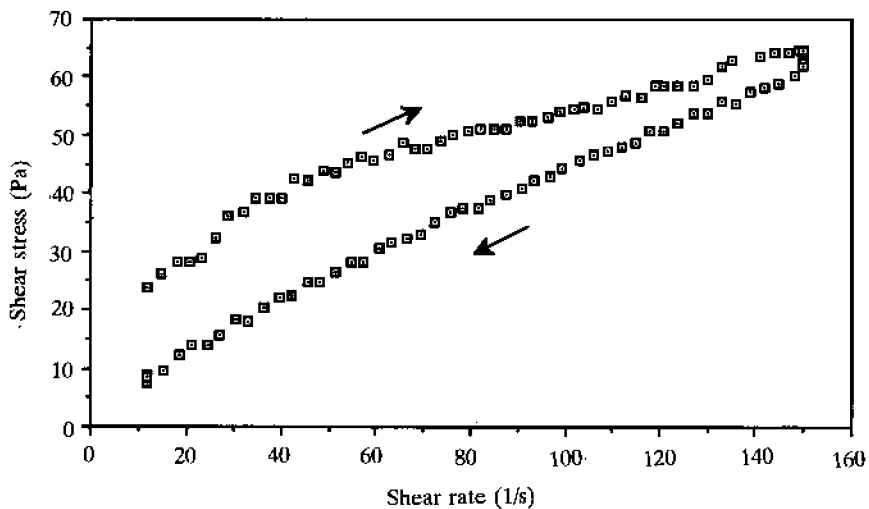


Fig. 4. The effect of shearing time on apparent viscosity (40 wt% & $T=20\text{ }^{\circ}\text{C}$).

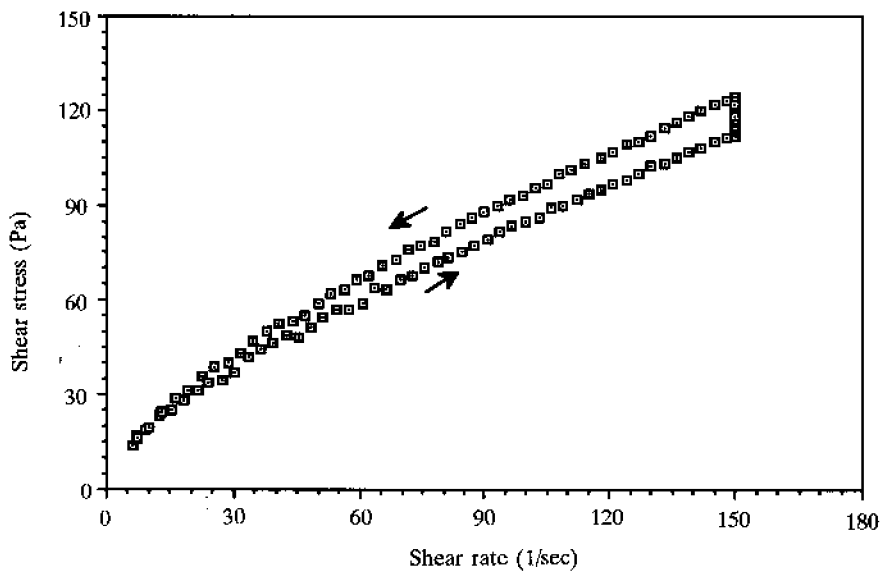


Fig. 5. The effect of shear rate and shear stress (40 wt% whey protein, $T=52\text{ }^{\circ}\text{C}$).

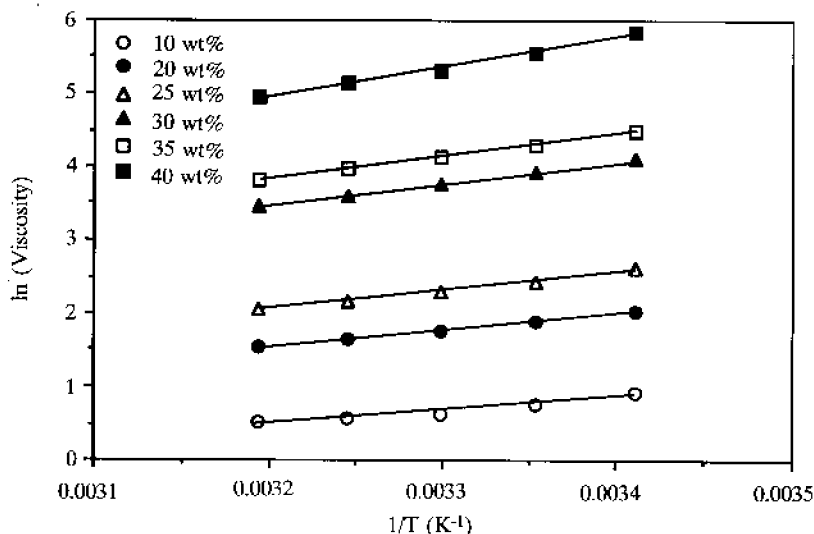


Fig. 6. The $\ln(\mu)$ vs. $1/T$ at different concentrations (pH 6.5 & $\dot{\gamma} = 500$ 1/s).

why solutions with shearing time [4,21,23,25-27].

The results presented here show that the apparent viscosity decreases with increasing temperature below 52 °C because of increases in intermolecular distance[28,29] and protein-protein hydrophobic interactions. Above 52 °C the increases in viscosity caused by unfolding and denaturing of the protein outweigh decreases in viscosity caused by temperature increases. According to Dewit and Klarenbeek[30], above 60 °C any protein structure changes are mostly irreversible. At temperatures below this, protein changes are reversible.

It can be seen that the viscosity of whey, which includes several different proteins, is very complex and is the result of the combined contribution of the hydrodynamic forces and interactions between protein particles. The changes in viscosity, and particularly the effect of shear rate on viscosity have a significant application in processes including pumping, spray drying and ultrafiltration.

ACKNOWLEDGEMENTS

The authors wish to thank the New Zealand Dairy Research Institute for the supply of the whey protein concentrate. M.R.A would also like to thank the Higher Education Ministry of Iran for financial support.

SYMBOLS

- C= Concentration (wt% whey)
- r^2 = Regression coefficient
- n = Power law index
- μ = Average viscosity for shear rate of 500 1/sec
- μ_w = Viscosity of water = 1 mPa.s at 20 °C
- $\dot{\gamma}$ = Shear rate (1/sec)
- E= Activation energy of flow (kJ/mol)
- R= Universal gas constant (kJ/mol.°K)
- T= Absolute temperature (°K)
- A= Arrhenius equation constant (mPa.s).

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