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Studies on Some Functional Characteristics of Whey Protein-Polysaccharide Complex

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Functional characteristics of whey protein-carboxymethyl cellulose (WP-CMC) was studied and compared with those of ultrafiltered whey protein concentrates (UF-WPC). WP-CMC complexes were highly soluble at neutral pH, but showed very less protein solubility at pH below isoelectric point of whey protein. The temperature did not show any significant change in the solubility. Higher buffering capacity was observed below pH 3.0 and between pH 5.7 and 6.3. The viscosity of the WP-CMC complex decreased with rise in temperature above 50°C, but UF-WPC indicated an increase in viscosity above 50°C. These complexes formed weak gels even at lower pH. Emulsion and foam solubility of WP-CMC complex were very high, as compared to UF-WPC.

Keywords : Whey protein, Carboxymethyl cellulose, Functional characteristics, Ultrafiltered whey protein concentrates.

The charged polysaccharides have a special ability to interact with food proteins. Significance of these interactions in food system for protein recovery, protein stabilisation and food texture modification have been well documented (Samant et al. 1993). Generally, the properties of such protein-hydrocolloid complexes differ considerably from those of individual polymers (Bimlesh and Malik 1993). In case of protein-anionic polysaccharide complexes, the conformation and charge ratio of the molecular component dictates the properties. Many functional properties can be controlled by complexing proteins with polysaccharides (Tolstoguzov 1990). The work carrried out by Asano (1996) suggests that carboxymethyl cellulose (CMC), which is a polysaccharide, interacts with several milk proteins in acidified milk. Subsequently, Hidalgo and Hansen (1971) developed the method of recovering the whey proteins by complexing with CMC.

The main objective of this study was to examine the physico-chemical properties of the whey protein-carboxymethyl cellulose complex. Such type of work will be helpful in further utilization of this complex in various formulated foods.

Materials and Methods

Recovery of whey protein-carboxymethyl cellulose (WP-CMC) complex: WP-CMC complex was recovered by using the method given by Mathur and Srinivasan (1979) with slight modification. The pH of cheese whey was adjusted to 3.2 and mixed with an equal volume of the acidulated water (pH 3.2), containing calculated amount (0.3%) of CMC (substitution range of 0.65 to 0.85).The precipitated complex was recovered by centrifugation, followed by dialysis and freeze-drying. Along with WP-CMC complex, the ultrafiltered whey protein concentrates (UF-WPC), obtained from Experimental Dairy, National Dairy Research Institute, were also analyzed for the sake of comparison.

Chemical analysis: The samples were analyzed for proteins (Morr et al. 1985), carbohydrates (Winzler1955), fat, ash and moisture contents (ISI Methods 1981).

Functional properties: Protein solubility was determined by the method described by Morr et al (1985) and data were subjected to statistical analysis. Buffering capacity (BC) was determined by titrating 0.5% solution of WP-CMC complex with 0.1 N HCl or 0.1 N NaOH and was calculated by the equation:

$$\frac{dB}{dpH} = \frac{\text{Milli-equivalent of titrant}}{\text{Gram sample} \times \text{pH}}$$

BC curve was drawn by plotting $\frac{dB}{dPH}$ vs. pH

Relative viscosity of aqueous solution of WP-CMC complex, having concentration varying between 2 and 10% (w/v), was determined between 20°C and 80°C, using falling Ball Hoppler's viscometer. The equation used was:

$$\text{Viscosity } n = T\,(S_B - S_L)\,K$$

where,

T= falling time of the ball,

S_B= specific gravity of the ball,

S_L= specific gravity of liquid used and

K= ball constant

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Gelling behaviour of these samples was observed by the method of Zirbel and Kinsella (1988) with 20% concentration in water.

For determining emulsion stability, emulsions were prepared with ultrasonic instrument (Branson Sonifier Distruptor, Model B-12), using 45 g water, 5 g soybean oil and 120 mg protein product. Immediately after sonification, the viscosity of the emulsion was determined, using Ostwald viscometer.

Foaming properties were examined, using a household mixer by whipping 75 ml of 3% (w/v) protein solution for 5 min at maximum speed (DeWit et al. 1988).

Results and Discussion

The WP-CMC complex was white in colour as compared to UF-WPC, which was slightly brownish. The former was more fluffy. The yields of WP-CMC complex and UF-WPC were 6.2 and 7.8 g/l cheese whey.

Chemical composition: The chemical composition of WP-CMC complex, given in Table 1, indicates that the protein contents in WP-CMC complex were slightly less than those of UF-WPC. WP-CMC complex contained more carbohydrates than ash and moisture contents. The average fat content in both the WPCs was almost similar.

Solubility: It is observed from Table 2 that protein solubility of WP-CMC complex was very much dependent on pH, as compared to UF-WPC. The complex had much more solubility at pH 7,0, than at pH 3.5. The UF-CMC also had more solubility at pH 7.0, but in this case the difference was of the order of about 10% only. The WPC manufactured by complexation or precipitation method generally had more solubility dependence upon pH, than the whey protein concentrates from other processes because of residual reagents, which precipitated positively charged protein molecule at or below isoelectric point (Delaney 1976). The residual amounts of the complexing reagents, which were perhaps present as anionic species, had no effect on the solubility of WPC at pH above the isoelectric point of the whey protein, when these proteins were also carrying negative charge. This is evident from the fact that at pH 7.0, the solubility of WP-CMC complex was higher than that of UF-WPC. Statistical analysis showed that per cent solubility of WP-CMC complex at temperature 20°, 30° and 40°C did not show any significant difference ($p > 0.05$), but in case of UF-CMC, the per cent solubility at those temperatures differed significantly ($p < 0.01$) (Table 2). The solubility was lower at 40°C than at 30°C in almost all the cases. This lower solubility at 40°C may be explained on the basis of the findings of Macritchie (1979), who reported that bovine serum albumin (BSA) was highly soluble in water at 30°C, but showed severe precipitation in temperature range between 40 and 45°C. This charged solubility at about 40°C paralleled the reversible partial unfolding of BSA, observed at 42 and 50°C (Lin and Koeing 1976).

pH and buffering capacity (BC): The initial pH value of the WP-CMC complex was low (4.5) in

TABLE 1. CHEMICAL COMPOSITION (g/100 g) OF WP-CMC AND COMPLEX) AND UF-WPC

	WP-CMC complex	UF-WPC
Protein, %	57.70 - 64.27	61.25 - 65.79
	(60.94)	(63.52)
Carbohydrate, %	17.13 - 18.50	4.06 - 6.46
	(17.82)	(5.26)
Fat, %	13.40 - 17.85	12.08 - 16.06
	(15.63)	(14.07)
Ash, %	1.11 - 2.690	3.88 - 5.04
	(1.86)	(4.97)
Moisture, %	1.65 - 2.75	5.16 - 6.92
	(2.20)	(6.09)

Values in parentheses indicate average of five samples

TABLE 2. SOME FUNCTIONAL PROPERTIES OF WHEY-PROTEIN-CARBOXYMEHTYL CELLULOSE COMPLEX AND ULTRAFILTERED WHEY PROTEIN CONCENTRATES

Functional properties	WP-CMC		UF-WPC	
(a) Solubility, %				
	pH		PH	
	3.5	7.0	3.5	7.0
Temperature (°C)				
20	14.15*	86.69*	56.79**	70.70**
30	16.47*	100.00*	74.18**	81.94**
40	15.69*	99.60*	67.49**	76.09**
(b) pH and buffering capacity				
Initial pH	4.85		5.63	
pH of peak in BC curve	6.30		7.0-7.8	
(c) Emulsion stability in terms of relative viscosity	2.56		1.35	
(d) Whipping properties				
Overrun, %	35.33		40.00	
Foam stablity	5.31		1.40	

* solubilities at different temperatures were not significantly different ($p > 0.05$)

** solubility differed with temperature significantly ($p < 0.01$)

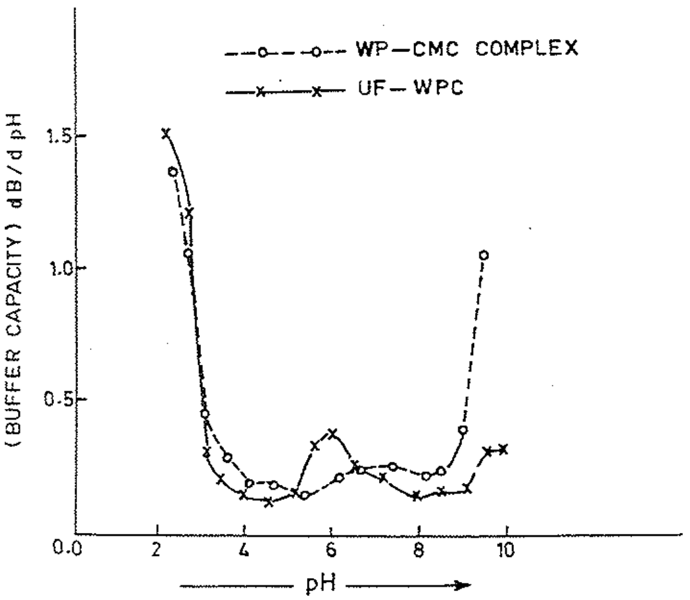

Fig. 1. Buffering capacity as a function of pH

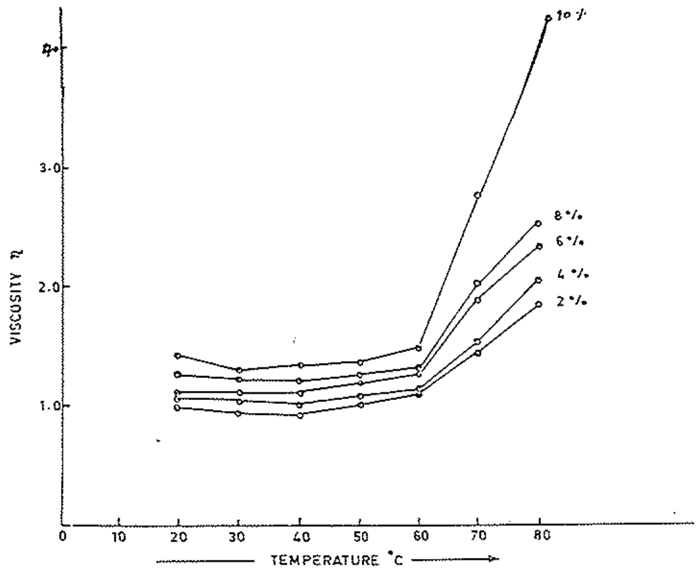

Fig 3. Viscosity of whey protein concentrates prepared by ultra-filtration as a function of temperature

comparison with UF-WPC (6.3), which is perhaps due to the method of preparation of these samples. It is shown in Fig. 1 that BC of WP-CMC complex was higher at values below pH 3.0 and above 6.0, while whey protein concentrates prepared by ultrafiltration showed higher BC below pH 4.0 and a broad peak in BC/pH curve was observed around 6.0. Buffering capacity data provided an indication of the type and concentration of the important ions that were retained in these whey protein concentrates.

Viscosity: The WP-CMC complex showed higher viscosity than WPC from other methods. This might be due to CMC being highly viscous. The complexes showed higher viscosity at low temperature and behaved more or less like gel at 10% concentration, as shown in Fig. 2. However, with the rise of temperature, the viscosities of these complexes decreased continuously, unlike those of the UF-WPC, when there was decrease initially and then (at around 50°C and above) increase due to denaturation of whey proteins (Fig. 3). In former case, it appeared that the effect of increase in viscosity due to denaturation of whey protein was balanced by the behaviour of CMC, because viscosity of a polysaccharide solution decreased with increase in temperature (Whitsler and Daniel 1985).

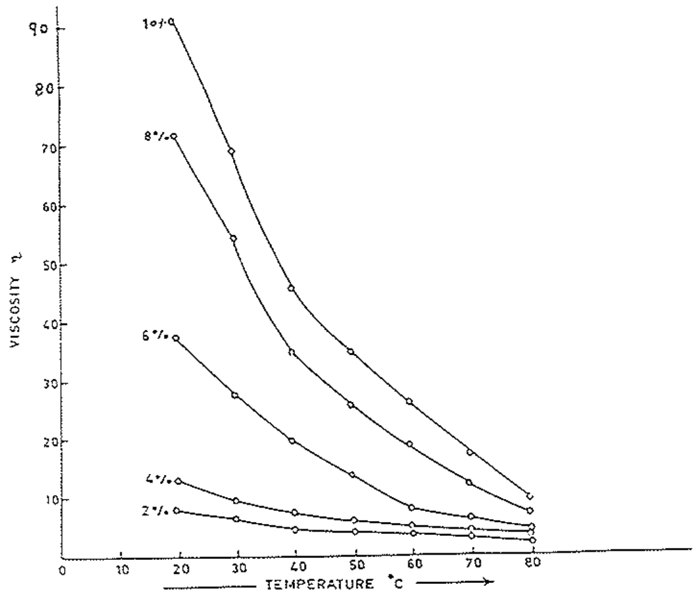

Fig. 2. Viscosity of whey protein-carboxy methyl cellulose complex as a function of temperature

Gelation: Whey protein-CMC complex, prepared from cheese whey, did produce gels, but these gels were very weak and fragile. It was not possible to cut sections from these gels, and study their textural characteristics with the help of Instron. But, UF-WPC produced gels which were quite hard and springy in nature. The formation of protein gels was due to protein network, which resulted from a balance between protein-protein and protein-solvent (water) interactions and attractive as well as repulsive forces between the adjacent polypeptide chain (Hermanson 1979). Around pH 4.5, the whey proteins are only slightly changed and bind a small amount of water. The small charge should help in formation of the network. Due to very small amount of water, which the proteins are carrying, a precipitate is obtained instead of a gel (Hiller and

Cheeseman 1979; Bimlesh and Malik 1994). It is interesting to note that pH of WP-CMC complex was around 4.5 and at this pH, there should not be any gel formation. The weak gel formed by WP-CMC complex may be, however, due to cross linking between -OH group of CMC with NH_2 or -COOH groups of whey proteins. Protein can form gel through interaction with anionic polysaccharide gelling agents (Lin 1977).

Emulsion stability: It is well established that proteins stabilise the fat particles in emulsion by forming a membrane around the oil particles and making the oil particles to carry similar charge. These charged particles cannot come close to each other and coalesce. The charge on the oil particles also increases the viscosity of system due to electroviscous effect. Therefore, the viscosity of the emulsion also gives a qualitative idea about the stability of the emulsion. Higher the viscosity, more stable is the emulsion. The viscosity of the emulsion stabilised with whey protein-CMC complex and UF-WPC complex was almost double than that of UF-WPC. This might be due to the fact that CMC binds with water and imparts viscosity to the aqueous phase and thus stabilizes the emulsion. The emulsion stability increases on transition from a protein to its complex with polysaccharide (Tolstoguzou1986).

Whipping properies: WP-CMC complex showed lower overrun, but better foam stability than UF-WPC as shown in Table 2. The higher overrun can be produced with higher protein solubility (Liano and Mangino 1987). But, WP-CMC complex dispersion had low pH, i.e., around 4.5 and solubility at this pH was very low (Table 2). Good foam stability can be explained on the basis of higher viscosity of aqueous solution of WP-CMC complex.

Conclusions

Complexation of whey protein with carboxymethyl cellulose changes the functional properties of these proteins to a greater extent. Due to carbohydrate complexation, the functional properties of whey proteins can be controlled in a particular range of pH, depending upon the food products. The study on protein-polysaccharide interaction reveals their potential, which can be well utilized to meet new technological requirements.

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