

Short Communication

Cationic Effect on the Electrolyte Flocculation of Cassava Starch Emulsion

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Abstract. The study to investigate, whether cassava starch emulsions are prone to flocculation by electrolytes and the role of the cationic valency in the instability showed that the electrolyte treated samples exhibited various degree of creaming and increase in globule size which depended on the cationic valency of the electrolyte, whereas the untreated samples hardly exhibited any evidence of creaming or changes in globules structure after 24 h of preparation. The trivalent cationic electrolyte (FeCl₃) gave the most pronounced effect, while the monovalent cationic electrolyte (NaCl) gave the least effect on the creaming and globule size increase indicating that the instability is associated with the adsorption of the cationic moiety of the electrolyte on the globules to neutralize anionic charges on the globules surfaces.

Keywords: cassava starch emulsion, instability, cationic effect

Starches form oil/water emulsions primarily by imparting viscosity to the aqueous emulsions and by forming a multi-molecular layer around the disperse globules. Maize starch BP usually forms unstable emulsions with coarse globules and is used in the extemporaneous preparation of enemas only (Trease and Evans, 1989). On the other hand, cassava starch forms highly viscous mucilages capable of stabilising aqueous emulsions and in fact, may be used as a substitute for acacia gum, provided a preservative is included in the formulations (Uhumwangho *et al.*, 2005). The limitation in the use of cassava starch in pharmaceutical formulations is the content of hydrocyanic (prussic) acid (Trease and Evans, 1989). This problem may be overcome by treating the starch with dilute aqueous sodium bicarbonate solution and washing several times with water until the washing is neutral to litmus. It is well known that emulsions stabilised by hydrocolloids (e.g., whey protein, acacia, sodium alginate) are readily flocculated by electrolytes (Silvestre *et al.*, 1999; Black and Popovich, 1981). However, the mechanism of the instability is not clear. The purpose of the present study was to investigate, whether cassava starch emulsions are prone to such electrolyte-induced instability and the mechanism of the instability by varying cationic valency of the electrolytes.

Cassava starch was extracted from the tubers of cassava plant (*Manihot utilissima*) following standard procedures for starch extraction (Trease and Evans, 1989). The hydrocyanic content was neutralised and the starch was used to form mucilage at 4% w/v. The test electrolytes were sodium chloride, calcium chloride and ferric chloride (all Analar grades, BDH, Poole, England).

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Preparation of the emulsions. Emulsions (o/w) were prepared by adding, arachis oil to the mucilage (50 mL, 4% w/v). Mucilage concentration <4% w/v formed thin emulsion that creamed rapidly, while mucilage concentration >4% w/v formed thick emulsion that was difficult to disperse.

Electrolyte treatment of the emulsions. Different concentrations of sodium chloride (0.005 to 0.05 M) were used to challenge the emulsion and the minimum concentration which exhibited measurable creaming after 24 h was used to study the flocculant effect of the other two multivalent cationic electrolytes. High creaming rate indicated a high flocculant effect of the test electrolyte.

Determining creaming rate. Emulsion (10 mL) in a glass measuring cylinder was allowed to stand for 24 h. At selected time intervals, the volume of the cream (supernatant) layer was recorded.

Globule size analysis. Photomicrographs were taken and all globules appearing in each micrograph were counted and sized with the aid of a photomicrograph of a calibrated stage slide. Mean globule size (\bar{x}) was calculated from the expression:

$$\bar{x} = \frac{\sum fx}{Wf} \quad (1)$$

Where, f is the frequency of each size x. The size analysis was carried out for fresh and aged (24 h) samples (both treated and untreated). The increase in globule size during storage (24 h) was taken as a measure of globule flocculation and coalescence and was used to score the flocculant effect of the electrolytes.

Statistical analysis. The resulting data were subjected to the Student t test $P > 0.05$ to test for significance of difference between paired data.

Electrolyte effect on the creaming rates. The creaming rate increased with increase in the electrolyte concentration from 0.01 M to 0.05 M (Table 1). Concentration < 0.01 M gave no measurable creaming even after 24 h. This concentration was taken as the minimum flocculant concentration of sodium chloride and used to compare the flocculant effect of multi-valent electrolytes (CaCl_2 and FeCl_3). The results (Fig. 1) showed that the trivalent cation electrolyte (FeCl_3) produced higher creaming rate than the divalent electrolyte cationic electrolyte (CaCl_2), which in turn produced higher creaming rate than the monovalent cationic electrolyte (NaCl). The untreated samples showed no measurable creaming after 24 h.

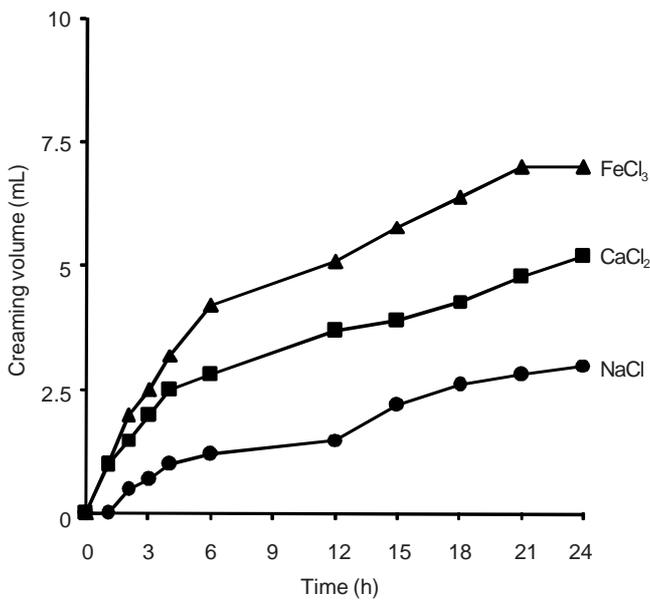


Fig. 1. Plot showing the creaming rate of emulsions treated with 0.01 M solutions of the electrolytes: NaCl (●), CaCl_2 (■) and FeCl_3 (▲).

Electrolyte effect on globule size. The globule sizes increased generally after 24 h in the electrolyte treated emulsions (Fig. 2a-c). It can be seen that the untreated aged sample hardly exhibited any change in the globule structure, whereas the treated sample conspicuously exhibited an increase in globule size and a corresponding decrease in globule number. The mean globule size in the fresh emulsions was 26.4 ± 6.1 nm. After treatment with equal molar concentration (0.01 M) of the

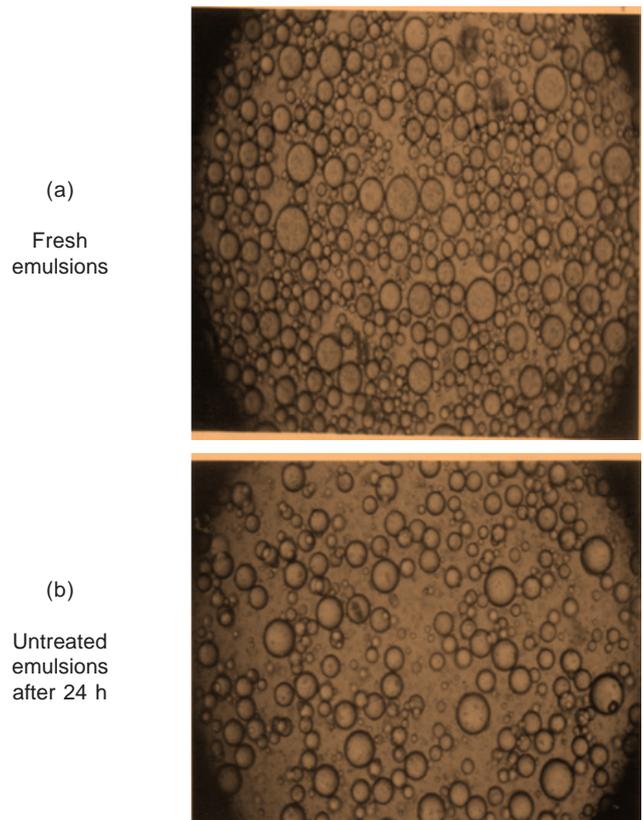


Fig. 2a & b. Photomicrographs (x 40) showing the globule structure of (a) fresh sample (b) untreated emulsions samples 24 h old, (test electrolyte FeCl_3 (0.01 M)).

Table 1. Effect of electrolyte (NaCl) concentration on creaming rate

Electrolyte concentration (M)	Creaming volume (mL/h)									
	1	2	3	4	6	12	15	20	24	
0.005	*	-	-	-	-	-	-	-	-	-
0.01	0.1±0.01	0.3±0.01	0.3±0.02	0.4±0.01	0.5±0.02	0.7±0.02	0.7±0.02	0.7±0.01	0.7±0.02	
0.02	0.2±0.03	0.4±0.02	0.5±0.02	0.6±0.02	0.6±0.03	0.9±0.01	1.0±0.01	1.0±0.02	1.0±0.03	
0.03	0.4±0.02	0.4±0.03	0.6±0.03	0.6±0.03	0.7±0.02	0.9±0.02	1.0±0.03	1.0±0.03	1.2±0.04	
0.05	0.4±0.01	0.5±0.02	0.6±0.02	0.7±0.01	0.9±0.03	1.0±0.02	1.2±0.02	1.3±0.04	1.5±0.02	

* = no measurable creaming volume.

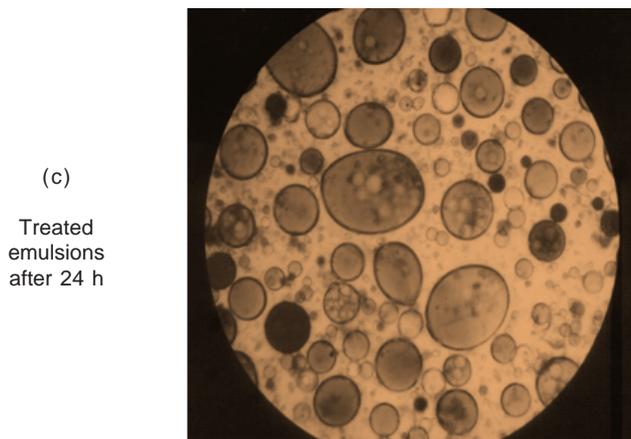


Fig. 2c. Photomicrographs (x 40) showing the globule structure of treated emulsion samples 24 h old, (test electrolyte FeCl_3 (0.01 M)).

electrolytes the mean globule size increased to 52 ± 4.2 mm (NaCl), 75 ± 3.2 mm (CaCl_2) and 82 ± 4 mm (FeCl_3). Statistical analysis revealed a statistically significant difference in the globule sizes of the fresh emulsions and the treated emulsions ($P < 0.05$). Thus, a higher cationic valency was associated with a higher flocculant effect of the electrolyte. Flocculation promotes creaming which ultimately results in coalescence, hence the increase in globule size observed in the electrolyte treated emulsion (Tcholakova *et al.*, 2005). Hydrocolloids such as the cassava starch are anionic polymers which carry negative charges (Sikora *et al.*, 2008). These polymers stabilize emulsion by forming a multimolecular layer around the disperse globules as well as imparting viscosity to the dispersion medium (Sikora *et al.*, 2008). Strong dependence of the flocculant effect of the electrolyte on the cationic valency suggests that the cations were adsorbed on the globule

surface to neutralise the anionic charges and hence bring about flocculation (Black and Popovich, 1981).

Conclusion

It is concluded that cassava starch emulsions are prone to flocculation by the trace amount of electrolytes; the higher the cationic valency of the electrolytes, the higher its flocculant effect. The implication is that cationic drugs or excipients cannot be incorporated in the emulsion system studied.

References

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