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Coacervation of Gelatin–XM6 Mixtures and their Use in Microencapsulation

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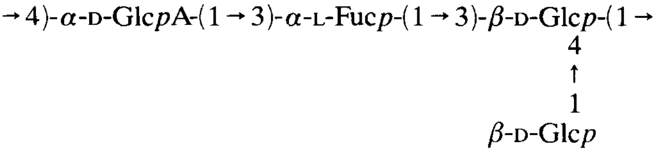
SUMMARY

Complex coacervation has been observed at low total polymer concentrations in mixtures of gelatin with the extracellular bacterial polysaccharide secreted by Enterobacter *(NCIB 11870). Coacervation only occurred within the pH range 3·0–4·5. Methods are described for the microencapsulation of oils and solid particles.*

INTRODUCTION

XM6 is the codename for an extracellular polysaccharide produced by the bacterium *Enterobacter* (NCIB 11870) (Nisbet *et al.*, 1984). The polymer is a branched anionic heteropolysaccharide (O'Neill *et al.*, 1986) composed of tetrasaccharide repeat units (Fig. 1). XM6 shows unusual gelation properties and has potential use as an industrial gelling agent. The polysaccharide may be dispersed in water and yields a viscous liquid. Thermoreversible gels are formed when the ionic strength of these liquids is raised by the addition of inorganic salts (Nisbet *et al.*, 1984). This article is concerned with a possible alternative industrial use for XM6. Studies have been made of complex coacervation of



$$\rightarrow 4)\text{-}\alpha\text{-D-Glc}p\text{A-}(1\rightarrow 3)\text{-}\alpha\text{-L-Fuc}p\text{-}(1\rightarrow 3)\text{-}\underset{\substack{4\\ \uparrow\\ 1\\ \beta\text{-D-Glc}p}}{\beta\text{-D-Glc}p}\text{-}(1\rightarrow$$

Fig. 1. Chemical repeat unit of XM6.

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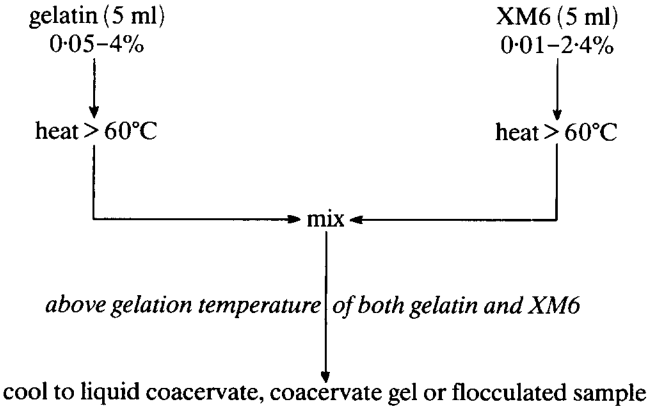
gelatin–XM6 mixtures. These data have been used to investigate potential uses for encapsulation of oils and solid particles.

EXPERIMENTAL

Samples of XM6 were a gift from Dr I. T. Taylor (ICI plc, Biological Products Business, Billingham, UK). Large-scale production, isolation and clarification of XM6 polysaccharide was carried out as described by O'Neill *et al.* (1986). An additional clarification step involved filtering hot (90°C) aqueous dispersions through 8-μm Millipore filters. Samples of pig-skin gelatin (Bloom 175, batch no. G2625) were supplied by Sigma Chemical Co. The isoionic point was measured by the method of Janus *et al.* (1951) and found to be at pH 8. This value is typical of an acid-treated pig-skin gelatin. The oils used in the encapsulation studies were sunflower oil and colourless paraffin. Aluminium powder (Aldrich Chemicals) was used as a representative solid core material.

Scheme I was used to investigate coacervation in gelatin–XM6 mixtures. Studies were confined to low total polymer concentrations at which the mixtures remained liquid upon cooling to room temperature (25°C). Cooling gelatin–XM6 mixtures often resulted in the formation of white precipitates or flocs which sedimented upon standing. Samples which became translucent upon cooling were examined under a microscope for evidence of coacervation and/or flocculation. A typical coacervate is shown as an inset in Fig. 2. Droplet diameters ranged in



Scheme I

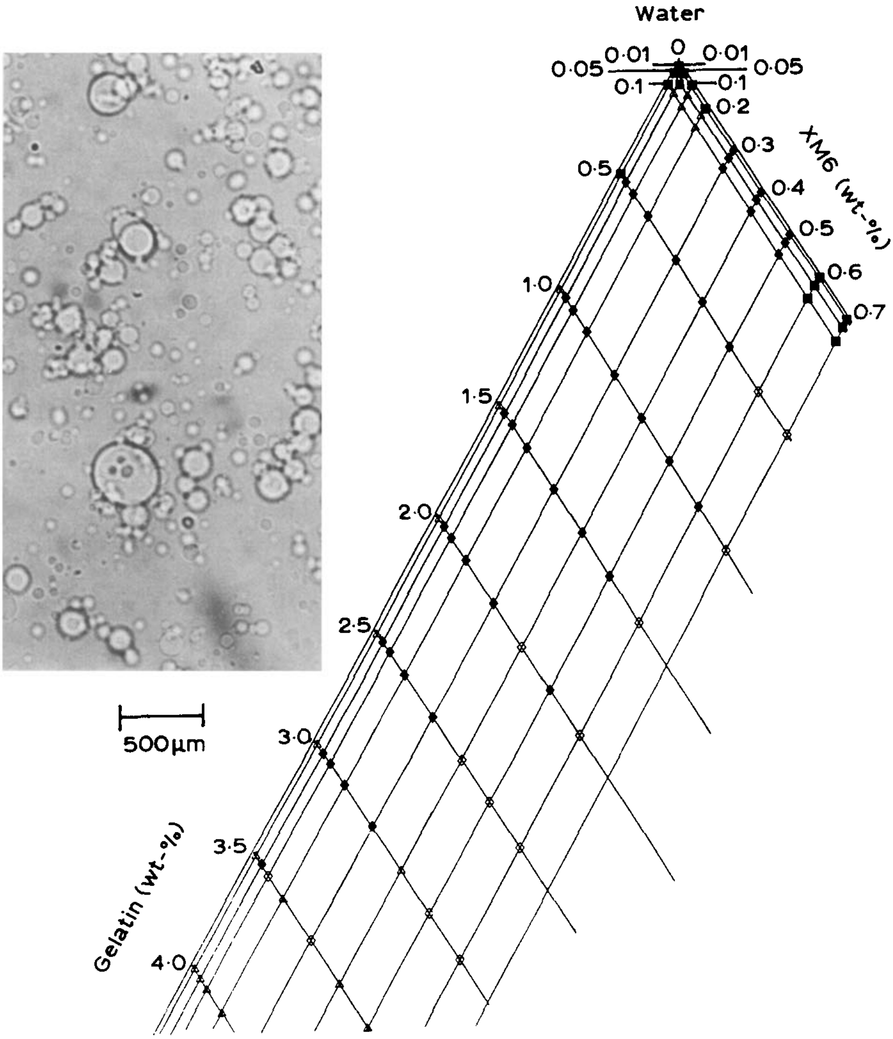
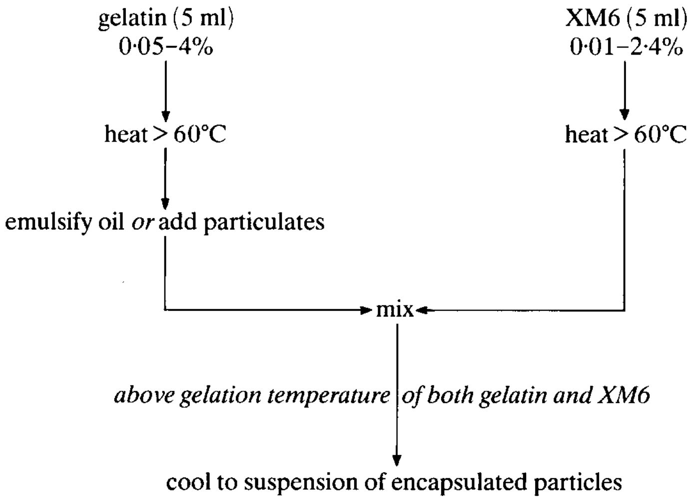


Fig. 2. Gelatin–XM6 coacervates. Diagram illustrating the coacervation region observed after mixing and cooling. ■, Liquid medium no coacervate; ◆, coacervates; ◇, coacervates plus flocs; △, flocculation. Insert shows a typical gelatin–XM6 coacervate.

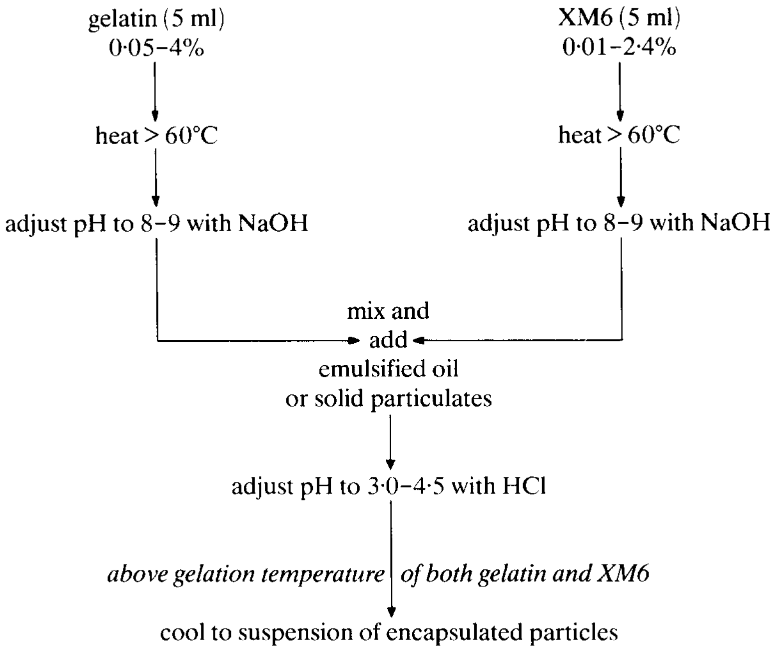
size from ≈ 1 to 400 μm. The region in which coacervation, essentially free of flocculation or precipitation, occurs on cooling is displayed in Fig. 2.

Coacervation may be broadly divided into two types (de Jong, 1949). Simple coacervation arises from the addition of suitable cosolutes to a polymer solution and is largely independent of the electrical charge on the polymer(s). Complex coacervation of a binary polymer mixture requires that one polymer is positively charged and that the other possesses a net negative charge. Thus complex coacervation will be restricted to a finite pH range. The effect of pH upon coacervation of gelatin–XM6 mixtures was probed by using a modification to scheme I. The pH of hot (> 60°C) solutions of gelatin and XM6 were adjusted to pH 8–9 by addition of sodium hydroxide. These solutions were then mixed, the pH reduced by addition of hydrochloric acid, the samples cooled to room temperature and examined for coacervation. Coacervation was only observed in the narrow pH range 3·0–4·5. The narrowness of the allowable pH range probably accounts for the fact that varying the initial pH prior to mixing, or the final pH after mixing, did not significantly alter the size distribution of coacervate droplets. The present studies have been carried out at low ionic strength. Detailed studies have not been made of the effects of cation type or ionic strength upon coacervation. Raising the ionic strength should promote association or gelation of XM6 (Nisbet *et al.*, 1984) and might be expected to restrict the useful coacervation region.

Two schemes (II and III) were used to encapsulate oils and solid particles. Photographs of encapsulated sunflower oil, paraffin and aluminium powder are shown in Fig. 3. Scheme III provides the easiest method for encapsulating core materials. Procedures for fixing the coats



Scheme II



Scheme III

and preparing slurries or dry powders of encapsulated materials have not been investigated in detail. Methods for fixing the polymer coats, concentrating the encapsulated particles into slurries and drying to produce powders are described in a related study on coacervation in gelatin–gellan gum mixtures and their use in microencapsulation (Chilvers & Morris, 1986).

CONCLUSIONS

Complex coacervation has been observed in gelatin–XM6 mixtures in the pH range 3·0–4·5. Methods are described for using such mixtures for encapsulation of oils or solid particulates.

ACKNOWLEDGEMENT

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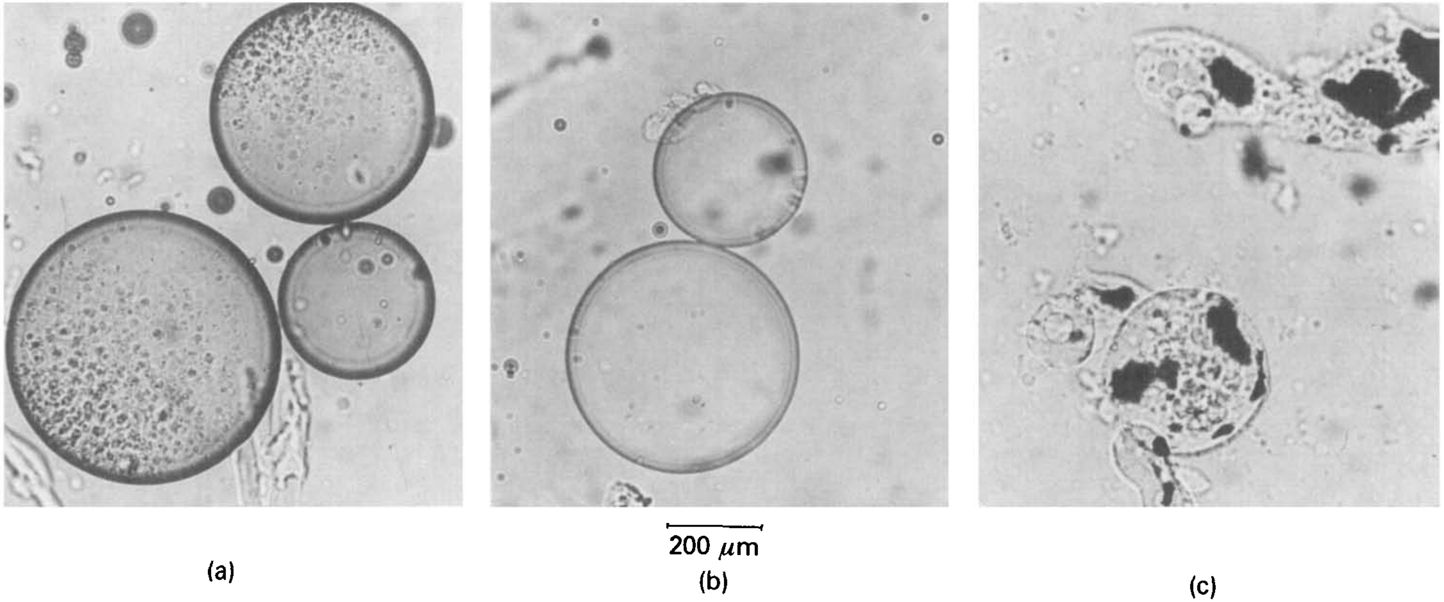

(a) (b) (c)

Fig. 3. Photographs of encapsulated materials. (a) Encapsulated sunflower oil; (b) encapsulated paraffin oil; and (c) encapsulated aluminium powder.

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