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The effect of microcapsule size on the oxidative decomposition of core material*

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The factors that affect the size of microcapsules and the oxidation of their benzaldehyde core have been examined. The pH of the preparation changed the overall size of the microcapsules which reached a maximum diameter at pH 4·1. The size of the core droplets also varied with the preparative pH and their oxidation rate depended on the bulk droplet size rather than their surface area. A rapid oxidation of benzaldehyde associated with the microcapsule wall resulted in a preliminary peak in the oxidation curve. Explanations for these phenomena are discussed.

The microencapsulation of small particles dispersed in coacervate droplets has been widely studied and of primary interest to previous workers has been the release of core material. But little attention has been paid to the concept of core stability. Luzzi & Gerraughty (1964) studied some factors affecting the diffusion of oils from microcapsule but supplied no information about the stability of the oils they used. Vitamin A palmitate has been reported to be stable in microcapsules (Bakan & Sloan, 1966) as have a number of other materials (N.C.R., 1970; Eurand, 1974).

Because of the structure of the microcapsule wall, particularly that of gelatin–gum acacia coacervates some diffusion of an oil core is inevitable and this could lead to the formation of a monolayer on the outside of the microcapsule. Luzzi & Gerraughty (1964) determined the permeability of the microcapsule wall and attempted to relate this to the resistance to breaking of the wall by the amount of oil that solvents could extract under specified test conditions.

If it is possible to protect the surface of an oil droplet by means of a strong microcapsule wall then this could confer protection against oxidation, even when primary free radicals are formed at the surface of the drop.

It has been found with the reference oils, benzaldehyde, methyl lineolate and cyclohexane, that reduction in the bulk volume of individual oil droplets by emulsification leads to a reduction in the rate of oxidation (Nixon, 1958). Benzaldehyde, which oxidizes rapidly, may be microencapsulated in a complex coacervate made from gelatin and gum acacia.

The present paper examines the effects of pH on the microcapsule size. As this changes so will the total surface area of the microcapsules and consequently the rate of diffusion of the oil out and oxygen in. The effect of these factors on the degree of stability of microencapsulated oils has been examined.

MATERIALS AND METHODS

Gelatin (Richard Hodgson & Sons, Ltd., Beverley, Yorks.) acid pretreated material, having the following characteristics: Bloom No. 256; pH of 2% w/w solution 4·3; viscosity (6 2/3% w/w, 40°) 7·4 cP; isoelectric point 9·0. *Acacia* B.P. 1963. *Benzaldehyde* (BDH Ltd.) Analar. The ultraviolet assay gave benzaldehyde 99·61%. Storage was under nitrogen in 10 ml ampoules. *Electrolytes*, Analar grade; *isopropanol* (May and Baker), general laboratory grade; *triple distilled water* pH 5·5.

Measurement of coacervate volume. This was directly measured at pH values from 3·0 to 5·0 using calibrated 10 ml centrifuge tubes after equilibration at 40°.

Absolute viscosity determination. The absolute viscosity of the equilibrium liquid at 10° was determined using a Hoppler-Viskosimeter (Type BH). Separation from the coacervate was allowed to take place over a period of 24 h at 40°. Measurements were made at pH values from 3·0 to 5·0. Measurements were made at 10° because the tubes were cooled to this temperature before separation of the equilibrium liquid.

Microcapsule preparation. Benzaldehyde was emulsified in 2% gum acacia solution by using 5–10 ml of distilled water and diluting to the required volume.

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The emulsion was stirred at 200 rev min^{-1}. The same volume of a 2% gelatin solution was slowly and steadily added whilst the stirrer speed was maintained. The interaction was at 40° ± 1°. The pH of the preparation was adjusted with either HCl or NaOH to a predetermined value of between 3·0 and 4·5. Formaldehyde was used for hardening the microcapsule wall. During the extraction process the product was washed three times with isopropanol over a 3 h period. The last portion of isopropanol was decanted, the microcapsules were dried in a stream of nitrogen and kept under it until required for the oxidation study. Unhardened microcapsules were prepared similarly but without the formaldehyde.

Determination of unoxidized benzaldehyde. Unoxidized benzaldehyde was extracted from the microcapsules by shaking with 5 ml of diethyl ether and adjusting to the required volume with water. The concentration was determined spectrophotometrically at 249·5 nm. An experimental blank was made using empty microcapsules and the above technique.

Particle size analysis and surface area determination. Because of the nature of the core material and the size of microcapsule produced, optical microscopy was the most convenient method for the microcapsule size analysis. Samples were mounted on clean slides and at least 300 microcapsules were measured at random by means of a calibrated eye piece. The results were expressed as number percent under size. The data obtained were also computed using the following equation to determine the surface area per unit volume.

$$S_v = \frac{6\Sigma nd^2}{\Sigma nd^3 \times 10^{-4}} \text{ cm}^2 \text{ cc}^{-1}$$

where d is the mean microcapsule diameter, n the number microcapsules in each size range, S_v is the specific surface area.

Calculation of oxygen uptake rate. A known weight of sample was dispersed in 2 ml of triple distilled water and shaken at 25 ± 0·1° in a Warburg respirometer and oxygen uptake measured. Changes in atmospheric pressure and temperature were corrected by means of a thermobarometer whose flask contained a similar dispersion but in which the microcapsules contained no core material, although otherwise prepared under identical conditions. The oxygen uptake of the same quantity of non-encapsulated benzaldehyde was also measured under identical conditions. An attempt was made to determine the quantity of unoxidized benzaldehyde remaining in the microcapsules or unencapsulated dispersion over the period of the oxidation experiments.

RESULTS AND DISCUSSION

Coacervation was found to be pH-dependent (Bungenberg de Jong, 1949; Luzzi & Gerraughty, 1964; Khalil, Nixon & Carless, 1967). Luzzi has confirmed Bungenberg's finding that coacervation does occur at a pH lower than the isoelectric point of gelatin. In the present study the pH of maximum coacervation was 4·1. At this pH where the absolute viscosity of the equilibrium liquid is at its minimum value (Fig. 1) and the coacervate is at a maximum, the greatest amount of colloid will be available

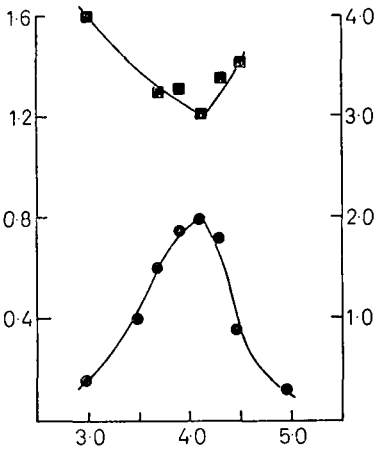

FIG. 1. Effect of pH on the coacervate volume and absolute viscosity of equilibrium liquid in the gelatin-Acacia coacervate system. Temp. 40°, ● coacervate volume (cm^3) (right-hand ordinate). ■ absolute viscosity (cP) (left-hand ordinate). Abscissa: pH.

in the coacervate phase and usable in the formation of the microcapsule wall. Changing the starting pH of the preparation produced microcapsules of different size. The microcapsule size was greatest at the pH of optimal coacervation and became smaller as the pH increased or decreased away from the optimal value (Table 1).

Yoshida & Thies (1967) have reported that swollen gelatin–gum arabic complexes are characterized by a network structure having junction points which involve secondary valancies and ionic bonds and behave like typical polyelectrolyte gels in that swelling is a function of pH. As with gelatin gels the complexes can be reversibly reformed by pH changes. These authors also found a similarity between gelatin solution and gelatin–gum arabic complexes and they suggested that the latter may

Table 1. *The effect of preparative pH on the size and specific surface area of benzaldehyde containing microcapsules.*

Preparative pH	Formalin hardened		Unhardened	
	a	b	a	b
4·5	96	366	78	384
4·3	145	313	136	310
4·1	155	264	148	300
3·8	124	325	111	349
3·5	93	445	61	575
3·0	59	764	43	952

(a) Mean size diameter, μm. (b) Specific surface area, $cm^2\ cc^{-1}$.

retain many of the characteristic features of the gelatin gels. That gelatin–gum arabic gels may have a gelatin gel structure was first postulated by Bungenberg de Jong & Landsmeer (1946, 1948).

The observed effect of pH on the microcapsules size has been discussed in relation to the effect of pH on the gelatin gel structure. Since Veis (1964) has suggested that groups such as NH_2 are completely protonated at all pH values below 6·0 the swelling changes could reflect variations in the number of free carboxylic sites (COO^-) within the gelatin gel. Below the isoelectric point gelatin contains an excess of unshielded amino groups owing to repressed ionization of the carboxylic group. Since the acacia retains its negative charge regardless of pH, the degree of interaction between the gelatin and the acacia is completely dependent on the gelatin amino sites. The optimum conditions for complex coacervation can therefore be achieved by adjusting the pH to a point at which maximum amounts of oppositely charged molecules of the two colloids are present. At pH 4·5 the microcapsule size was at a minimum (Table 1), due to a lowering of amino sites in the gelatin (Yoshida & Thies, 1967) and so the interaction between the two colloids was not complete. Consequently this could reduce the available gelatin–acacia coacervate available for microencapsulation. Decreasing the pH below 4·1 led once again to increasing imbalance of groupings between the interacting colloids. At pH lower than 3·0 and greater than 4·5 no microcapsules could be formed with the present system.

The microcapsule size at a given pH is slightly larger for those which have been formalin hardened, possibly because shrinkage or swelling is prevented (Tabor, 1968). With the unhardened walls there is the possibility of the gelatin molecules being forced into a closer configuration during the cooling at 5°, thus producing a more dense wall and a smaller microcapsule. Decrease in size may also be due to slight solution of the unhardened wall material during the cooling period, brought about by stirring.

The microcapsule wall is a very open porous structure but without any definite pores through it, and it is not completely impervious to the passage of oxygen or the diffusion of core material. That this latter occurs can be easily detected by odour of the oil. It is obvious that oxidative decomposition, whilst it may be decreased, will not be completely prevented. The amount of benzaldehyde remaining in the microcapsules was determined over seven days (Table 2) at the end of which 73% of the benzaldehyde in the microcapsules remained unoxidized but only 46·6% of the solution of benzaldehyde remained unoxidized.

Table 2. *Determination of benzaldehyde remaining unoxidized in unhardened microcapsules and in solution over a period of seven days when shaken with triple distilled water on the Warburg apparatus.*

Time (days)	% unoxidized benzaldehyde in microcapsules (a)	% benzaldehyde unoxidized in solution (b)
0	100·00	100·00
1	100·00	98·31
2	91·97	94·92
5	82·14	47·46
7	73·21	46·61

Temperature 27 ± 0·1°; Benzaldehyde concentration: (a) 10 mg/100 mg of microcapsules; (b) 5 mg ml^{-1} in the solution.

Figs 2, 4 show the oxidation in different microcapsule sizes. The induction period was taken as a value of 200 μl oxygen uptake. Despite this a true induction period was difficult to assess because of the complications caused by the initial rapid oxidation of benzaldehyde associated with the microcapsule wall. This complicated behaviour is shown by the existence of preliminary peaks (Figs 2 and 4). By extrapolating the main portion of the curve to zero and by determining the time for 200 μl oxygen uptake an empirical induction period could be assessed.

During the microencapsulation and recovery some of the benzaldehyde becomes associated with the microcapsule wall. When the microcapsules are washed with the dehydrating agent most of this is removed but a residue of wall-associated benzaldehyde remains. This unencapsulated oil oxidizes first and

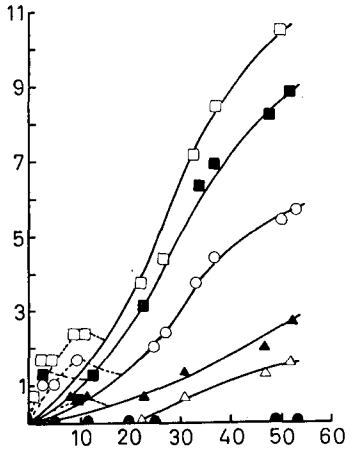

FIG. 2. Effect of size on the oxygen uptake of formalin-treated microcapsules. Temp. 25 ± 0·1°. Oxidizing system 100 mg microcapsules in 2 ml triple distilled water. Mean microcapsule size μm, ● 59; △ 93; ▲ 96; ○ 124; ■ 145; □ 155. Ordinate: Oxygen uptake μl $\times 10^{-3}$ litre^{-1} of dispersion. Abscissa: Time (h).

because it is not protected the oxidation is rapid and produces the preliminary peak. The amount of surface free benzaldehyde appears to be inversely proportional to microcapsule size the preliminary peak is definitely higher with larger microcapsules and in all experiments made it fell along with microcapsule size. Once the primary oxidation is completed, the benzaldehyde within the microcapsule, which has been slowly diffusing though the wall, begins to increase the internal pressure within the Warburg flasks, resulting in an apparent fall in the oxygen taken. This accounts for the initial peak. Preliminary oxidation was found with both formalin-hardened and unhardened microcapsules (Figs 2, 3) but with a smaller total preliminary amount of oxygen uptake in the unhardened capsules, suggesting that more of the benzaldehyde was removed from the non-formalized walls during processing. The oxidation of encapsulated benzaldehyde at a given microcapsule size shows a much slower oxidative decomposition for the unhardened sample, than for the formalin-hardened material. As the microcapsules were suspended in triple distilled water at 25° the unhardened microcapsule wall hydrates and forms a gelatinous barrier to the diffusion of oxygen and the open porous nature of the wall was lost and with it the possibility of definite pores. In formalin-treated material the wall allowed the ready passage of oxygen in and of benzaldehyde out. Consequently a higher oxidation rate was obtained. Diffusion through the coacervate coat may well occur through the intermolecular space of the coiled structure, as well as through the vacuoles present as a result of the coacervation process. It was found by Nixon (1958) and Swarbrick (1963) that reducing the bulk volume of the individual entities in the form of an emulsion could lead to a slowing down of oxidation rate. The higher oxidation rate with larger microcapsules correlates with the bulk amount of encapsulated core material.

Microcapsules of large diameter contain a proportionally larger amount of encapsulated benzalde-

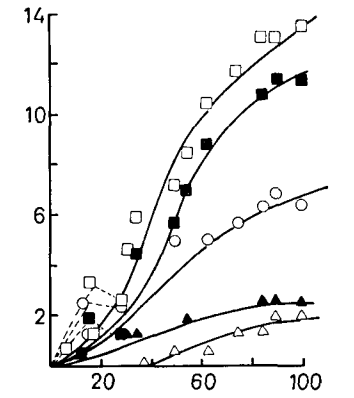

FIG. 3. Effect of size on the uptake of formalin untreated microcapsules. Temp. 25 ± 0·1° C, oxidizing system: 100 mg microcapsules in 2 ml triple distilled water, mean microcapsules size μm, △ 61; ▲ 78; ○ 111; ■ 136; □ 148. Ordinate and abscissa as for Fig. 2.

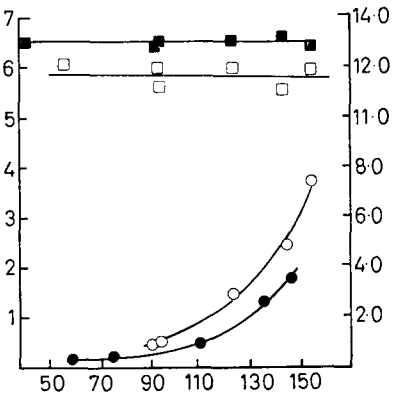

FIG. 4 The relationship between amount of encapsulated benzaldehyde in different microcapsule sizes and the oxidation rate. ■ Amount of benzaldehyde in formalin untreated sample (100 mg); □ amount of benzaldehyde in formalin treated sample (100 mg); ○ rate of oxidation in formalin treated sample; ● rate of oxidation in untreated sample. Left-hand ordinate: Oxidation rate (μl × 10^{-2} litre^{-1} h^{-1}). Right-hand ordinate: Amount of encapsulated benzaldehyde (mg). Abscissa: Mean microcapsule size (μm).

hyde, frequently in individual droplets, which is more rapidly oxidized when compared with the same amount of benzaldehyde distributed in smaller microcapsule (Fig. 4), even though the latter have a larger overall surface area (Table 1). This is because the propagation reaction takes place readily, whilst termination reactions, because of the large number of individual chains involved within the oxidizing droplet, are less likely than in small droplets. With small microcapsules or those containing a number of small oil droplets, the chance of chain termination will be greatly increased. The oxidation rate is independent of microcapsule surface area but the bulk droplet size of the encapsulated material appears to be a factor in the oxidative decomposition.

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