

## Factors Affecting Retention in Spray-Drying Microencapsulation of Volatile Materials

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Microencapsulation of volatile materials (aroma) was evaluated by using model systems in which gum arabic was the wall material and various esters were the core materials. The outer and inner structure of spray-dried microcapsules and the structural changes induced by exposure to various relative humidity (RH) levels were studied by SEM. The influence of capsule composition and drying conditions on the retention of the volatiles was evaluated. It was found that high retention levels, up to 90%, can be achieved. High solids concentration and high drying temperatures enhance retention, as long as there is no structural damage during preparation. Increase of the ester load in the feed emulsion adversely affects the retention. Aroma losses occur during the early stages of the drying process by stripping of volatile droplets. The losses are enhanced by internal mixing in the drying capsule. The retention of volatiles by spray-dried microcapsules was also studied as a function of storage at increasing relative humidity. At relative humidity below 64% the structure of the capsules was not damaged, and high retention levels of more than 85% were obtained. Increasing the relative humidity to 75–97% led to gradual dissolution of the capsule walls, and retention dropped sharply. The structure was completely destroyed at RH of 97%, leading to total loss of the volatiles.

Microencapsulation is a technique whereby liquid droplets or solid particles are packed into continuous individual shells. The shells, or "walls" as they are called, are designed to protect the encapsulated material from factors that may cause its deterioration. By a different approach, the wall is designed to permit controlled release of the encapsulated material ("core") under desired conditions.

Important applications of microencapsulation in the food industry involve materials such as volatile compounds, essential oils, and oleoresins. Encapsulation of these sensitive materials makes it possible to incorporate them in dry form so that they are protected by the walls against evaporation, oxidation, and chemical reaction. In the case of aroma compound microencapsulation, the full organoleptic profile of the product is thus preserved until the product is used, and high quality and commercial value can be ensured.

Numerous techniques for various materials have been developed (Herbig, 1970; Madan, 1978; Goodwin and Somerville, 1974; Fanger, 1974; Gutcho, 1979; Taylor, 1983; Dziezak, 1988). Techniques for microencapsulation of food ingredients and the potential use of the technology in the food industry have been discussed in the literature by Todd (1970), Balassa (1971), Graves (1972), McKernan (1972, 1973), Bakan (1973), Werner (1980), Andres (1981), Pagington (1985), Reineccius and Risch (1986), Szente and Szejtli (1986), Youngs (1986), Chen et al. (1988), and others. The application of microencapsulation processes in the food industry involves some special considerations, primarily those related to the solvent and to the wall material which should be Generally Recognized as Safe (GRAS). The published information concerning

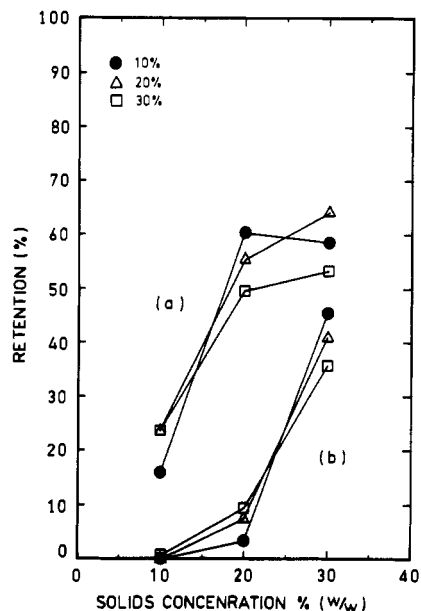
microencapsulation of food materials is mainly qualitative. Quantitative data are scanty, because most of the technology has been developed by commercial research organizations and is protected by patents.

Because spray-drying is a well-known technology in the food industry, it is at the present the common microencapsulation technique in use. Successful spray-drying microencapsulation in general, and of volatiles in particular, depends on achieving high retention of the core material during processing and storage. Retention of volatiles during drying processes has been treated by many investigators, and several theories have been postulated. These studies involved volatiles, mostly alcohols, and natural polymers like dextrans (Ranz and Marshall, 1952; Marshall and Seltzer, 1950; Kirschbaum, 1952; Brooks, 1965; Menting and Hoogstad, 1967; Thijssen and Rulkens, 1968). Volatile concentrations in these models were of typical aroma compound levels in natural products, such as fruit juices. The factors considered were feed temperature (Sivetz and Foote, 1963; Rulkens and Thijssen, 1967), particle size (Brooks, 1965; Rulkens and Thijssen, 1967), solids concentration in the inlet feed (Sivetz and Foote, 1963; Brooks, 1965; Menting and Hoogstad, 1967; Rulkens and Thijssen, 1967; Reineccius and Coulter, 1969; Blakebrough and Morgan, 1973), drying air temperature (Rulkens and Thijssen, 1967; Bomben, 1973; Blakebrough and Morgan, 1973), and the nature and concentration of the volatile to be retained (Brooks, 1965; Rulkens and Thijssen, 1967). Recently, several papers concerning the microencapsulation of volatile compounds and natural essential oils were published (Risch and Reineccius, 1988). In these the effects of process conditions, emulsion composition, and nature of wall and core materials on the retention of the volatiles were discussed, and microencapsulation techniques such as spray-drying, coacervation, and extrusion, as well as more recently developed techniques such as molecular inclusion, were evaluated.

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**Figure 1.** Retention of (a) ethyl caproate and (b) ethyl butyrate by gum arabic during spray-drying microencapsulation as a function of initial solids and ester concentration. Drying air temperature was 150 °C.

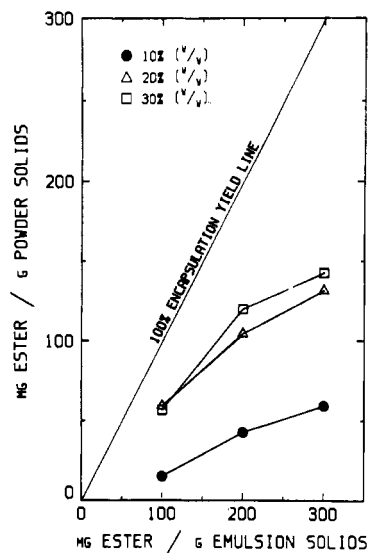
In the present work we have studied the influence of some of the above-mentioned parameters on the retention of model aroma compounds (esters) during spray-drying microencapsulation. Retention of volatiles by spray-dried microcapsules during storage was evaluated as a function of humidity to which they were exposed. These results were compared to microstructural information from scanning electron microscopy (SEM).

## MATERIALS AND METHODS

Microcapsules were prepared by spray-drying emulsions in which the continuous phase was a solution of the wall polymer and the dispersed phase was the core material. In most experiments the wall polymer was gum arabic (from Sharon Laboratories). In some cases sodium alginate (Merck) or gelatin (Hormel) was incorporated into the wall phase (analytical grade, Frutarom). All the wall polymers were of food grade quality. The esters used as core materials were ethyl propionate, ethyl butyrate, ethyl valerate, ethyl caproate, and methyl anthranilate. Wall polymers and esters were of commercial grade. The esters were emulsified into the continuous phase by homogenization for 5 min using a Type X100 laboratory disperser (Interlabs, App. GmbH). Viscosity of the wall solutions or of the emulsions was measured by using a Brookfield viscometer Model LTV (Brookfield Engineering Laboratory Inc.). Drying of the emulsions was carried out in a Mobile Minor Niro-Atomizer (Copenhagen) spray-dryer. The feed rate was 15 g/min and atomization pressure 6 atm; inlet and outlet air temperatures were usually 150 and 90 °C, respectively, or as specified otherwise.

Retention of the esters during drying was calculated as percent of the original volatiles found in the capsules at the end of the drying process. Two grams of emulsion or powder was dispersed in 100 mL of water (40 °C). Five milliliters of this dispersion was diluted to 50 mL with a 50% aqueous ethanol solution. The concentration of esters in this solution was then determined according to the method of Peleg (1970). The efficiency or yield of the microencapsulation process was defined as the ratio of ester content in the dry product (grams of ester/grams of solids) to its content in the emulsion (grams of ester/grams of solids).

To determine the effect of humidity on the retention of volatiles, we placed in closed glass vessels dishes, kept at 25 °C, containing samples of about 1 g of microcapsules and dishes of saturated salt solutions, chosen to give relative humidities in the range 11–97% according to the method of Rockland (1960).



**Figure 2.** Encapsulation yield: ethyl caproate retained by gum arabic via spray-drying microencapsulation as a function of initial solids concentration and ester load.

Water uptake was followed by weighing. Changes in ester content were studied by the method described above. These parameters were monitored until equilibration was achieved (about 30 days). Retention of volatiles by the humidified capsules was expressed as percent of the initial ester content. Structural changes caused by humidification were studied by SEM.

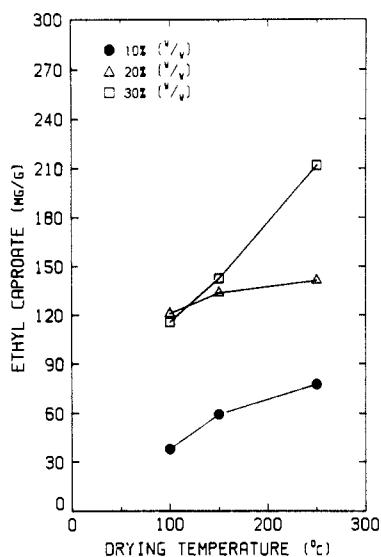
The outer and inner structures of the microcapsules were examined by scanning electron microscopy. For the study of the outer structure of the microcapsules, the particles were mounted on SEM stubs by double-sided adhesive tape. The specimen was then sputter-coated with a 15-nm gold layer by using an E515 SEM coating unit (Polaron). To study their inner structure, capsules were embedded in Lowicryl HM-20 resin (Polaron). The polymerized blocks were fractured, and the inner structure of the capsules in the fracture plane was examined in the SEM after the specimen had been gold-coated as described above. The specimens were examined in a JEOL T200 scanning electron microscope at 25 kV in the secondary electron imaging (SEI) mode. More details about microcapsule specimen preparation and scanning electron microscopy of these specimens are given by Rosenberg et al. (1984a, 1985, 1988).

## RESULTS

Retention as function of solids concentration in the emulsion and of the initial ester concentration on a dry basis (DB, i.e., grams of ester/grams of solids in the emulsion) is shown in Figure 1 for ethyl caproate and ethyl butyrate. The encapsulation yield of ethyl caproate is plotted in Figure 2. We see that increase of solids concentration resulted in steeply increased retention. Similar results were reported by us previously (Rosenberg and Kopelman, 1983; Rosenberg et al., 1984b) and by Reineccius and Bangs (1985). Under the same conditions retention of ethyl caproate was better than retention of ethyl butyrate. The latter showed zero retention with 10% solids concentration. In the case of ethyl butyrate, at a constant solids concentration, different initial ester loads led to very similar retentions. This indicates that the retention is mainly determined by the solids concentration, and, as can be seen in Figure 1, only by increasing the solids concentration could higher ester loads be encapsulated. In the case of ethyl caproate (which is almost insoluble in water) the final ester load in the capsules is a function of the solids concentration and of the initial ester load. At a constant solids concentration, higher final ester load could be achieved by increasing the initial ester load in the emulsion. Retention exper-

**Table I. Effect of Wall System Viscosity on Retention of Ethyl Caproate in Spray-Drying Microencapsulation**

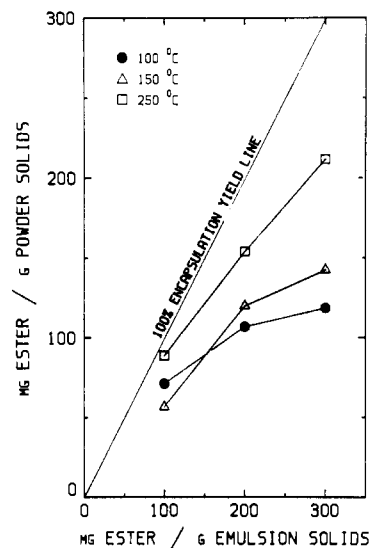
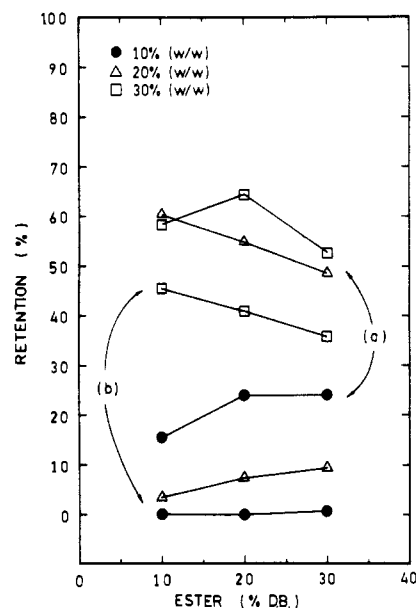
system	solids			viscosity at 20 °C, cP	ethyl caproate (15% DB in feed), retention %
	total solids	gum arabic	sodium alginate		
1	10	10		16	23
2	10	9	1	34	32
3	10	8	2	175	35
4	10	7	3	420	26
5	10	6	4	780	19
6	20	20		36	48
7	20	19	1	74	56
8	20	18	2	232	58
9	20	17	3	640	42
10	20	16	4	890	37
11	30	30		82	74
12	30	29	1	124	79
13	30	28	2	290	33
14	30	27	3	880	53
15	30	28	4	1360	49

**Figure 3.** Effect of drying air temperature on ethyl caproate retention by gum arabic during spray-drying microencapsulation. Ester concentration in the emulsion was 30% DB. Solids concentrations was 10–30% w/w.

iments with ethyl propionate and ethyl valerate (not shown here) yielded the following results: for ethyl propionate, no retention was obtained below 30% solids, and only 5% retention was recorded at 30% solids; in the case of ethyl valerate, the retention values were between those of ethyl butyrate and ethyl caproate.

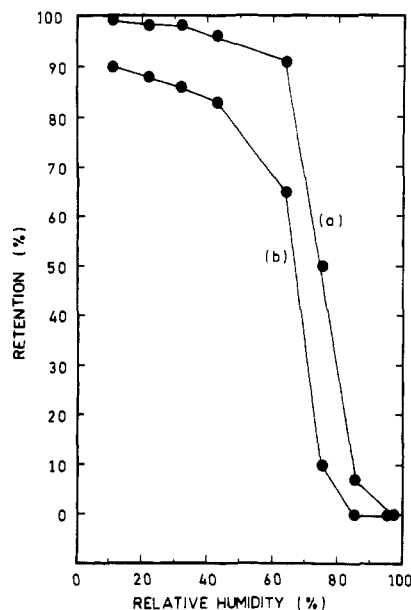
The effect of viscosity of the emulsion continuous phase on retention is shown in Table I. Increasing the viscosity by means of sodium alginate improved retention up to an optimum, beyond which retention levels dropped.

Figures 3 and 4 show the effect of drying air temperature on the retention of ethyl caproate during spray-drying microencapsulation. Retention increased by increasing the inlet air temperature; this effect was stronger at higher solids concentration. The influence of drying temperature on volatile retention (ethyl caprylate) was previously reported by us (Rosenberg et al., 1984b). The influence of drying temperature on microencapsulation by spray-drying of orange essential oil was reported by Anker and Reineccius (1988). The results of the present work are in agreement with the results of Reineccius and Bangs (1982). Figure 5 shows that retention decreased with ester concentration increase. In some cases (i.e., ethyl butyrate) retention was only little affected by the initial ester concentration.

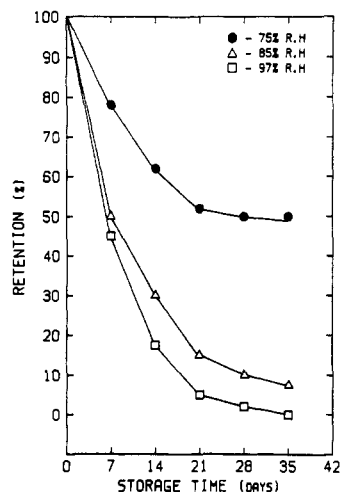
**Figure 4.** Encapsulation yield: ethyl caproate retained by gum arabic (30% w/w) during spray-drying microencapsulation as a function of air drying temperature and initial ester load.**Figure 5.** Retention of (a) ethyl caproate and (b) ethyl butyrate by gum arabic (10–30% w/w) during spray-drying microencapsulation as a function of initial ester concentration. Drying air temperature was 150 °C.

Figures 6 and 7 show how retention changes as a function of storage at different relative humidities (RH). High retention was obtained up to 64% RH. Increase to 75% RH led to a steep drop of ester retention. Total loss of volatiles was recorded at RH of 97%. Retention values of ethyl butyrate were lower than those of ethyl caproate. The initial ester load in the systems described in the above figures was 200 mg/g. In Figure 8 we show that water sorption isotherms of gum arabic microcapsules containing volatiles (15% ethyl caproate) are of type II according to the BET classification (Brunauer et al., 1938). An almost identical curve was found for “empty” gum arabic capsules.

Examples of the morphology of spray-dried microcapsules as revealed by SEM are given in Figure 9. Figure 9a shows a typical sample of gum arabic microcapsules. These are spherical bodies with outer surfaces free of cracks and pores. The only defects are dents due to shrinkage of the droplets during the early stages of the drying pro-



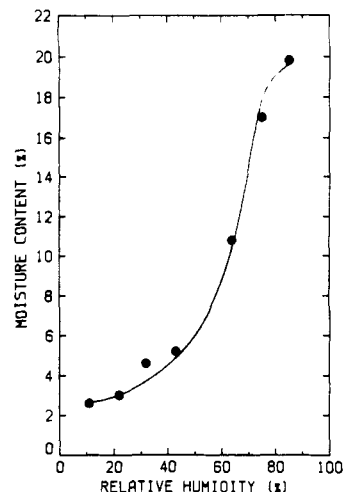
**Figure 6.** Retention of (a) ethyl caproate and (b) ethyl butyrate by gum arabic spray-dried microcapsules after storage (25 °C) in a humidified environment as a function of relative humidity. Initial ester content was 200 mg/g.



**Figure 7.** Retention of ethyl caproate by gum arabic spray-dried microcapsules as a function of storage time at different relative humidities and 25 °C.

cess (Greenwald, 1980; Rosenberg et al., 1985). The inner microstructure of microcapsules containing ethyl caproate is shown in Figure 9b. The ester is dispersed in the capsule wall as small droplets or "pools" that are similar in size (0.5–2  $\mu\text{m}$ ) to their counterparts in the emulsion as was established by light microscopy prior to drying. In some cases we observed a large void in the center of the capsule. Formation of the void is related to expansion of the capsules during the later stages of the drying process (Greenwald, 1980; Rosenberg et al., 1985, 1988). The inner structure of microcapsules in which 0% retention was found is shown in Figure 9c. No core material droplets are seen. This indicates that the loss of the volatiles occurred before the solidification of the wall.

Figure 10a shows typical structural changes during humidification of microcapsules, up to 64% RH. Although no drastic changes were detected, water uptake caused some swelling and bridging of the capsules. Further increase of RH in the 75–92% range caused progressive dissolution of the wall polymer (Figure 10b), until at 97% RH a paste was formed (Figure 10c). The microstruc-



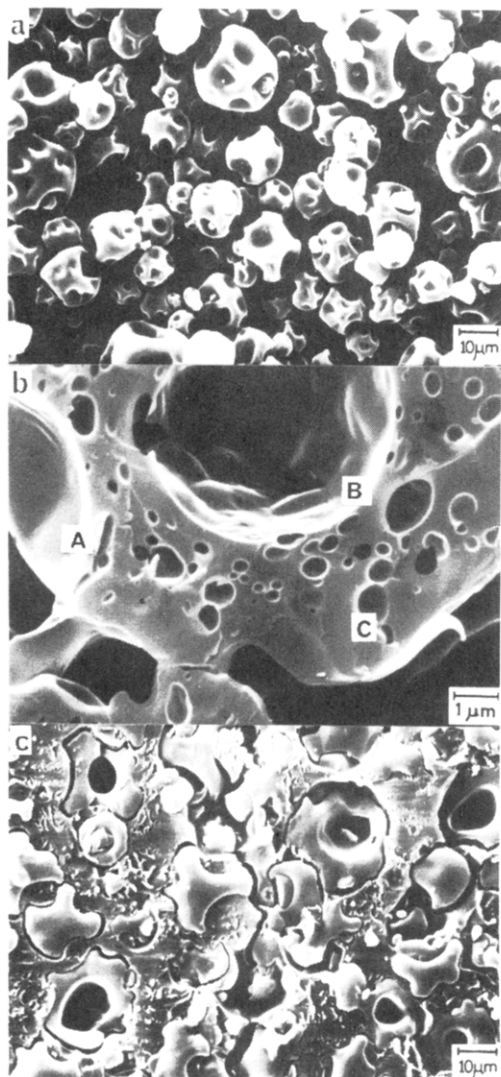
**Figure 8.** Water sorption isotherm at 25 °C for gum arabic spray-dried microcapsules containing ethyl caproate (25% DB).

ture of spray-dried microcapsule is described in more detail by Rosenberg et al. (1988).

## DISCUSSION

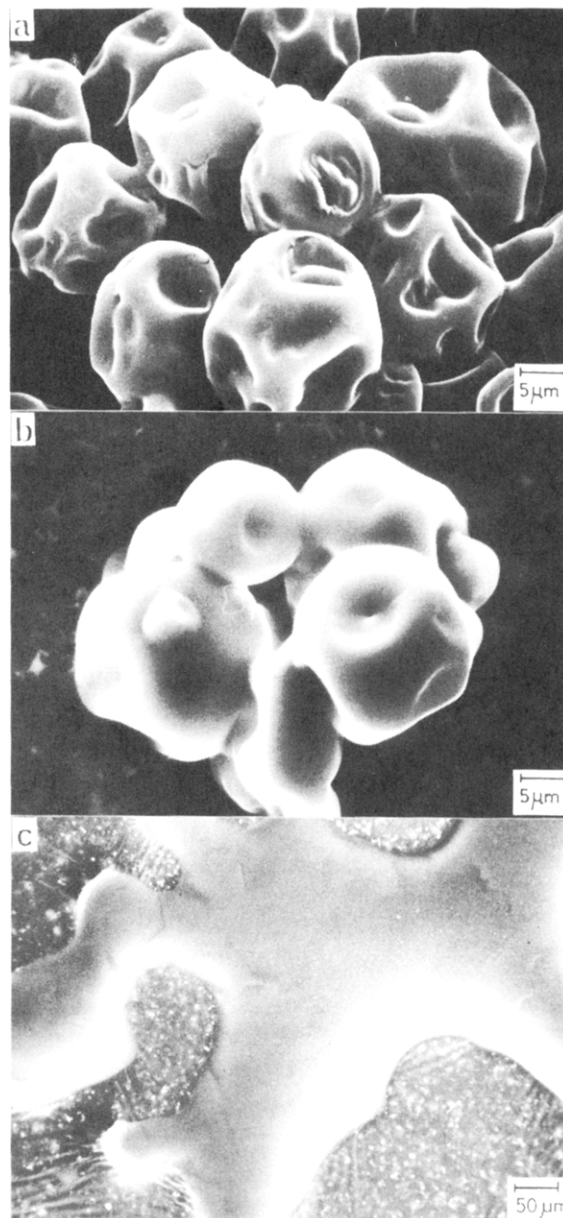
Several theories have been developed to explain the retention of volatiles during drying of food materials. Volatile losses are often less than what would be expected from volatility data. Brooks (1965) and Thijssen and Rulkens (1968) have shown that the solids concentration and the quantitative ratio between volatiles and solids affect very strongly volatile retention during spray-drying. Volatile losses during spray-drying are associated not only with the interaction between the drying droplets and the hot air but also with the process of droplet formation (atomization). The theory and practice of atomization, and evaporation from droplets containing volatiles, have been discussed previously by Marshall and Seltzer (1950), Ranz and Marshall (1952), and Kirschbaum (1952). Menting and Hoogstad (1967) have shown that volatile materials can leave the drying droplets until a crust forms around the droplets, or until the termination of the first stage of the drying process, i.e., the so-called constant-rate stage. Further losses can occur only if the volatiles can pass through the crust by means of diffusion in the solid or through pores or channels. According to this explanation, solids concentration and drying temperature are very important because of their effect on crust formation. A "selective diffusion theory" has been presented by Brooks (1965) and by Rulkens and Thijssen (1967), who suggested that the diffusion coefficients of water and volatiles are reduced as water concentration decreases due to drying. As a result of differences in molecular weight of water and volatiles, the reduction in the diffusivity of the volatiles is more pronounced than that of water. Once the crust has formed, volatiles diffusivity is so low that for all practical purposes the volatiles are entrapped in the drying solid matrix, while water can still diffuse through the crust. The crust therefore becomes effectively a selective membrane.

In the present work we have studied the effect of solids and ester concentration and of drying air temperature on volatiles retention during spray-drying microencapsulation. The influence of solids concentration on ester retention can be explained by its effect on crust formation and drying rate. Increasing the soluble solids concentration reduces the time for dry skin (crust) formation around the drying droplet (capsule); thus, the losses of the volatiles are reduced. The selective diffusivity the-



**Figure 9.** (a) SEM micrograph of gum arabic spray-dried microcapsules containing ethyl caproate. Solids and ester concentrations in the emulsion were 20% (w/w) and 15% (DB), respectively. Drying air temperature was 150 °C. (b) Typical inner structure of gum arabic spray-dried microcapsules containing ethyl caproate. Solids and ester concentrations in the emulsion were 20% (w/w) and 15% (DB), respectively. Drying temperature was 150 °C. (A) Capsule wall; (B) central void; (C) ester sites. (c) Inner structure of spray-dried microcapsules. Emulsion composition: gum arabic 20% (w/w), ethyl butyrate 10% (DB). Retention level after drying was 0%. Drying air temperature was 150 °C.

ory can explain the losses of volatiles that are at least partially water soluble and thus can diffuse with water through the gum matrix during the early stages of the drying process. This is the case of ethyl propionate or ethyl butyrate. But when esters such as ethyl caproate are encapsulated, their lower polarity causes them to organize as small pools in the capsules. Because it is unlikely that only molecular diffusion controls retention, we assume that loss of such volatiles is a result of stripping during the early stages of drying. Such losses are enhanced by internal mixing that may bring the ester to the surface of the capsule and thus cause its partial loss to the drying air. Retention of ethyl butyrate or ethyl propionate is controlled by a combination of molecular diffusivity of the water-soluble fractions of the esters and by droplet stripping. Until sufficient water is lost from the drying capsule, and as long as the capsule remains in the constant-rate stage of drying, volatile losses may occur. Once the capsule has solidified, the ester droplets are



**Figure 10.** Spray-dried gum arabic microcapsules containing methyl anthranilate (200 mg/g) after equilibration at (a) 43%, (b) 75%, and (c) 97% RH.

locked in the dry matrix, and volatile loss stops. Polar volatile materials are also held in the dry matrix material by hydrogen bonding.

Solids concentration affects viscosity and thus is very important in determining volatile losses. The viscosity of the system in its wet form governs the movement of the volatiles to the surface of the drying capsules. Thus, viscosity may be increased to an optimal value to improve retention. Further increase in viscosity causes decrease of ester retention. This is a result of increase in residence time in the atomizer and difficulties in droplet formation. Before droplets form in the atomizer, the emulsion is highly turbulent, and volatile loss is enhanced by internal mixing (Kieckbusch, 1978; Kieckbusch and King, 1980; Zarkarian, 1979). At that state volatile losses are governed by their relative volatility (Marshall and Seltzer, 1950). Increasing the viscosity to the optimum reduces internal mixing and thus enhances the retention. Beyond that level, the residence time of the emulsion under high turbulence prior to actual atomization and droplets formation becomes too long, and losses of aroma com-

pounds are high. Similar results were found by Reineccius and Bangs (1985) and by Reineccius (1988).

The type of solids used also affects the retention of volatiles. When esters were encapsulated in several maltodextrins (Rosenberg et al., 1984a,b; Rosenberg, 1985), poorer results compared to those achieved with gum arabic were obtained. Combination of gum arabic and various maltodextrins yielded lower retentions compared to those of systems consisting of gum arabic alone at the same solids concentration. The superior properties of gum arabic can be explained by its emulsification properties and its tendency to form films at the interfaces between the emulsion phases. Although the superior properties of gum arabic related to flavor encapsulation are known, due to problems related to its price, availability, and impurities associated with it, efforts are made to find other natural polymers that will make it possible to encapsulate flavors with similar efficiency as gum arabic (Leahy et al., 1983; Bangs and Reineccius, 1988; Kenyon and Anderson, 1988; Inglett et al., 1988; Thevenet, 1988; Trubiano and Lacourse, 1988; Reineccius, 1988; King, 1988).

Higher drying temperature caused increase in encapsulation yield and volatile retention. Increasing air temperature increases drying rates and reduces the duration of the constant-rate stage of the drying process. Higher inlet air temperature also decreases the time for internal mixing and thus enhances retention. The effects of drying temperature on the microcapsules structure has been discussed elsewhere (Rosenberg et al., 1985, 1988). Suffice it to say here that in some cases the combination of high solids concentration and high drying air temperature yielded cracked capsules. This effect can be explained by the substantial expansion of the drying capsules by heating at the final stages of the process. Thus, increasing drying air temperature to improve volatile retention should be evaluated carefully in light of possible adverse effects it may have on the integrity of the capsules. It should be noted, however, that when thermolabile core materials are encapsulated, increase in retention through increasing drying temperatures may be accompanied by degradation of the core materials. In such cases lower drying temperatures should be used.

As ester concentrations in the feed emulsion increase, retention decreases. This reduction is linked to the way the volatile core material (as in the case of low polarity esters) is organized in the capsule. Increasing the initial load of the ester in the emulsion causes an increase in the concentration of ester droplets in the wall. This increases the ester fraction that is exposed to the drying air during microcapsule formation and thus reduces retention. With increasing amounts of ester in the drying capsule the average path from each droplet to the surface is reduced, and hence volatile losses during the stages in which internal mixing exists are higher. Also, as larger amounts of ester are exposed at the outer surface of the capsule during crust formation, more ester is lost. Analysis of the effect of solids concentration and drying temperature on the encapsulating yield indicates that retention reduction is not a result of saturation in terms of the capability of the solids to retain the volatiles, but may be considered a packing problem.

Ester properties also affect the ester's retention. We have found that highly water soluble esters are retained less well than esters of lower polarity. As water solubility increases, ester losses during spray-drying microencapsulation increase due to the ability of the esters to diffuse through the wet polymer even at late stages of the drying process. When partially water soluble esters

are encapsulated, the system is more sensitive to solids concentration, and retention is reduced.

Our experiments to determine the effect of relative humidity on retention of volatiles by the microcapsules indicate that as long as the individual structure of the capsule is intact, high retention of volatiles is maintained. However, once the capsule structure is damaged by water uptake, volatiles are increasingly exposed, and retention drops. The low retention of partially water soluble esters can be explained by their ability to migrate through the sorbed water layers even at low water concentration in the humidified system. The similarity in water sorption patterns found in capsules with and without core material indicates that the volatiles are indeed locked inside the capsules and thus do not affect water uptake. If core material were exposed, a difference between the two kinds of capsules should have been observed due to the difference in polarity. This is in agreement with the scanning electron microscopy results.

## CONCLUSIONS

High retention of volatiles can be achieved during spray-drying microencapsulation. The retention depends on capsule composition and drying conditions. As long as no structural damage is induced, high solids concentrations and drying temperatures enhance volatiles retention. Wall polymers, which form high-solids solutions with viscosity that allows good atomization and droplet formation, are suitable for microencapsulation by spray drying. Wall polymers should have good emulsification and drying properties. The core material is organized within the capsule in small droplets embedded in the polymer wall. The volatiles are protected and retained by the walls of the capsule as long as the capsule structure is intact. Once the structure is destroyed, as in the case of water uptake at high RH, the capsules lose their volatiles content. Proper choice of capsule composition and drying conditions can lead to a dry product that retains high loads of volatile material.

## ACKNOWLEDGMENT

This research was supported by the Fund for the Promotion of Research at the Technion and by the Israeli National Council for Research and Development. We thank Judith Schmidt and Berta Shdemati for their invaluable help in preparing the manuscript.

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Received for review June 26, 1989. Accepted January 23, 1990.

**Registry No.** Ethyl propionate, 105-37-3; ethyl butyrate, 105-54-4; ethyl valerate, 539-82-2; ethyl caproate, 123-66-0; methyl anthranilate, 134-20-3; gum arabic, 9000-01-5; sodium alginate, 9005-38-3.