

Production of Oil-Containing Crosslinked Poly(vinyl alcohol) Microcapsules by Phase Separation: Effect of Process Parameters on the Capsule Size Distribution

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SYNOPSIS

Oil-containing poly(vinyl alcohol) (PVA) microcapsules in the size range of 5–20 μm were prepared by the simple coacervation of PVA followed by chemical crosslinking of the coacervated PVA membrane with glutaraldehyde. Coacervation of the aqueous polymer solution was achieved by the addition of a phase separation inducer (e.g., sodium sulfate). PVA of different grades (e.g., molecular weight and degree of hydrolysis) was utilized both as stabilizer and wall-forming material. Dispersion of the oil phase in the aqueous PVA solution was effected by a homogenizer. The effects of the various process parameters, such as the agitation speed, the type and concentration of PVA, the volume ratio of the internal oil phase to the external aqueous phase, the viscosity of the oil phase as well as the electrolyte concentration in the aqueous solution, on the stability and the size distribution of the emulsion droplets and microcapsules were experimentally investigated. It was shown that high agitation rates and low interfacial tension (e.g., high PVA concentrations) resulted in a significant reduction of the size of the emulsion droplets and microcapsules. On the other hand, as the viscosity and the amount of the dispersed oil phase increased, the capsule size increased. Finally, it was found that the concentration of the electrolyte significantly affected the stability of the (o/w) emulsion, the size and concentration of coacervated PVA colloidal aggregates, as well as the morphology of the polymer wall membrane formed by the adsorption of the polymer-rich phase to the oil/water interface. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Since the release characteristics of liquid-containing microcapsules largely depend on their size, the morphology, and the thickness of the capsules' polymer wall, it is essential to know how to control these properties in terms of the production conditions. Thus, a well-controlled microencapsulation process should typically lead to the production of microcapsules having a narrow capsule size distribution and exhibiting a desired release profile.

In the preparation of oil-containing microcapsules by the simple coacervation method, the dispersion of the organic phase in the continuous aqueous phase is the determining step in establishing the size dis-

tribution of the final microcapsules. This is influenced by the geometrical characteristics of the agitation system, the agitation quality (e.g., agitation speed, type and concentration of stabilizers), as well as the physicochemical properties of the dispersed and continuous phases. It is thus essential that the dispersed liquid droplets are sized for a period of time before the formation of the capsules' polymer wall.

In general, when an organic liquid phase is dispersed in water, after a certain period of time a dynamic equilibrium is attained between the drop coalescence and the drop breakage rate. Coalescence of the emulsion droplets is usually affected by the addition of surface-active agents. In many microencapsulation techniques, water-soluble polymers are used as stabilizers to depress the droplet coalescence frequency.¹ The adsorption of the polymer to the

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surface of the oil droplets lowers the interfacial tension between the two immiscible liquids, thus giving rise to steric stabilization forces.^{2,3}

Partially hydrolyzed polyvinyl alcohol has been employed extensively as a steric stabilizer imparting emulsion stability.^{2,4} The hydrophobic parts of the poly(vinyl alcohol) (PVA) polymer chains coming in contact with the hydrophobic oil phase adopt conformations toward the droplet surface, thus generating a protective hydrophobic layer around the droplets. The emulsion stability largely depends on the PVA type (e.g., molecular weight and degree of hydrolysis) and its concentration. By varying the acetate content (i.e., the degree of hydrolysis), one can alter the hydrophobicity of the PVA stabilizer. The steric stabilization properties of PVA have been analyzed by several investigators.⁵⁻⁹ Recently, Chatzi and Kiparissides⁸ employed a model system of 50% v/v *n*-butyl chloride in water to investigate the effects of the PVA type and agitation rate on the droplet size distribution. They developed a generalized numerical algorithm to simulate the steady-state drop size distribution of liquid-liquid dispersions in order to elucidate the breakage and coalescence mechanisms as a function of the physical and interfacial characteristics of the system.

PVA has also been used as a film-forming material in several microencapsulation processes. Aqueous PVA solutions have been utilized to prepare, using phase separation methods, microcapsules containing hydrophobic liquids. The coacervated polymer membrane is subsequently reacted with aldehydes or dialdehydes to obtain a chemically crosslinked polymer capsule wall.^{4,10} Several authors¹¹⁻¹⁸ have analyzed the effects of the agitation rate and the concentration of the surface-active agent on the mean diameter of the microcapsules. In general, high agitation speeds and emulsifier concentrations result in a decrease of the microcapsule mean size.

In the present work the stability and the size distribution of (o/w) emulsions and oil-containing microcapsules are investigated. Specifically, the effects of the agitation rate, type and concentration of PVA, type and amount of the dispersed oil phase, and amount of electrolyte in the polymer aqueous solution on the drop size distribution are experimentally analyzed. Finally, a quantitative correlation is developed to relate the Sauter mean diameter of the emulsion droplets with the agitation rate, the concentration of PVA, and the ratio of the encapsulated oil to the continuous aqueous phase.

EXPERIMENTAL

Materials

PVA (Gohsenol, Nippon Gohsei) of various grades (e.g., degree of hydrolysis and molecular weight) was utilized both as stabilizer and film-forming material. Sodium sulfate of reagent grade (Mallinckrodt Chemical Works) was employed as phase inducer. Silicon oils (polydimethylsiloxanes, Fluka Chemie AG) of different viscosities were chosen as liquid core materials. The crosslinking of PVA was carried out under acidic conditions (e.g., sulfuric acid, Merck, 96%, anhydrous methanol, Mallinckrodt Chemical Works, and acetic acid, Merck, 100%, all of analytical grade) using a glutaraldehyde solution (TAAB, EM 25% vol). An oil-soluble dye (SUDAN III, Solvent Red 23, Aldrich Chemie) was added to the oil phase to assess the efficiency of the encapsulation process. All materials were used as received.

Preparation of (o/w) Emulsions

One hundred milliliters of an aqueous PVA solution were introduced into a specially designed dispersion vessel made of borosilicate glass with special constructed indentations on its inner surface to prevent problems of vortexing and overflowing (KINEMATICA AG). Subsequently, a small amount of silicon oil (e.g., 10 mL) was added dropwise into the aqueous polymer solution. The emulsification was effected with the aid of a Polytron homogenizing device consisting of a dispersion unit and a dispersion aggregate while the agitation rate was controlled by a speed controller. The emulsion was allowed to stir at room temperature, for a total of 10 min, in order to obtain a steady-state droplet size distribution.

Phase Separation Behavior of PVA Solutions

The temperature at which a homogeneous polymer solution separates into two phases is known as the cloud point temperature of the solution and marks the onset of the formation of a polymer-rich phase and of a diluted one. The polymer-rich phase may consist of microscopic colloidal aggregates, which adsorb to the surface of the hydrophobic oil droplets, thus leading to the formation of a polymer membrane around them. The formation of the polymer membrane around the dispersed oily droplets largely depends on the size and concentration of the colloidal polymer aggregates. The PVA type (e.g., molecular weight and degree of hydrolysis) and concentration, the concentration of the electrolyte in

the aqueous solution, and the rate of temperature increase are the most critical parameters affecting the size and the concentration of the colloidal polymer aggregates and, thus, the thickness and the morphology of the polymer membrane formed around the oil droplets.

A series of experiments was carried out to determine the cloud point temperature of several PVA solutions as a function of the electrolyte concentration. The onset of phase separation was optically observed and the cloud point temperature was recorded. The results of the phase separation experiments are reported in Table I. It can be seen that as the PVA to salt mass ratio decreases and the concentration of PVA aqueous solution increases, the cloud point temperature decreases.

The Microencapsulation Procedure

Oil-containing microcapsules in the size range of 5–20 μm were prepared by the coacervation/crosslinking method, which included the following steps: (1) dispersion of the oil phase in an aqueous PVA solution, (2) addition of the electrolyte phase inducer (e.g., sodium sulfate), and (3) crosslinking of the coacervated polymer membrane with glutaraldehyde.

The (o/w) emulsion formed with the aid of a Polytron homogenizer was transferred into a jacketed reaction vessel having a volume capacity of 250 mL. The reactor was equipped with a stainless steel six-blade turbine impeller and fitted with four equally spaced vertical stainless steel baffles. Water from a constant-temperature Neslab RTE-210 bath was steadily circulated through the vessel's jacket to maintain the reactor content at the desired tem-

perature (e.g., 10°C). The (o/w) emulsion was stirred at a constant agitation rate.

Initially, 30 mL of a sodium sulfate solution (e.g., 20% w/v) were slowly added to the (o/w) emulsion maintained at a constant temperature of 10°C. The final aqueous PVA–sodium sulfate solution had a cloud point temperature of about 25°C. Coacervation was brought about by gradually increasing (e.g., 1°C/min) the temperature of the (o/w) emulsion from 10 to 25°C. Following the phase separation of the aqueous polymer solution and the coverage of the oil droplets by the coacervated polymer-rich phase, crosslinking of the capsules' polymer membrane was carried out by adding into the dispersion 12 mL of a solution, consisting of methanol (16.67% vol), acetic acid (5% vol), sulfuric acid (0.167% vol), and glutaraldehyde (4.167% vol).¹⁹ The crosslinking reaction occurred at 25°C for about 24 h. A schematic description of the various steps followed for the production of oil-containing microcapsules is given in Figure 1.

Droplet Size Measurements

For the measurement of the droplet (capsule) size distribution, a Malvern laser diffraction particle sizer Model 2605c interfaced with an Olivetti M24 computer was used. The particle size analyzer was equipped with a measurement cell. A lens with focal length of 63 mm capable of detecting particles in the size range of 1.4–118 μm was attached to the optical measurement unit. The primary output of the instrument was the relative volume size distribution of the droplets stored in 32 size classes uniformly spaced on a logarithmic scale. The Sauter mean diameter, d_{32} , of the droplets was selected as

Table I Cloud Point Temperatures of Various PVA–Sodium Sulfate Aqueous Solutions

PVA : Salt Mass Ratio	Cloud Point (°C) $C_{\text{PVA}} = 0.5\% \text{ w/v}$	Cloud Point (°C) $C_{\text{PVA}} = 1\% \text{ w/v}$	Cloud Point (°C) $C_{\text{PVA}} = 1.5\% \text{ w/v}$
1 : 1	—	> 50	> 50
1 : 2	—	> 50	> 50
1 : 3	—	> 50	38
1 : 4	—	48–50	20–21
1 : 5	> 50	31–33	10
1 : 6	> 50	25	< 10
1 : 7	> 50	18	< 10
1 : 8	50	8–10	< 10
1 : 9	42–44	< 10	—
1 : 10	36	< 10	—

Molecular weight of PVA: 60,000; degree of hydrolysis of PVA: 95–97%-mol.

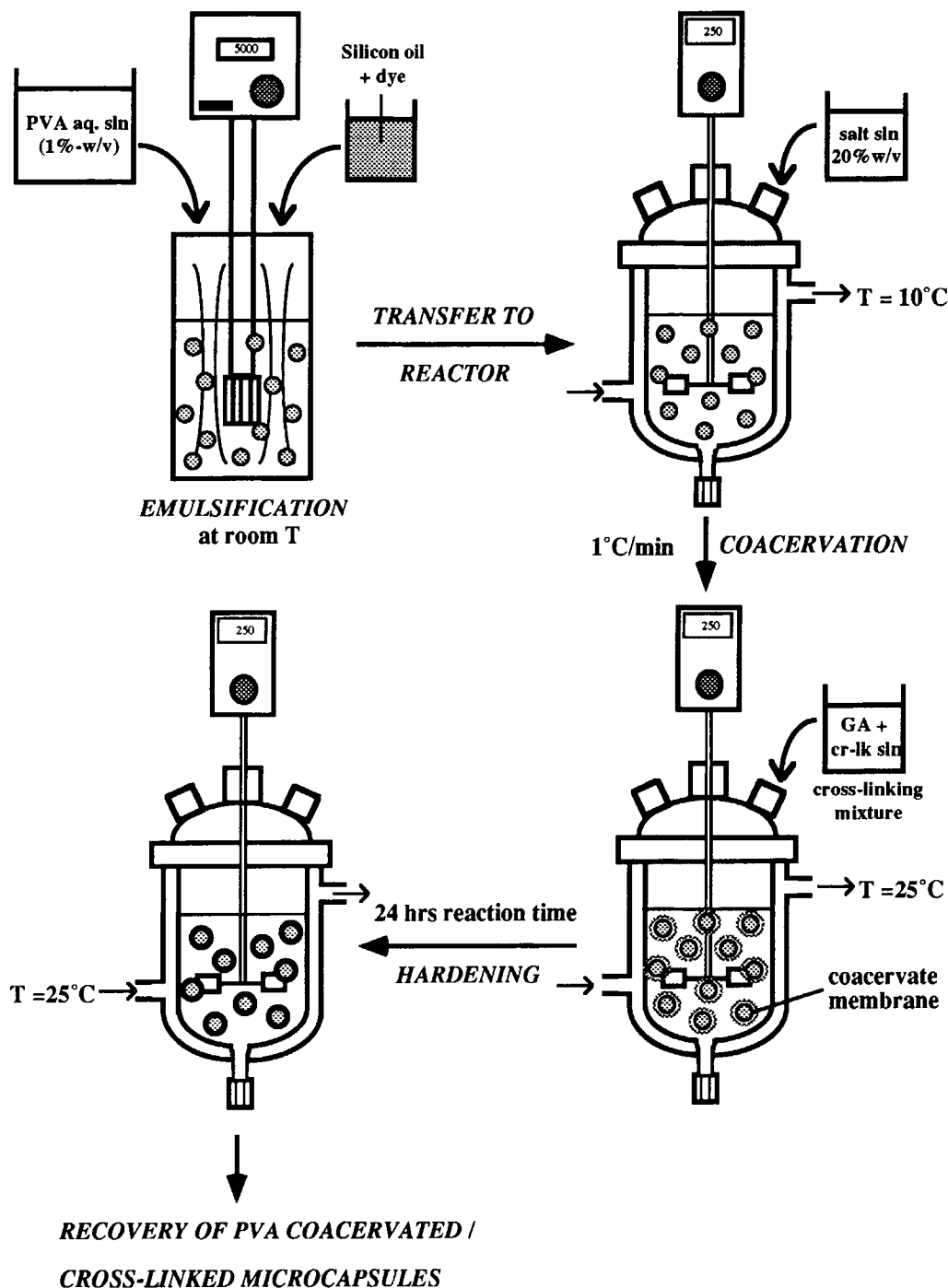


Figure 1 Schematic representation of the various stages of the production of PVA microcapsules by the coacervation/crosslinking method.

the characteristic mode of the distribution to assess the effects of the various process parameters on the droplet (microcapsule) size distribution; d_{32} was calculated from the measured volume frequency using the following equations:

$$d_{32} = \frac{\sum_i f_i d_i^3}{\sum_i f_i d_i^2}; \quad f_i = \frac{f_{vi} \frac{\pi d_i^3}{6}}{\sum_i f_{vi} \frac{\pi d_i^3}{6}} \quad (1)$$

where f_{vi} is the measured volume frequency and f_i is the normalized number frequency of the droplets having diameters in the size range of d_i to $d_i + \Delta d_i$.

Optical examination of the (o/w) emulsions as well as of the final microcapsules was carried out using a Leitz Mettalux 3 microscope. The system was supplied with suitable software for advanced image analysis of the optical photographs (Image ProPlus, version 1.1).

Process Variables and Operational Conditions

The most important process parameters influencing the size (e.g., Sauter mean diameter) of the oil droplets (microcapsules) are the agitation speed, the molecular weight and the degree of hydrolysis of PVA, the concentration of PVA, the viscosity and the amount of the dispersed oil phase, and the concentration of the phase separation inducer electrolyte. While studying the effect of one variable, the values of all others were kept constant. Table II summarizes the experimental conditions selected in the present study. From Table II, one can notice that eight PVA grades of different molecular weight (e.g., $M_n \sim 25,000$ – $100,000$) and degree of hydrolysis (71–100% mol) were employed. In all experiments, the PVA concentration in the aqueous phase varied from 0.05 to 5% w/v. Four grades of silicon oil with viscosities in the range of 12 to 1070 cp were tested. The agitation speed varied from 1000 to 10,000 rpm. The volume ratio of the emulsified oil to the aqueous continuous phase (φ) ranged from 0.01 to 0.5. The ionic strength of the aqueous phase was adjusted by the addition of a 20% w/v sodium sulfate aqueous solution. Thus, the mass ratio of PVA to the salt could be changed from 1 : 1 to 1 : 10.

RESULTS AND DISCUSSION

In most controlled release applications, the release of the liquid core material is largely influenced by the size distribution of the microcapsules, the morphology of the capsules' polymer wall, and the environmental conditions (e.g., pH, ionic strength) of the release medium. In the present study, the effect of selected process parameters on the microcapsule size distribution has experimentally been assessed. In the coacervation process, control of the capsule size distribution is difficult, since the stability of the emulsion is strongly affected by small changes in the environmental conditions (e.g., temperature, electrolyte concentration) of the continuous phase. As the size of the oil droplets decreases, the quality of the protective polymer membrane formed around the droplets deteriorates and the extent of microcapsule agglomeration increases. In fact, one cannot easily obtain discrete and stable microcapsules in the size range of 1–5 μm by the simple coacervation/crosslinking method.²⁰

The Effect of the Agitation Rate

A great number of articles have been published dealing with the experimental investigation of the effect of agitation rate on the droplet size distribution in liquid–liquid dispersion systems.^{9,12,13,16–18} In general, the mean size of the droplets in a liquid–liquid dispersion is determined by the balance between the turbulent forces tending to break up the droplets and the interfacial tension and viscosity forces holding a droplet together.

The effect of the agitation rate on the size distribution and the Sauter mean diameter of the oil

Table II Experimental Conditions Employed for the Preparation of o/w Emulsions and Microcapsules

Agitation Rate (rpm)	PVA Type		C_{PVA} (% w/v)	Viscosity of Oil (cp)	Oil Volume Fraction	Mass Ratio of PVA : Salt
	MW	Deg. Hydrolysis (% mol)				
1,000	25,000	98.5–100	0.05	12	0.01	1 : 1
2,000	60,000	95–97	0.1	53	0.05	1 : 2
3,000	60,000	98–99	0.5	378	0.10	1 : 3
4,000	100,000	97.5–98.5	1	1070	0.50	1 : 4
5,000	25,000	86.5–89	2			1 : 5
6,000	80,000	86.5–89	3			1 : 6
7,000	70,000	78.5–81.5	4			1 : 7
8,000	25,000	71–74	5			1 : 8
9,000						1 : 9
10,000						1 : 10

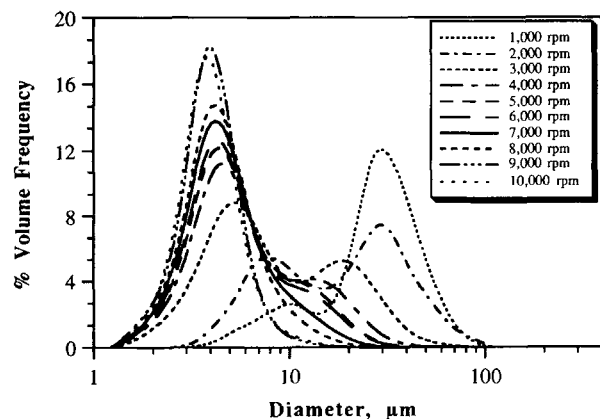


Figure 2 Effect of agitation rate on the drop size distribution of (o/w) emulsions. PVA concentration: 1% w/v; oil volume fraction: 0.05; oil viscosity: 12 cp.

droplets for a 5% vol silicon oil in water system and a 1% w/v PVA concentration is depicted in Figures 2 and 3. It is apparent that as the agitation rate increases, the droplet size distribution shifts to smaller diameters since the turbulent kinetic energy associated with the drop breakage process increases. It is interesting to notice that, at low stirring rates, the droplet size distribution exhibits a bimodal form, which changes to a more symmetrical one (e.g., unimodal) at higher agitation rates (see Fig. 2). However, at agitation speeds above 7000 rpm, no significant variation of the drop size distribution is observed with the agitation rate. This is also shown in Figure 3, where the Sauter mean diameter is plotted with respect to the agitation rate. It is evident that as the agitation rate increases, the Sauter mean diameter sharply decreases to a limiting value of about 5 μm .

The Effect of PVA

The interfacial tension of the oil/water system will depend on temperature and the type and concentration of PVA.^{5,6,8,21,22} In general, at low PVA concentrations (e.g., less than 10^{-4} g/L) the interfacial tension is relatively independent of the PVA concentration. At intermediate concentrations (e.g., 10^{-4} to 10^{-1} g/L) the interfacial tension exhibits an almost linear decrease with the logarithm of the PVA concentration. Finally, at higher concentrations (e.g., above 10^{-1} g/L) the interfacial tension reaches a limiting value.⁸ The observed break point of the interfacial tension at PVA concentrations in the range of 10^{-4} to 10^{-3} g/L marks the onset of almost complete coverage of the oil phase by the PVA molecules having an extended conformation. Lankveld

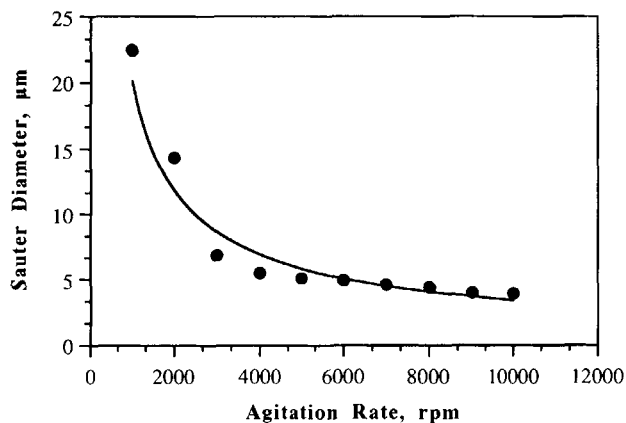


Figure 3 Effect of agitation rate on the Sauter mean diameter of (o/w) emulsions. (Experimental conditions as in Fig. 2.)

and Lyklema⁵ suggested that the observed variation of the interfacial tension with the PVA concentration is related to the number of adsorbed polymer segments per unit area of the liquid-liquid interface, the interaction free energy per segment in the loops of the adsorbed polymer molecules, and the average loop length. The combined effect of segmental adsorption as well as loop interaction tends to decrease the interfacial tension due to the appearance of steric repulsion forces. On the other hand, the observed limiting value of the interfacial tension at higher polymer concentrations coincides with the completion of the polymer adsorption (e.g., formation of a polymer monolayer around the oil droplets) and the appearance of strong repulsion forces.²³

The effect of PVA concentration on the size distribution and the Sauter mean diameter of the oil droplets is shown in Figures 4 and 5, respectively.

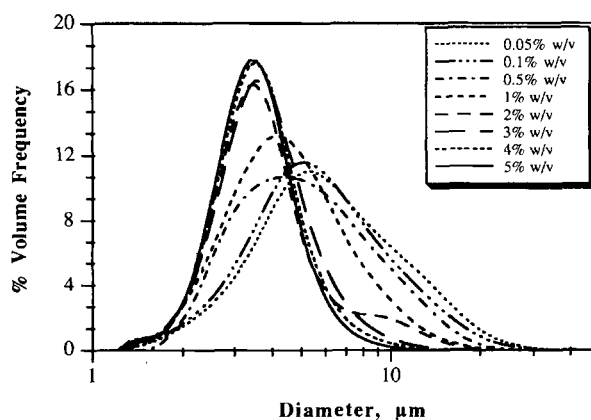


Figure 4 Effect of PVA concentration on the drop size distribution of (o/w) emulsions. Agitation rate: 8000 rpm; oil volume fraction: 0.05; oil viscosity: 12 cp.

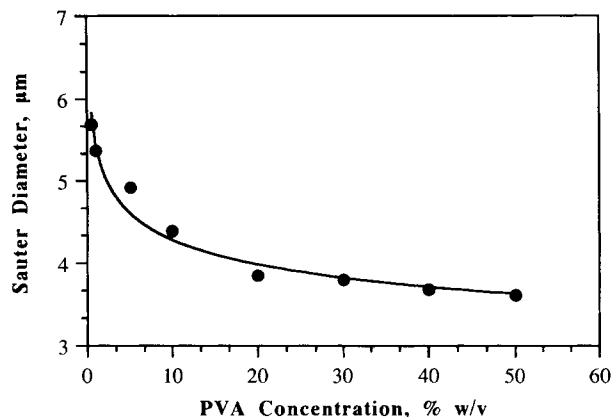


Figure 5 Effect of PVA concentration on the Sauter mean diameter of (o/w) emulsions. (Experimental conditions as in Fig. 2.)

Figure 4 illustrates that the drop size distribution becomes narrower and more symmetrical as the PVA concentration increases. It is important to point out that above a certain PVA concentration (e.g., of about 2% w/v) the drop size distribution (Fig. 4) and the Sauter mean diameter (Fig. 5) do not vary significantly, which is due to the limiting value of the interfacial tension at higher PVA concentrations. In general, the dependence of the drop size distribution on the amount of PVA stabilizer decreases as the stabilizer concentration increases.

The effect of the PVA type (e.g., degree of hydrolysis and molecular weight) on the interfacial tension and the drop size distribution in liquid-liquid dispersions has been discussed by several investigators. Lankveld and Lyklema^{5,6} studied the effects of the acetate content and molecular weight of PVA on the polymer adsorption for a paraffin-water system. They showed that as the molecular weight of the PVA increased, the PVA stabilizer became more surface active (e.g., the interfacial tension was decreased). Moreover, they found that PVA samples with a high vinyl acetate content exhibited a more surface-active behavior than PVA with a high degree of hydrolysis. Scholtens and Bijsterbosch²⁴ studied the adsorption behavior of partially hydrolyzed PVA for a water-1, butanol system. They also observed a reduction in the interfacial tension of the system as the acetate content of the PVA increased. They concluded that the efficiency of the PVA in lowering the interfacial tension was directly related to the lyophilic-lyophobic balance of polymer chains determined by the degree of hydrolysis of PVA.

The effect of PVA type on the size distribution and the Sauter mean diameter of the (o/w) emulsions is depicted in Figure 6 and Table III. As the

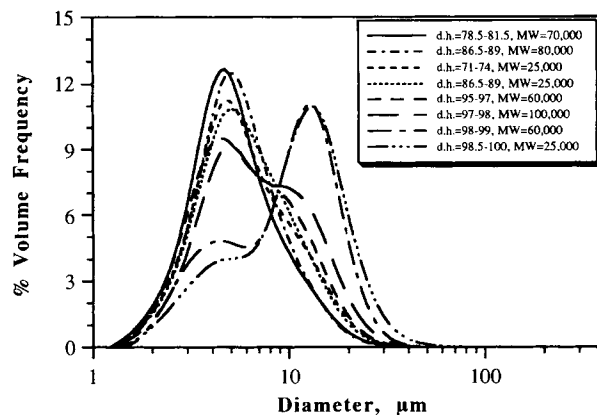


Figure 6 Effect of PVA type on the drop size distribution of (o/w) emulsions. Agitation rate: 5000 rpm; PVA concentration: 1% w/v; oil volume fraction: 0.05; oil viscosity: 12 cp.

acetate content of the PVA increases, the resistance to drop breakage decreases, leading to a decrease of the mean droplet size.⁸ Furthermore, partially hydrolyzed PVA of high molecular weight adsorbs more strongly to the oil/water interface than PVA of low molecular weight, which results in lowering the interfacial tension of the oil-water system.⁴

The Effect of the Oil Phase

A variety of correlations have been published relating the Sauter mean diameter of the droplets, d_{32} , to the vessel geometry and the physical properties of the dispersion system.²⁵ The most well-known correlation is described by eq. (2):

$$d_{32}/D_I = b(1 + c\phi)(N_{We})^{-0.6} \quad (2)$$

where $N_{We} = \rho_c(N^*)^2 D_I^3 / \sigma$ is the Weber number of

Table III Effect of the PVA Type on the Sauter Mean Diameter of the Emulsion Droplets and Microcapsules

Molecular Weight	Degree of Hydrolysis (% mol)	Sauter Mean Diameter, d_{32} (μm)
25,000	71-74	4,966
25,000	86.5-89	5,521
25,000	98.5-100	8,342
60,000	95-97	7,524
60,000	98-99	6,129
70,000	78.5-81.5	5,184
80,000	86.5-89	5,415
100,000	97.5-98.5	5,503

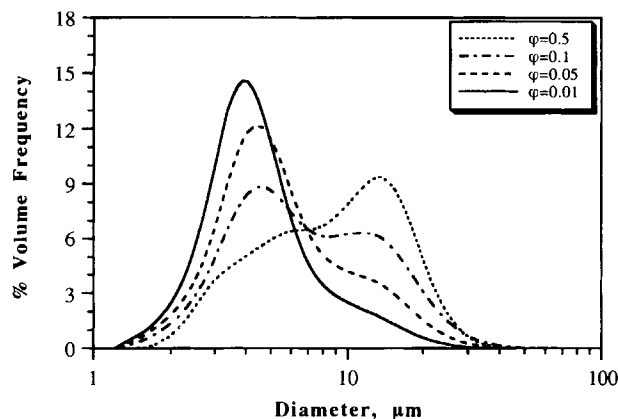


Figure 7 Effect of the volume fraction of the emulsified oil phase on the drop size distribution of (o/w) emulsions. Agitation rate: 5000 rpm; PVA concentration: 1% w/v; oil viscosity: 12 cp.

the main flow, D_I is the diameter of the impeller, N^* is the impeller speed, ρ_c is the density of the continuous phase, σ is the interfacial tension, b and c are correlation parameters, and φ is the dispersed phase volume fraction. Thus, the Sauter mean diameter, d_{32} , will depend on the physicochemical properties of the system, the turbulence intensity, and the dispersed phase fraction, φ . Note that the term $(1 + c\varphi)$ reflects the influence of the dispersed phase volume in damping down the overall level of turbulence intensity. Alternatively, the net “damping effect” of the dispersed phase on the intensity of turbulence can be expressed as a reduction of the effective agitation rate by a factor of $(1 + \varphi)^{26}$:

$$N_{\text{eff}}^* = N^*/(1 + \varphi) \quad (3)$$

Figure 7 illustrates the effect of dispersed phase volume fraction, φ , on the drop size distribution. It is evident that as φ increases, the drop size distribution shifts to larger diameters and becomes broader. In fact, the distribution changes from a symmetrical form to a bimodal one. This is in accordance with the results of Figures 2 and 3 and the predictions of eqs. (2) and (3), which show that the Sauter mean diameter increases with an increase of φ (e.g., decrease of N^*).

It has been postulated that drop breakage in turbulent fields may be caused by viscous shear forces, by turbulent pressure fluctuations, and/or by relative velocity fluctuations.²⁵ In general, high-viscosity liquids, when stirred, exhibit a greater resistance to breakage and deformation than low-viscosity fluids. Consequently, they form larger and more stable emulsion droplets compared to the low-viscosity

ones. In general, an increase in the droplet size distribution is observed when the viscosity of the internal phase is increased. Figure 8 depicts the effect of the silicon oil viscosity on the size distribution of the droplets for a constant agitation rate of 6000 rpm and a PVA concentration of 1% w/v. It can be seen that as the viscosity of the oil phase increases, the distribution becomes broader and shifts to larger diameters. Sanghvi and Nairn^{14,15} studied the effect of the internal phase viscosity on the formation of emulsified droplets and reported a similar behavior.

The Effect of the Electrolyte Concentration

The effect of electrolyte concentration on the coacervation of gelatin was investigated by Rosenblat et al.¹¹ They found that high agitation rates were required during the phase separation and cooling stages of the process, to produce small and stable microcapsules. The mechanism of coacervation and phase separation as well as the interfacial interactions in polymer aqueous media were also investigated by Van Oss.²⁷ He observed that the mechanism operative in coacervation would lead to flocculation whenever the limits of polymer solubility were transgressed.

The thermodynamic stability efficiency of polymeric surface-active agents in the presence of strong electrolytes largely depends on the chemical nature of the anchor polymer, the nature of the stabilized colloidal particles or droplets, and the solvency efficiency of the dispersion medium for the stabilizing polymeric moieties.^{28,29} Following the investigation of the phase separation behavior of PVA polymer solution, it is anticipated that the mechanism operative in coacervation readily lead to flocculation

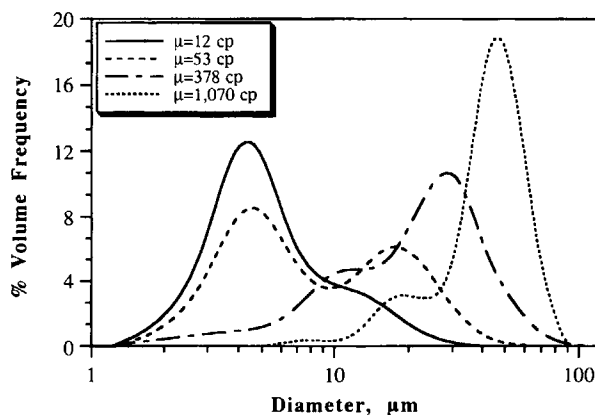


Figure 8 Effect of oil viscosity on the drop size distribution of (o/w) emulsions. Agitation rate: 6000 rpm; PVA concentration: 1% w/v; oil volume fraction: 0.05.

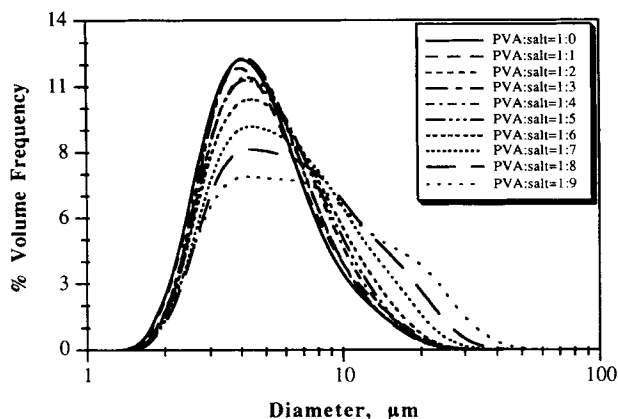


Figure 9 Effect of the electrolyte concentration on the drop size distribution of (o/w) emulsions. Agitation rate: 7000 rpm; PVA concentration: 0.5% w/v; oil volume fraction: 0.01; oil viscosity: 12 cp.

whenever the solubility limit of PVA chains is exceeded due to an increase in the electrolyte concentration.

In Table I, the cloud point temperatures of three PVA solutions (e.g., $C_{\text{PVA}} = 0.5\%$, 1%, and 1.5% w/v) are reported as a function of the sodium sulfate concentration. At low PVA concentrations (e.g., $C_{\text{PVA}} = 0.5\%$ w/v), phase separation occurs at relatively high temperatures (e.g., $>50^\circ\text{C}$) and high salt concentrations (e.g., PVA : salt ratios $> 1 : 5$). However, as the PVA concentration increases, the cloud point temperatures of the solution sharply decreases and phase separation occurs at lower PVA : salt mass ratios.

In general, an increase in the electrolyte concentration lowers the solubility of the PVA chains in the aqueous phase due to the "salting out" effect.^{3,4,28} As a result, monomer units on the same PVA polymer chain first start interacting with their nearest neighbors, followed by association with surrounding chains (e.g., formation of polymer aggregates). At the cloud point temperature, the PVA chains are imparting strong attraction forces, which can lead to the destabilization of the oil-in-water emulsion system.

As previously discussed, coacervation is brought about either by gradually increasing the temperature of the (o/w) emulsion, which contains a predetermined amount of the electrolyte, to its cloud point temperature or by gradually increasing the electrolyte concentration while maintaining the (o/w) emulsion at a constant temperature. In Figure 9, the effect of the electrolyte concentration on the drop size distribution of the (o/w) emulsion and its stability is illustrated for a 0.5%-w/v PVA solution at

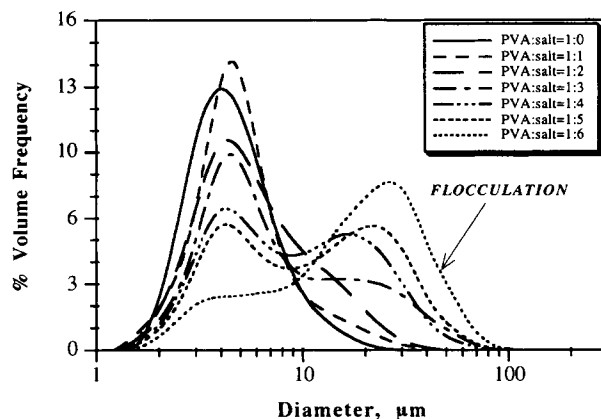


Figure 10 Effect of the electrolyte concentration on the drop size distribution of (o/w) emulsions. Agitation rate: 7000 rpm; PVA concentration: 1% w/v; oil volume fraction: 0.01; oil viscosity: 12 cp.

25°C . Since in all investigated cases the cloud-point temperature of the PVA–sodium sulfate–water solution was above 35°C (see cloud point temperatures in Table I), the formation of a coacervated PVA membrane around the oil droplets was not feasible. Note that as the electrolyte concentration increases, the droplet size distribution shifts to larger diameters. This is due to a decrease of the steric stabilizing efficiency of PVA at higher salt concentrations, which increases the droplet coalescence rate.

In Figures 10 and 11, the effect of the electrolyte concentration on the stability of the produced microcapsules is depicted for two PVA concentrations (e.g., 1% w/v and 1.5% w/v). It is apparent that as the PVA to salt ratio decreases, the drop flocculation increases, leading initially to a bimodal distribution

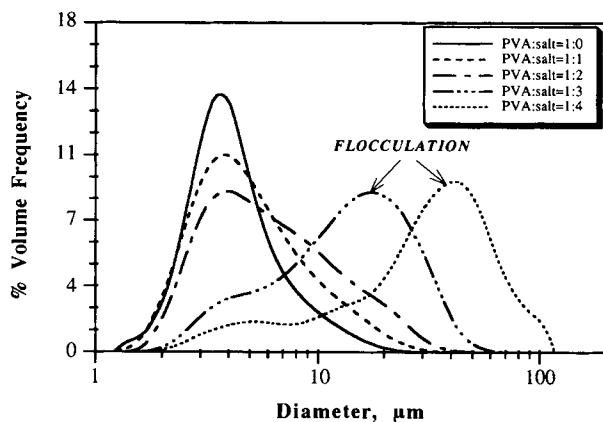


Figure 11 Effect of the electrolyte concentration on the drop size distribution of (o/w) emulsions. Agitation rate: 7000 rpm, PVA concentration: 1.5% w/v; oil volume fraction: 0.01; oil viscosity: 12 cp.

and, finally, to a completely aggregated system. Notice that, according to the results of Table I, a 1% w/v aqueous PVA solution exhibits a cloud point temperature of 25°C for a PVA : salt mass ratio of 1 : 6, while a 1.5% w/v aqueous PVA solution will have a cloud point temperature of 25°C for a PVA : salt mass ratio slightly above 1 : 4.

Finally, Figure 12 depicts the effect of the salt : PVA mass ratio on the stability of the (o/w) emulsions for different PVA concentrations at a constant temperature of 25°C. Note that in order to obtain a stable emulsion and, thus, stable microcapsules, the concentration of the phase inducer should not exceed a critical value for a given PVA concentration.

Model Developments

For low values of φ and assuming that the drop breakage is the dominant mechanism, Eq. (2) becomes³⁰⁻³²

$$d_{32}/D_I = b(N_{We})^{-0.6} \quad (4)$$

On the other hand, assuming that the drop size is determined by the drop coalescence process, it can be shown that the Sauter mean drop diameter will be given by the following relation^{30,31}:

$$d_{32}/D_I = k(\sigma D_I)^{-0.375}(N_{We})^{-0.375} \quad (5)$$

The steady-state Sauter mean droplet diameters measured under different experimental conditions (e.g., agitation rates, volume fraction of the dispersed oil phase, and PVA concentrations) were fitted to the following empirical correlation using a nonlinear least-squares algorithm:

$$d_{32} = 3362 \cdot (1 + 4.67\varphi) \cdot N^{-0.77} \cdot C_{PVA}^{-0.103} \quad (6)$$

where d_{32} is the Sauter mean diameter in μm , N is the agitation speed in rpm, C_{PVA} is the PVA concentration in % w/v, and φ is the volume fraction of the oil phase. Notice that Eq. (6) shows that d_{32} is proportional to $N^{-0.77}$, which is consistent with Eq. (5) as far as the dependence of d_{32} on N is concerned. As a result, drop coalescence might be the dominant mechanism in the formation of the (o/w) emulsions.

Generally, the present experimental results are in agreement with previously reported results^{9,13,18} regarding the dependence of the Sauter mean drop diameter on the agitation rate, the volume fraction of the dispersed phase, and the stabilizer concentration.

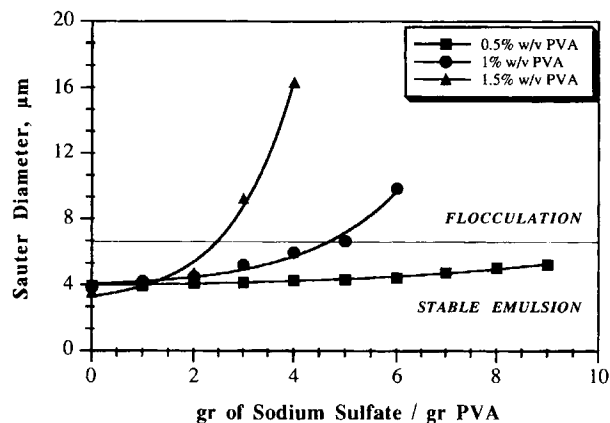


Figure 12 Effect of PVA concentration on the Sauter mean diameter of (o/w) emulsions for different mass ratios of sodium sulfate to PVA.

Production of Microcapsules

The size and morphology of the microcapsules produced by the coacervation process are subjected to a number of physical and chemical parameters, including the geometrical characteristics of the agitation quality (e.g., agitation speed, type and concentration of stabilizers) as well as the physico-chemical properties of the dispersed and continuous phases.

The gradual introduction of a phase separation inducer into an aqueous polymer solution results in the formation of minute coacervate droplets containing a higher concentration of the polymer, as compared with that in the bulk solution. As the concentration of the phase inducer agent increases, the size of the coacervate droplets increases due to the coalescence of the primary droplets. In the absence of stirring, the coalescence of the primary colloidal droplets continues unabatedly, leading to the formation of very large coacervate droplets and, finally, to macroscopic phase separation.¹ In Figure 13 the coalescence of the coacervate PVA droplets is depicted as a function of the concentration of the sodium sulfate. It can be seen that as the concentration of the electrolyte increases, the size of the coacervate droplets increases too.

By appropriate selection of the controlling process variables (e.g., agitation rate, type and concentration of the stabilizer, type and concentration of the electrolyte), formation of small coacervate droplets in the desired size range (of about 100 nm) can be achieved. In the present study, stable microcapsules were produced by adjusting the emulsification conditions (e.g., agitation rate, oil volume fraction) and maintaining the concentration of the phase inducer

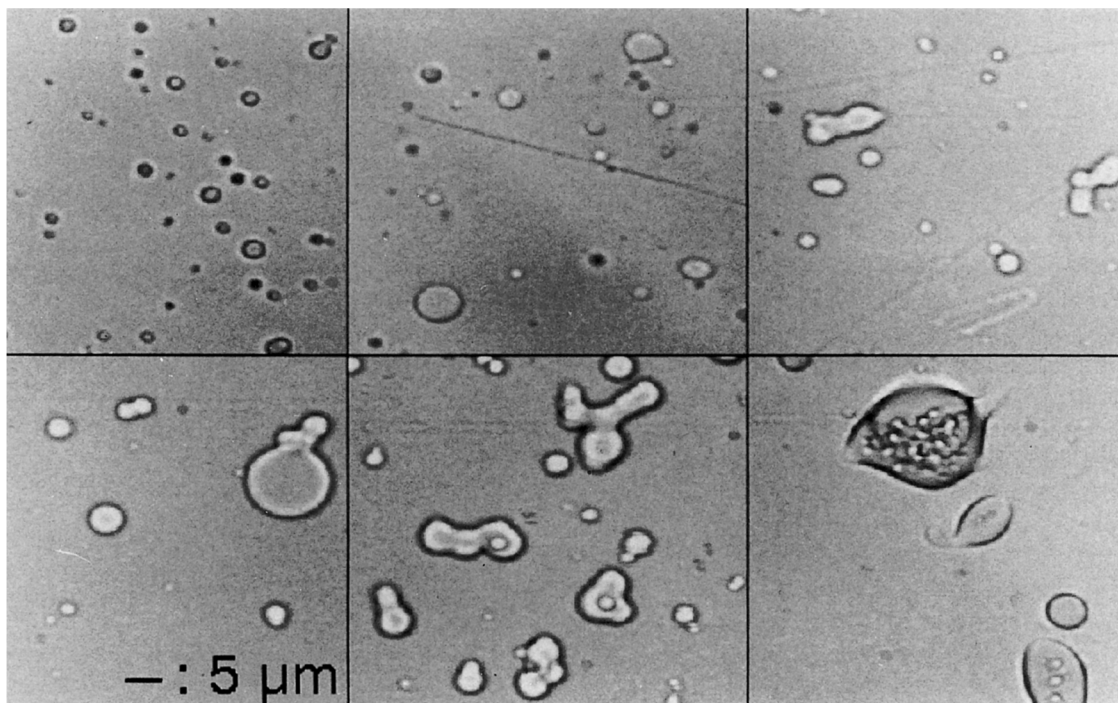


Figure 13 Effect of the electrolyte concentration on the coalescence of the coacervate droplets.

below the experimentally determined critical flocculation point. Optical microscope observations revealed that discrete and spherical microcapsules were produced (Fig. 14) under the selected optimal process conditions. Finally, Figure 15 shows a comparison between the size distribution of the emulsion

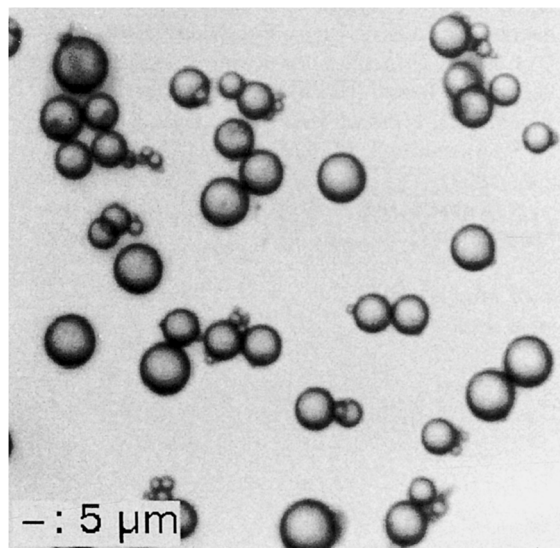


Figure 14 Oil-containing PVA microcapsules produced by coacervation and crosslinking.

droplets and the final microcapsules. Apparently, there is a small difference between the two distributions, which proves that no significant drop coalescence occurs during the coacervation process under the selected conditions.

CONCLUSIONS

Oil-containing polyvinyl alcohol microcapsules in the size range of 5–20 μm were prepared by the

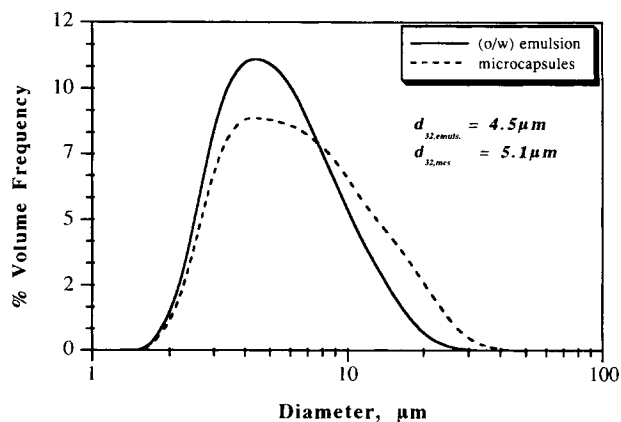


Figure 15 Comparison between the size distributions of the microcapsules and the (o/w) emulsion droplets.

emulsification of different silicon oils in aqueous PVA solutions and the subsequent confinement of the oil droplets by a combined coacervation/cross-linking process. The Sauter mean diameter of the emulsion droplets was found to be directly proportional to the volume fraction of the emulsified phase and proportional to $N^{-0.77}$ and $C^{-0.103}$ with respect to the agitation rate and the PVA concentration, respectively. Moreover, the Sauter mean drop diameter decreased by increasing the viscosity of the internal phase. The size distribution of the (o/w) emulsions and the Sauter mean diameter of the emulsion droplets were also dependent on the molecular weight and the degree of hydrolysis of the PVA stabilizer. The experimental results showed that partially hydrolyzed/high-molecular-weight PVA grades were more effective in stabilizing the (o/w) emulsions, leading to more uniform size distributions. Finally, it was shown that the addition of the phase inducer electrolyte to the sterically stabilized (o/w) emulsion significantly affected the size distribution and stability of the oil droplets and of the final microcapsules.

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