Microencapsulation in Polyurea Shell by Interfacial Polycondensation

A model and a simple measurement technique for time of encapsulation have been developed to study the microencapsulation of butachlor in polyurea shell by means of interfacial polymerization. The model is based on diffusion of the hydrophilic monomer through the polymeric shell with an interfacial reaction at the inner surface while the measurement technique is based on the indirect determination of the concentration of the hydrophilic monomer in the continuous phase by monitoring the pH. Measurements show that capsule sizes ranging from 1 to 20 μm can be produced, and the surface to volume mean size varies only from 2 to 6 μm for a large variation in rpm of the agitator. Time of encapsulation is found to be approximately proportional to the microcapsule size, and it varies from 150 to 300 s. Both the data and the model were used to discern that the process is kinetically-controlled by and large. It is also shown that time of encapsulation varies with the square of the capsule size in a diffusion-controlled regime.

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Introduction

Microencapsulation in a polymeric shell by means of interfacial polycondensation is an important technique for encapsulating active agents such as biological species and pesticides (Chang, 1964; Koestler, 1980). This technique has been shown to be very convenient and useful for encapsulating water-immiscible pesticides (Beestman and Deming, 1981, 1983). Consider, for example, the present case of microencapsulation of a preemergence herbicide, Butachlor, in polyurea shell. In this case, Butachlor containing a hydrophobic monomer, hexamethylene-1,6-diisocyanate (HMDI) is dispersed in a continuous aqueous phase containing a salt of lignin sulfonate (preferably sodium salt) which acts as a surfactant. Formation of polyurea wall takes place at the interface of each droplet and water when a hydrophillic monomer like hexamethylene-1,6-diamine (HMDA) is added to the aqueous phase. This microencapsulation (or in short, encapsulation) process goes to completion in a few minutes (Beestman and Deming, 1983).

The most widely used application of these microcapsules is the controlled or sustained release of the encapsulated active agent. The functional performance of the microcapasules in this application to a great extent depends on the morphology and the surface characteristics of the polymeric shell as well as on their size range. Both of these important characteristics (size range and shell morphology) of the microcapsules, in turn, depend on the process materials and the process conditions. If the shell formation is conducted under a kinetic-controlled regime with multifunctional monomers, for example, one obtains a highly crosslinked polymer with extremely low permeability. Hence, there is a need to develop a sound analysis capable of predicting the various features of the process. It is also needed to develop an experimental technique to measure the time of encapsulation (t_e)—an important information in the design of encapsulator. Reported studies on these aspects are limited only to a few publications (Koestler, 1980; Sirdesai and Khilar, 1988). These studies offer neither a comprehensive model to describe the process nor a convenient technique to measure the time of encapsulation.

In this paper, we first report a kinetic model for describing the dynamics of this encapsulation process. This model can be used to predict the controlling regime of the interfacial polymerization process as well as the time required for completion of this process. We then report the development of a simple and convenient technique of monitoring the pH of the continuous phase to measure the time of encapsulation. The model and the measurements are then used to elucidate some interesting features of the process.

Theoretical Studies

Pearson and Williams (1985) treated the case of the interfacial polymerization of an isocyanate with a diol using pseudo-

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steady state and unsteady state modeling approaches, featuring diffusion of one of the monomers through the polymer shell surrounding the other monomer droplet and a surface reaction between the two at the inner boundary of the shell. Sirdesai and Khilar (1988) treated the encapsulation process along similar lines in a quasisteady-state approach, accounting for the fact that in this case the solution inside the droplet is not a pure monomer, but a solution. In both studies, the monomer in the continuous phase was assumed to be in abundant supply so that its concentration remained essentially constant in time.

In order to determine the encapsulation kinetics, one needs to monitor either the thickness of the polymer shell or the concentration of one of the monomers with time. The concentration of the continuous-phase monomer is obviously the most convenient to measure. A realistic theoretical treatment has to therefore recognize the variation in concentration of the continuous-phase monomer. The analysis presented in this work, while essentially similar in approach to the work described above, accounts for this concentration variation. Small shell thicknesses allow analytical integration of the rate expression and derivation of a criterion for kinetic control. The rate expressions, appropriately simplified for this special case, allow determination of the rate constant by linear fitting procedures.

Figure 1 shows schematically the sequence of events in the encapsulation of a single drop. Butachlor (the material to be encapsulated) with some dissolved monomer A (hydrophobic) is dispersed as fine drops in water with the aid of an emulsifier. As soon as monomer B (HMDA) is added to the continuous phase, the reaction begins at the surface of the drops, leading to the formation of a polyurea shell encasing the drops. At subsequent times, B has to diffuse through the growing shell [for systems such as the one in question, A is likely to be insoluble in the polymer (see Pearson and Williams, 1985)] before it can contact A and react at the inner surface of the shell. The polymer swells with the continuous phase as it forms. The reaction ceases when monomer A (assumed to be the stoichiometrically-limiting monomer) is exhausted.

The salient assumptions are as follows:

1. All of the droplets are assumed to have the same radius r_o (at time $t = 0$). Where a size distribution of droplets is involved, the surface-to-volume mean radius may be used in place of r_o.

2. Diffusion of B through the polymer shell and interfacial reaction are the only rate processes considered. External mass transfer rate is likely to be quite rapid in the agitated system being employed. Diffusion of A within the drop is assumed to be rapid enough not to be rate-limiting.

3. Since monomer B can diffuse through the polymer as well as any micropores present in the shell, an effective diffusivity D_B is used to describe its diffusion. D_B is assumed to be independent of shell thickness.

4. The movement rate of the inner boundary due to polymer formation is assumed to be small in comparison with the diffusion rate of B so that, so far as the diffusion of B is concerned, a pseudosteady-state approximation is valid. The applicability of the pseudosteady-state approximation (PSSA) to problems of this type has been discussed at length in the literature on fluid-solid reactions. Bischoff (1963, 1965) concluded that the PSSA could lead to errors if the concentration of the diffusing species was comparable to the molar density of the solid, as in the case of liquid-solid systems. However, a rigorous treatment of the problem requires recognition of the fact that the movement of the boundary results in a convective flux in addition to the diffusive flux. Taking this into account, Lindman and Simonsson (1979) demonstrated that the PSSA, which ignored the transient term as well as the convective term, was a good approximation even in liquid-solid systems, except at very high conversions when the boundary was approaching the center of the sphere. In any event, it is obvious that, under reaction control, the concentration profile of B in the shell being nearly flat, the PSSA should apply well.

5. The polymer is assumed to contain equal moles of A and B.

The interfacial kinetics are assumed to be governed by the second-order rate expression and for a drop, one can write,

$$\frac{1}{4\pi r_i^2}\frac{dn_A}{dt} = k \cdot C_{Ae} \cdot C_{Be} \tag{1}$$

where C_{Ae} and C_{Be} are volumetric concentrations at the inner radius of the shell, r_i, and n_A is the moles of A in the drop at any time t. While a slightly different kinetic form was used by Sirdesai and Khilar (1988), it can be shown that for the conditions of this problem (concentration of HMDI $\ll$ concentration of Butachlor), the two forms are analogous. Both forms are seen in the literature.

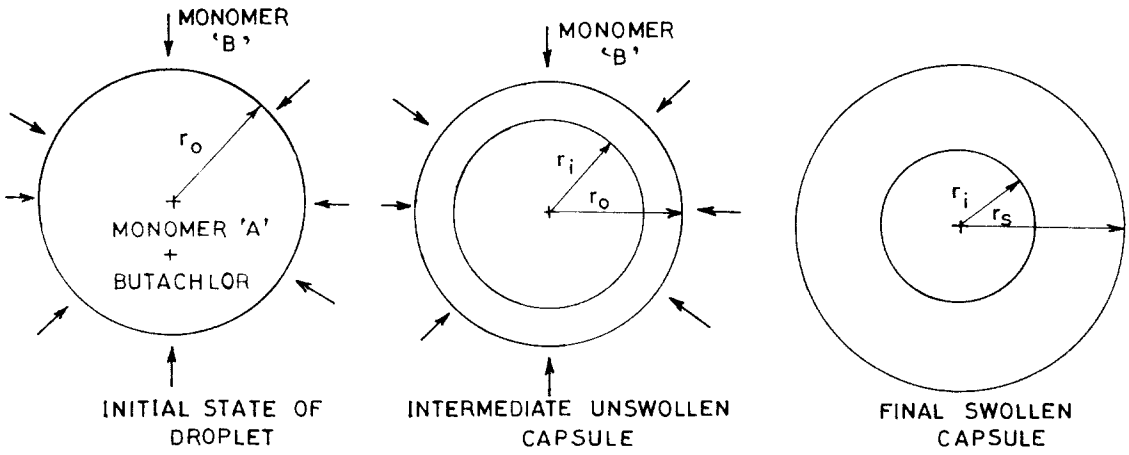

Figure 1. Formation of a microcapsule.

If the original radius of the drop is r_o, diffusion of monomer B through the polymeric shell obeys the following equations at any time t, under the pseudosteady-state assumption.

$$\frac{D_B}{r^2}\frac{d}{dr}\left(r^2\frac{dc_B}{dr}\right)=0 \tag{2}$$

with

$$C_B = KC_{Bs} \quad \text{at} \quad r = r_s$$

and

$$D_B\frac{dc_B}{dr}\bigg|_{r=r_i} = kC_{Ae}C_{Be} \quad \text{at} \quad r = r_i \tag{3}$$

Here, r_s given by

$$r_s = [r_i^3 + \alpha(r_o^3 - r_i^3)]^{1/3} \tag{4}$$

is the outer radius of the forming microcapsule (which differs from r_o because of swelling), α is the swelling factor, C_{Bs} is the concentration of monomer B in the continuous phase, and K is the partition coefficient for monomer B between the continuous and polymer phases. Note that the concentrations of A and B are referred to the phase in which they are present and not to total dispersion volume (Thus, C_B is the kmoles of B per unit volume of the continuous phase etc.).

The above equation can be solved for the instantaneous concentration profile of B in the polymeric shell:

$$C_B = KC_{Bs}\left[\frac{\dfrac{4\pi r_i D_B}{3kn_A}+\dfrac{1}{r_i}-\dfrac{1}{r}}{\dfrac{4\pi r_i D_B}{3kn_A}+\dfrac{1}{r_i}-\dfrac{1}{r_s}}\right] \tag{5}$$

Now this can be used to obtain expressions for the variation of C_{Bs} and r_i with time. Thus, a balance for B in the continuous phase yields,

$$-V_C\frac{dC_{Bs}}{dt} = N\left[4\pi r_s^2\cdot D_B\frac{dC_B}{dr}\right]_{r=r_s}$$

$$(C_{Bs} = C_{Bo} \quad \text{at} \quad t = 0) \tag{6}$$

The growth rate of the polymer shell can be equated to the consumption rate of the reactants:

$$-\zeta_p\cdot 4\pi r_i^2\frac{dr_i}{dt} = -M_A\frac{dn_A}{dt} - \frac{M_B V_C}{N}\frac{dC_{Bs}}{dt} \tag{7}$$

$$(r_i = r_o \quad \text{at} \quad t = 0).$$

Here the moles of monomer B present in the polymer shell has been neglected in comparison with that in the continuous phase since the volume ratio of the latter to the polymer is very large.

We may define a conversion X of B as,

$$X = \frac{C_{Bo} - C_{Bs}}{C_{Bo}}$$

and make use of the stoichiometry of the reaction to write,

$$(V_C/N)C_{Bo}dx = (V_C/N)(-dC_{Bs}) = (-dn_A) \tag{8}$$

From Eqs. 7 and 8 we have a relation between n_A, C_{Bs}, and r_i at any instant:

$$\frac{V_C}{N}C_{Bo}X = n_{Ao} - n_A = \frac{\zeta_p}{M_A + M_B}\frac{4}{3}\pi(r_o^3 - r_i^3) \tag{9}$$

Equation 7, with Eqs. 6 and 8 can now be used to derive the movement rate of the inner boundary which can be integrated to give the time required for any conversion X (at which the position of the inner boundary $r_i(X)$ is given by Eq. 9

$$t_X = \frac{\zeta_p}{M_A + M_B}\left[\frac{4\pi}{3kK}\int_{r_i(x)}^{r_o}\frac{r_i^3}{n_A C_{Bs}}dr_i + \frac{1}{KD_B}\int_{r_i(x)}^{r_o}\frac{r_i}{C_{Bs}}\left(1-\frac{r_i}{r_s}\right)dr_i\right] \tag{10}$$

Equation 10 has been written so that the first integral within the brackets gives the time if the overall rate is controlled by kinetics and the second, if diffusion is the controlling phenomenon. If experimental data happen to fall in either of the two extreme cases, only one of the two rate parameters (k and D_B) is of relevance and can be extracted from a fitting procedure.

Encapsulation kinetics for small shell thicknesses

When shell thicknesses $(r_s - r_i)$ are small relative to the capsule radius, r_s/r_i and $r_o/r_i \longrightarrow 1$ and the following approximations are permissible:

$$\frac{r_i}{r_s} = \left[1+\alpha\left(\frac{r_o^3}{r_i^3}-1\right)\right]^{-1/3} \simeq 1 - \frac{\alpha}{3}\left(\frac{r_o^3}{r_i^3}-1\right) \tag{11}$$

and

$$\frac{r_i}{r_o} = \left[1 - \frac{V_C C_{Bo}(M_A + M_B)}{V_D\zeta_P}X\right]^{1/3} \simeq 1 - \frac{1}{3}\left(\frac{V_C C_{Bo}(M_A + M_B)}{V_D\zeta_P}\right)X \tag{12}$$

The rate equation (Eq. 1) can then be analytically integrated, using Eqs. 5 and 9. The following relationship between time (t) and conversion (X) is obtained.

$$t = -\frac{2}{\beta}X - \frac{3\phi/\beta}{(1-a)(3+ab)}\ln\frac{a-X}{a} - \frac{3\phi + (3+2b)(a-1)}{\beta(a-1)(3+b)}\ln(1-X) + \frac{3}{b\beta}\left(\frac{\phi b^2 + 3(3+ab)}{(3+b)(3+ab)}\right)\ln\left(1+\frac{bX}{3}\right) \tag{13}$$

where

$$\phi = \frac{3D_B\zeta_P V_D^2}{\alpha r_o(M_A + M_B)k(V_C C_{Bo})^2} \tag{13a}$$

$$\beta = \frac{9(KD_B)\zeta_P V_D^2}{\alpha r_o^2 (M_A + M_B) V_C^2 C_{Bo}} \tag{13b}$$

$$b = \frac{V_C C_{Bo}(M_A + M_B)}{V_D \zeta_P} \tag{13c}$$

and

$$a = \frac{N n_{Ao}}{V_C C_{Bo}} \tag{13d}$$

The rate parameters k and D_B are embedded in the groups ϕ and β, which may be estimated by fitting Eq. 13 to experimental conversion-time data by a nonlinear regression procedure.

Case of kinetic control

We may expect kinetic control to prevail when the potential rate of chemical reaction is much smaller than that of diffusion. Recognizing that Kinetic rate (expressed in kmoles of B(or A)/$m^2 \cdot s$) $= k \cdot C_{Ae} \cdot KC_{Bo}(1 - X)$ in the absence of any diffusion resistance and

$$\text{Diffusion flux} = \frac{D_B \cdot KC_{Bo}(1 - X)}{(r_s - r_i)}$$

in the absence of any kinetic resistance, we can derive the following criterion for kinetic control:

$$\phi \gg X(a - X)\left(1 + \frac{2bX}{3}\right) \tag{14}$$

When B is the limiting monomer, the driving force for both rate processes decreases at high conversions, and kinetic control can be assumed over the whole encapsulation period only if Eq. 14 is valid at $X = 1$. Under these conditions, the conversion-time relationship simplifies to,

$$t = \frac{r_o}{(Kk)C_{Bo}}\left[\frac{1}{(a-1)(3+ab)}\ln\frac{a - X}{a} - \frac{1}{(a-1)(3+b)}\ln(1 - X) + \frac{b}{(3+b)(3+ab)}\ln\left(1 + \frac{bx}{3}\right)\right] = \left(\frac{r_o}{KkC_{Bo}}\right) \cdot Y \tag{15}$$

The quantity within brackets on the righthand side, Y, can be calculated and plotted against t, and the interfacial reaction rate constant k can be calculated from the slope of the resulting straight line.

Case of diffusion control

The rate-controlling phenomenon will be diffusion if

$$\phi \ll X(a - X)\left(1 + \frac{2bX}{3}\right) \tag{16}$$

All encapsulation processes are kinetically-controlled at $t = 0$, as Eqs. 14 and 16 show, since no polymer shell has formed to offer a diffusional resistance. Depending on the value of ϕ, a process may subsequently become limited by diffusion, if the inequality in Eq. 16 is satisfied. If a process can be said to be definitely diffusion-controlled beyond a conversion X_o, the conversion-time relationship for $X > X_o$ is given by,

$$t = \frac{1}{\beta}\left[-2(X - X_o) + \left(\frac{3 + 2b}{3 + b}\right)\ln\frac{1 - X_o}{1 - X} + \frac{9}{(3+b)b}\ln\frac{\left(1 + \frac{bX}{3}\right)}{\left(1 + \frac{bX_o}{3}\right)}\right] \tag{17}$$

As with Eq. 15, Eq. 17 can be used to recover the value of the rate parameter under conditions of diffusion control.

It may also be noted from Eqs. 15 and 17 that, the time required for a definite conversion is proportional to the drop radius r_o in the case of kinetic control and proportional to r_o^2 in the case of diffusion control.

Experimental Studies

Experiments to produce polyurea microcapsules encapsulating Butachlor were conducted essentially using the procedures developed by Beestman and Deming (1983). Two major measurements were done in this experimental work—the concentration of HMDA in the continuous phase (which can then be related to the extent of encapsulation), and the size of the microcapsules. The details of these two measurements are briefly presented in a later part of this section.

Materials used

- *Butachlor:* purity > 90% (supplied by Sudarshan Chemical Industries, India)
- *Hexamethylene-1,6-diisocyanate (HMDI):* purity > 95% (supplied by Fluka, Switzerland)
- *Hexamethylene-1,6-diamaine (HMDA):* purity > 99% (supplied by E. Merck)
- *Sodium lignosulfonate:* obtained by evaporation of black liquor from paper mill

Procedure

In a typical experiment, 1 g of sodium lignosulfonate was mixed with 100 mL of water in a glass beaker using a glass agitator with propeller-type blades. This formed the aqueous phase. The organic phase was prepared by mixing 2 g of HMDI monomer in 50 g of butachlor. This organic phase was then dispersed in the aqueous phase taken in a 1-L beaker, by using a high-speed blender (Remi Motors Ltd., Model L 56-3 of 1 hp (0.746 kW) and 8,000 rpm, provided with a shrouded, four-blade pitched turbine agitator). The speed of the agitator was kept constant and measured by a digital tachometer. After about 30 minutes of agitation, the speed was reduced and simultaneously 0.35g of HMDA was added to the aqueous phase. Time was reckoned from the instant of addition. The pH of the continuous phase was monitored by a pH electrode (immersed before HMDA addition) and a pH meter (Phillips, India, Model PP 9046). Since HMDA forms a basic solution in water, the pH

rose to a value of approximately 11.0 when HMDA was added and then decreased gradually as HMDA was consumed by the reaction. Temperature was maintained at 30°C during the encapsulation process. The size distribution of the capsules were measured by using a Coulter counter. These procedural steps were repeated for all experiments.

Measurement of time of encapsulation

A measurement technique for time of encapsulation can be based on either monitoring the thickness of polyurea shell or monitoring the concentration of one of the monomers. Measurement of the thickness of the inwardly growing shell, as well as the concentration of HMDI in the droplet phase, is rather difficult. Therefore, a technique can be based on measuring the concentration of HMDA in the continuous phase. There is, however, no simple technique to measure the concentration of HMDA on-line. These considerations led us to use the present technique of pH measurement of the continuous phase. The pH can be related to the concentration of HMDA. These concentration vs. time data can be used to obtain a time of encapsulation. In the scheme proposed by Beestman and Deming (1983), HMDI is the stoichiometrically-limiting monomer, and HMDA is in large excess. Therefore, the concentration of HMDA and hence the pH of continuous phase vary but little during the course of encapsulation and conversion measurement would be subject to large error. Hence the recipe suggested by Beestman and Deming (1983) was modified to make monomer *B* (HMDA) the stoichiometrically-limiting one, while keeping the total quantity of polymer formed the same.

Figure 2 shows the typical variation in pH of the continuous phase during the encapsulation process. In this case, the concentration of HMDA varied from 0.03 kmol/m^3 to a very low value. One observes from the figure that pH decreases considerably, from a value of about 11 to about 7.6. These pH values were converted to concentration of HMDA by the following procedure. For solutions of HMDA in deionized water, consideration of ionic equilibria for HMDA leads to a relation between concentration and pH. Such calculations show that the pH would be expected to vary from 11.66 to 7 as the HMDA concentration varies from 0.03 M to 0.0 (Yadav, 1988). Actual measurements of pH in different solutions of HMDA, with the emulsifier and Butachlor also added in the amounts used in the experiments (HMDI was left out in order to eliminate the possibility of reaction), gave a pH-C curve very similar in form to the theoretical curve, but the measured pH's were always lower than the calculated ones. This was thought to be due to small levels of dissociating impurities. The theoretical calculations were therefore modified to account for the following equilibrium in addition to those of HMDA:

$$BH \rightleftharpoons B^- + H^+; \qquad K_B = \frac{(C_B^-)(C_H^+)}{C_{BH}}$$

Here *BH* is an unknown impurity. Thus, the effect of the sum total of ionic equilibria, other than those of HMDA and H_2O, is lumped in K_B and the concentration C_I of the impurity. The resulting theoretical equation could be fitted very well to the experimental data by using a nonlinear parameter estimation routine and C_I and K_B were estimated. This calibration equation was used to convert pH to concentration. To account for small differences in the initial pH (which should be a constant in every case) between experiments which sometimes existed, the concentration C_I was calculated from the initial pH (pH at time 0) in every run. Figure 3 shows the theoretical curve for pure HMDA solutions as well as the modified calculations and experimental data for the actual system used in the experiments.

Measurement of capsule size

The size of microcapsule was measured by means of a Coulter counter. An aqueous electrolyte solution containing 1.8×10^{-4} kmol of sodium chloride was used. A drop of Coulter dispersant was used to disperse the sample. An orifice tube of 100 μm was used in the measurement.

It is found that the size of the microcapsules produced ranges from 1 to 20 μm.

A standard extrapolation procedure based on logarithmic linearity between the particle diameter and the corresponding volume of the microcapsules was used to obtain counts for particle diameters of 2 to 1 μm.

The discrete capsule-size distribution data were then used to calculate a pertinent mean capsule size. It is discerned that surface to volume mean size (Sauter mean) would be more appropriate to relate the size with time of encapsulation. Table 1 presents the surface to volume mean size measured in different experimental runs. In this set of runs (R1 to R8) which also

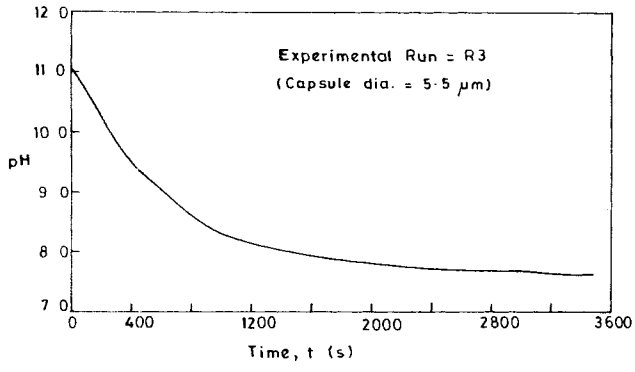

Figure 2. Typical variation in pH during encapsulation.

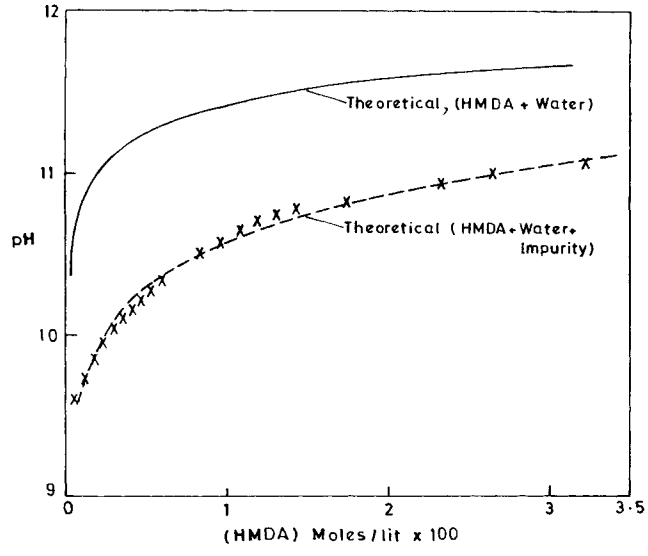

Figure 3. pH concentration of HMDA relationship.

Table 1. Surface to Volume Mean Capsule Size

Run No.	Surface to Vol. Mean Capsule Dia. (μm)	Time of Encapsulation (to $X_{(\bar{s})}$95%)	Reaction Constant (K)
R1	5.8	250	2.09×10^{-7}
R2	3.6	150	1.73×10^{-7}
R3	5.5	305	1.37×10^{-7}
R4	5.2	180	
R5	3.8	250	1.27×10^{-7}
R6	2.9	240	1.17×10^{-7}
R7	5.3	230	2.00×10^{-7}
R8	2.2	180	

includes repeats, only rpm of the agitator was varied from 200 to 3,000. In general, it is found that higher rpm produced, lower capsule size. Since the rpm could not be measured accurately, it is not reported. The other entries of the Table 1, on time of encapsulation for 95% conversion and reaction constant will be discussed later.

Results and Discussion

While it was not possible to maintain the conditions of emulsification strictly constant in all the experiments, since the sizes of the capsules produced were directly measured, this was of minor consequence. It appeared, however, that the drop (and hence the final capsule) diameters were quite insensitive to the stirrer speed at the emulsifier concentrations used and the particles obtained were roughly of the same size range in all experiments (1 to 20 μm) in spite of the stirrer speeds being quite different. The initial concentrations of the two monomers, C_{Ao} and C_{Bo}, were 0.15 and 0.0302 kmol/m^3 in all experiments. The swelling factor α for a similar polymer has been reported as 1.6 by Pearson and Williams (1985). Typical values of the interfacial reaction rate constant and diffusivity may also be calculated from the data in literature. Thus the work of Pearson and Williams (1985) suggests a value of 1.04×10^{-7} m^4/kmol · s for the rate constant consistent with Eq. 1. While their work was on the reaction between a polyether diol and a polyfunctional isocyanate (functionality 2.2), the rate constant for the present system is likely to be of the same order. A typical value for the diffusivity of a molecule such as HMDA through a swollen polymer would lie in the range 10^{-12}–10^{-15} m^2/s (Crank and Park, 1968). Accounting for possible pinholes in the polymer shell, we may anticipate a value of 10^{-10}–10^{-14} for the effective diffusivity of HMDA through the shell. The density of the polymer, ζ_p, was taken as 1,000 kg/m^3.

A value for ϕ may be calculated and inequality (Eq. 14) checked for the above values of the parameters. Corresponding to the minimum and maximum value of D_B above, value of ϕ would be expected to lie in the range 61 to 6.1×10^5 for a capsule of 6 μm diameter. The righthand side in Eq. 14 has a maximum value of about 4 (at $X = 1$). Therefore, we may expect that the conditions employed in our experiments are such that kinetic control prevails throughout.

In Figure 4 are plotted the values of the time taken for 95% conversion as a function of the capsule radius (surface to volume mean). The range of capsule sizes covered is small and the scatter is large, but a tendency for linearity is discernible. Since capsule-size measurements are made on extremely small sample sizes, getting a representative sample poses problems and errors

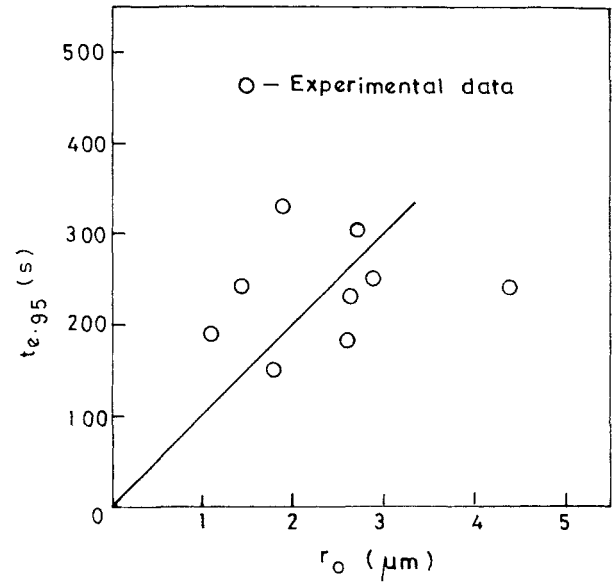

Figure 4. Encapsulation time based on 95% conversion vs. surface to volume mean capsule size.

in the measured size are likely to be large. The extrapolation technique could also introduce some errors. Hence, a much wider range of particle sizes needs to be covered than has been possible in this work to establish conclusively the dependence of time on size.

Conversion-time data were fitted to Eq. 13 (which makes no assumptions about the controlling regime), and the values of ϕ and β that gave the best fit were estimated using a nonlinear parameter estimation package. It was observed that Eq. 13 fitted the data quite well. However, while the values of (kK) estimated were within a narrow range, the fit was insensitive to the value of KD_B used, over a few orders of magnitude, thus again suggesting that kinetics was the rate-controlling phenomenon.

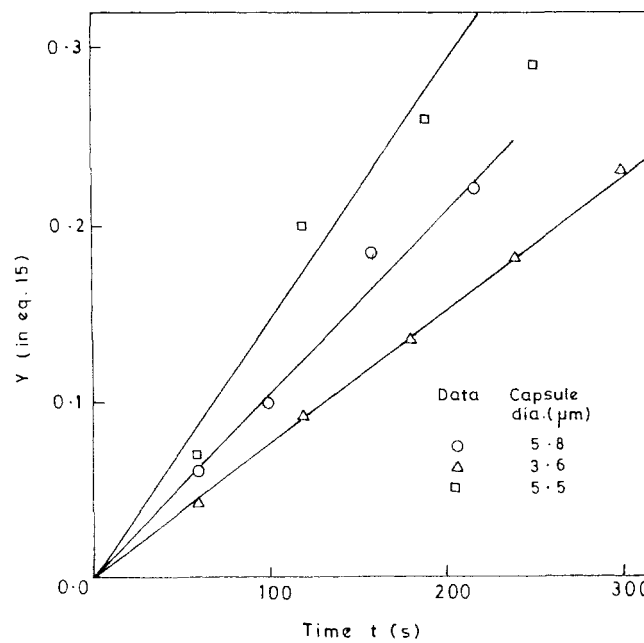

Figure 5. Plots of Eq. 15 showing kinetic control.

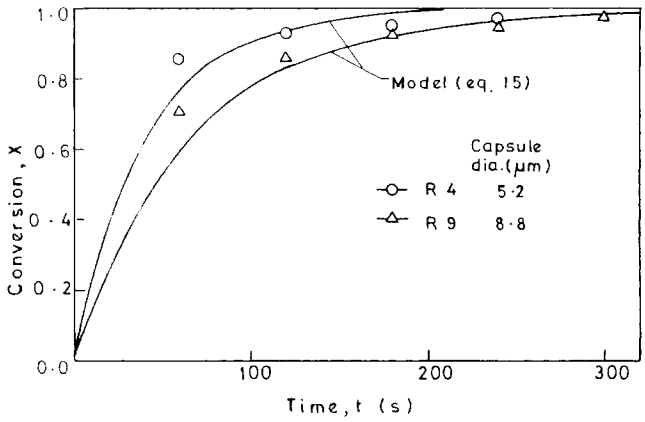

Figure 6. Predictions of Eq. 15 vs. experimental data.

Finally, the data were plotted as suggested by Eq. 15 for kinetic control. These plots, of which three are shown in Figure 5, showed a satisfactory linearity in most cases. The values of (Kk) calculated from the slopes of these lines using the measured Sauter mean diameter are tabulated in Table 1. The limitations of the pH technique for following the process and the problems explained above in measuring the proper size of microcapsules are probably responsible for the spread of values in Table 1. The value of Kk is estimated at around 1.2×10^{-7}–2×10^{-7} m^4/kmol · s. If K, the partition coefficient, is estimated assuming that the phase which swells the polymer is the same as the continuous phase [$K = (\alpha - 1)/\alpha = 0.375$], a value of 3.2×10^{-7}–5.3×10^{-7} m^4/kmol · s is obtained for the rate constant, which is of the same order as reported by Pearson and Williams (1985) for a similar system.

Figure 6 shows some simulations of the conversion-time behavior using Eq. 15 and their comparison with experimental data. A value of 1.6×10^{-7} m^4/kmol · s for Kk (average of the values in Table 1) has been used in the simulation. Reasonable agreement is seen between the simulations and data.

Conclusions

Following conclusions emerge from this study:

1. A mathematical model based on diffusion of HMDA in polymeric shell with interfacial reaction can be used to study the dynamics of the microencapsulation of Butachlor in polyurea shell by means of interfacial polymerization.

2. Time of encapsulation can be estimated by monitoring the pH of the continuous phase. This technique is, however, limited to cases where the continuous-phase monomer decreases by more than tenfold in the concentration range below 0.03 kmol · m^{-3}.

3. It is shown both experimentally and theoretically that time of encapsulation depends on the size of the microcapsule. It is approximately proportional to the size in the kinetically-controlled regime while it is proportional to the square of size in the diffusion-controlled regime.

4. It is found, under the conditions studied, that microencapsulation in a very thin polyurea shell is a kinetically-controlled process. The rate of the interfacial polycondensation reaction has been estimated to be 3.2×10^{-7}–5.3×10^{-7} m^4/kmol · s.

5. The capsule size is weakly dependent on the rpm and, in most cases, the capsule sizes vary from 1 to 20 μm.

6. Time of encapsulation based on 95% conversion of continuous-phase monomer varies from 150 to 300 s for surface to volume mean capsule size ranging from 2.2 to 5.8 μm.

Acknowledgment

One of the authors, KCK, thanks the members of the PAC on Chemical Engineering constituted by DST, New Delhi, for fostering his initial interest in this subject of encapsulation of agrochemicals.

Notation

a = defined in Eq. 13d
A = hydrophobic monomer, HMDI
B = hydrophobic monomer, HMDA
b = defined in Eq. 13c
C_A = concentration of monomer A in the liquid core at any time t, kmol · m^{-3}
C_{Ao} = initial concentration of monomer A in the liquid core, kmol · m^{-3}
C_{Ae} = concentration of monomer A at the inner radius of the shell, kmole · m^{-3}
C_B = concentration of monomer B in the polymer shell, kmol · m^{-3}
C_{Be} = concentration of monomer B at the reaction zone, kmol · m^{-3}
C_{Bs} = concentration of monomer B in the bulk solution, kmol · m^{-3}
D_B = effective diffusivity of monomer B, m^2 · s^{-1}
k = overall second-order reaction rate constant, m^4 · kmol^{-1} · s^{-1}
K = partition coefficient of monomer B between aqueous and polymer phase
M_A = molecular weight of monomer A, kg · kmol^{-1}
M_B = molecular weight of monomer B, kg · kmol^{-1}
n_A = moles of monomer A in a drop, kmol
N = number of drops in the system
r = any radius of shell between r_i and r_s at time t, m
r_i = inside radius of capsule at any time t, m
$r_f(X)$ = inside radius of capsule at any conversion X, m
r_o = initial outside radius of capsule, m
r_s = outside radius of capsule at any time t, m
t_e = time of encapsulation, s
t_x = time required for a conversion X, s
V_c = volume of the continuous phase, m^3
V_D = volume of the dispersed phase, m^3
X = fractional conversion of monomer B
Y = function of conversion defined in Eq. 15

Greek letters

ζ_p = density of polyurea formed, kg · m^{-3}
α = volumetric swelling factor
β = defined in Eq. 13b
ϕ = defined in Eq. 13a

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Manuscript received May 12, 1989.