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Removal of Residual Monomers from Polymer Emulsions by Steam Stripping

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ABSTRACT

Removal rates of residual monomers from polymer emulsions by batch steam stripping were modeled. Model parameters were emulsion batch charge, steam sparge rate, emulsion solids content, and phase–equilibrium relationships for systems containing monomer, polymer, and water. Experiments in which steam was sparged into a column partially filled with emulsion were performed to verify the model. The model and data showed good agreement. Theory and experiments demonstrated that monomer desorption was dependent upon steam sparge rate and solids content, whereas temperatures had little effect on monomer removal.

INTRODUCTION

Emulsion polymerization is a predominant process for manufacturing acrylic copolymers, SBR (styrene-butadiene rubber), polyvinyl acetate, and other radical-chain-based polymers. Emulsion polymerization is advantageous over other reaction routes because (i) viscosities of polymer emulsions are relatively low which facilitates processing, (ii) water acts as a diluent for removing heats of reaction, (iii) the latex product itself can sometimes be sold as a product, and (iv) the small size of emulsion particles allows low residual monomer levels to be attained.

Even low levels of unreacted monomer in the final product, however, can pose problems. Residual levels of monomers can prevent the entry of polymer into markets where organoleptic properties are important. The loss of unreacted monomer during isolation of the polymer can represent a significant yield loss over time. Finally, regulations restricting releases of volatile organic compounds into the environment during isolation are becoming more stringent.

Steam stripping is one means of removing residual monomers from polymer emulsions. The steam stripping of emulsions is similar to devolatilizing solutions except that emulsions consist of two phases: an aqueous phase and a polymer (solid) phase. Because of this added complexity, no methods for predicting monomer removal rates during steam stripping currently exist. Englund (1) and Omi et al. (2) both predict that the concentration of monomer in an emulsion changes by a first-order relationship when a constant steam sparge rate is used. The removal-rate constants, however, must be determined empirically by experiments. This paper will show how residual monomer removal rates can instead be determined from readily obtainable thermodynamic properties.

THEORY

Consider the sparged system shown in Fig. 1. A species balance on the system can be written as

$$\frac{d}{dt}\left(\frac{zS}{M_A} + \tilde{x}\tilde{L}\right) = -\tilde{G}\tilde{y} \tag{1}$$

where $\tilde{G}$ = sparge rate of steam, kgmol/s
$\tilde{L}$ = moles liquid in vessel, kgmol
M_A = molecular weight of monomer, kg/kg·mol
S = mass solids (polymer) in vessel, kg
t = time, seconds
$\tilde{x}$ = mole fraction monomer in liquid phase
$\tilde{y}$ = mole fraction monomer in vapor phase
z = mass fraction monomer in the polymer phase

The diameter of an emulsion solid particle is on the order of 100 nm and the diffusivity of the monomer in the polymer phase is of the order of 10^{-10} cm^2/s. Hence, there is little resistance to mass transfer in the polymer phase. Diffusion out of the polymer and into the liquid is very rapid, and we can assume that the solid and liquid phases are at equilibrium. The diffusion rate of monomer through the aqueous phase depends

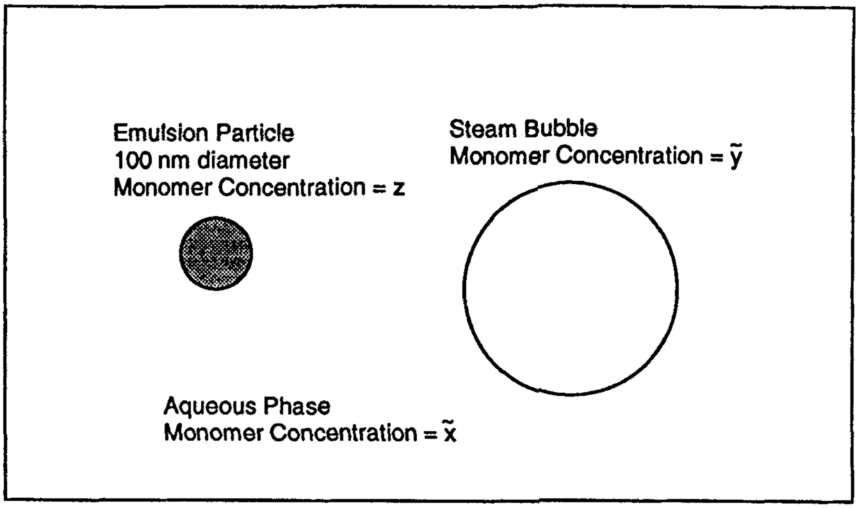

FIG. 1 System containing emulsion with steam sparge.

primarily upon how far the hydrocarbon molecules must travel through the water and how much interfacial area exists between the liquid and vapor phases. If our sparged system is sufficiently mixed and it is at its boiling point, we can also assume that equilibrium exists between the liquid and vapor phases. We introduce the following equilibrium relationships:

$$\tilde{y} = (H/P)\tilde{x} \tag{2}$$

$$z = Kx \tag{3}$$

where H = Henry's law coefficient for monomer in water, Pa
K = distribution coefficient for monomer between polymer and liquid phases = z/x
P = system pressure, Pa

Equation (2) is Henry's law which is valid for low levels of monomer in the aqueous phase. Equation (3) assumes that the relationship between monomer concentration in the polymer phase of an emulsion and its concentration in the liquid phase is linear. The distribution coefficient K is a ratio of liquid-phase to solid-phase activity coefficients modified to give a mass basis. Substituting Eqs. (2) and (3) into Eq. (1) yields

$$\frac{d}{dt}\left(\frac{zS}{M_A} + \frac{z\tilde{L}M_L}{M_A K}\right) = -\frac{\tilde{G}HM_L z}{KPM_A} \tag{4}$$

where M_L is the liquid-phase molecular weight. For low monomer levels, H and K are independent of monomer concentration, and Eq. (4) can be rewritten as

$$\frac{1}{z}\frac{dz}{dt}\left(S + \frac{L}{K}\right) = -\frac{G(H/P)M_L}{KM_G} \tag{5}$$

where M_G is the molecular weight of the gas phase. For low levels of monomer, M_G and M_L are both nearly equal to the molecular weight of water, and the terms cancel. After simplifying, Eq. (5) can be integrated to give

$$\ln\left(\frac{z}{z_0}\right) = -\frac{G(H/P)t}{KS + L} \tag{6}$$

where the subscript 0 denotes the initial monomer concentration. It is convenient to rewrite Eq. (6) in terms of the emulsion charge in kilograms, E, and the emulsion solids content, X. With

$$S = XE \tag{7}$$

and

$$L = (1 - X)E \tag{8}$$

the denominator of Eq. (6) can be rewritten as

$$KS + L = E[X(K - 1) + 1] \tag{9}$$

Substitution of Eq. (9) into Eq. (6) gives

$$\ln\left(\frac{z}{z_0}\right) = -\frac{G(H/P)t}{E[X(K - 1) + 1]} \tag{10}$$

Equation (10) shows that the rate of monomer removal is a function of the steam sparge rate, the emulsion solids content, the batch charge of emulsion, and the phase equilibria of the three-phase system. Because the phase relationships are linear, it is also true that

$$\ln\left(\frac{w}{w_0}\right) = -\frac{G(H/P)t}{E[X(K - 1) + 1]} \tag{11}$$

where w is the mass fraction of monomer in the emulsion.

PHASE EQUILIBRIA

An acrylic copolymer based on methyl methacrylate (MMA) and ethyl acrylate (EA) was used in this study. Henry's law constants and polymer–liquid phase distribution coefficients for acrylic monomers determined from in-house data and regressions are shown in Figs. 2 and 3, respectively.

For stripping calculations it is convenient to define a linear equilibrium relationship between the concentration of a volatile compound in the vapor phase and its concentration in the condensed phase. Such a relationship is valid for residual levels of monomers and is given by

$$y = mw \tag{12}$$

where

$$m = \frac{(H/P)}{[X(K - 1) + 1]} \tag{13}$$

While it is relatively easy to remove volatile organic compounds from water by steam stripping, removing organics from polymer emulsions is much more difficult. This can be seen in Fig. 4 where the slope of the equilibrium line is plotted against temperature for MMA in water and

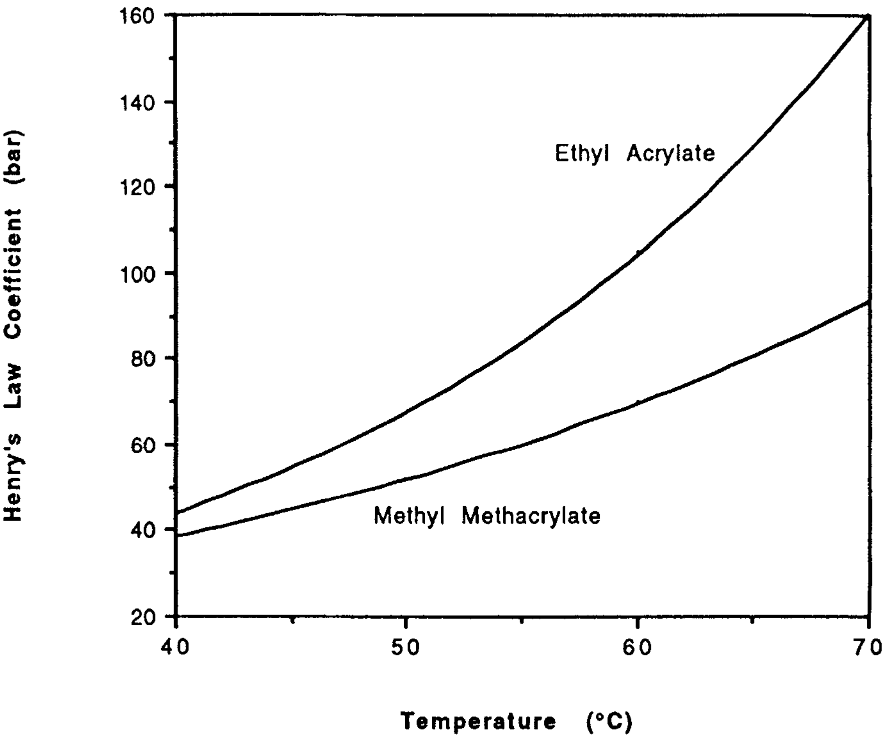

FIG. 2 Henry's law coefficient for acrylic monomers in water.

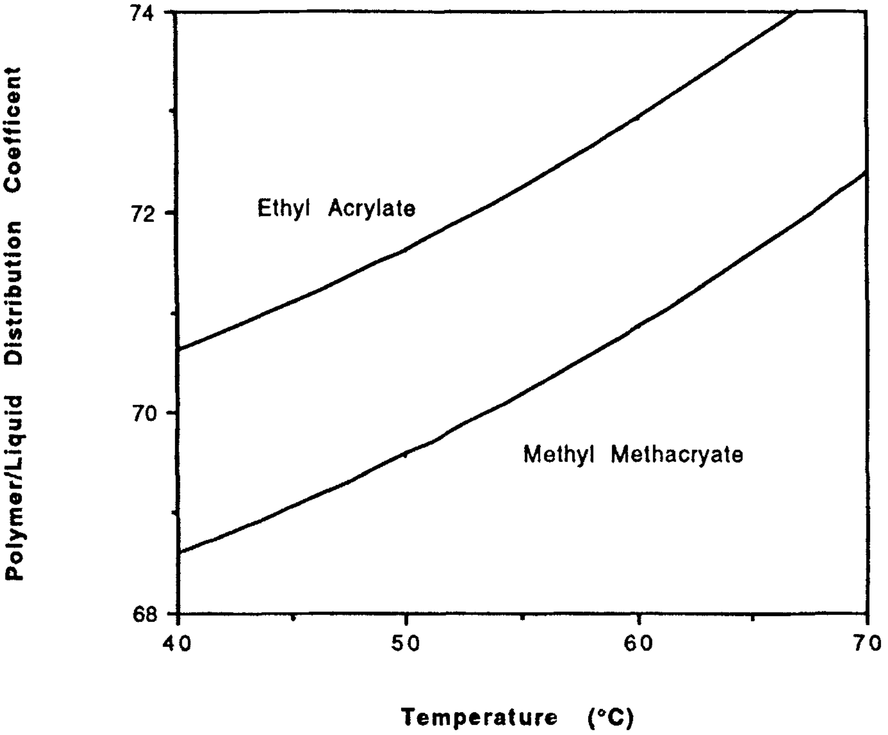

FIG. 3 Distribution of MMA and EA between acrylic copolymer and water.

for MMA in an emulsion containing 50% acrylic copolymer. Because the monomer prefers the polymer phase over the aqueous phase by about 50:1, its vapor-phase partial pressure is greatly reduced. In addition, we see that the slope of the equilibrium line is much less dependent on temperature. Conditions that make it more favorable for the monomer to occupy the vapor phase also cause the equilibrium monomer content in the polymer to increase. Monomer removal rates during vacuum steam-stripping are thus expected to be independent of temperature.

EQUIPMENT

Figure 5 is a schematic of the experimental apparatus used in this study. The apparatus consisted of a 100-mm diameter, 1.2-m tall glass column equipped with an agitator and baffles, a condenser, a steam generator and sparger, a sampling bomb, and a vacuum pump. The lower portion of the

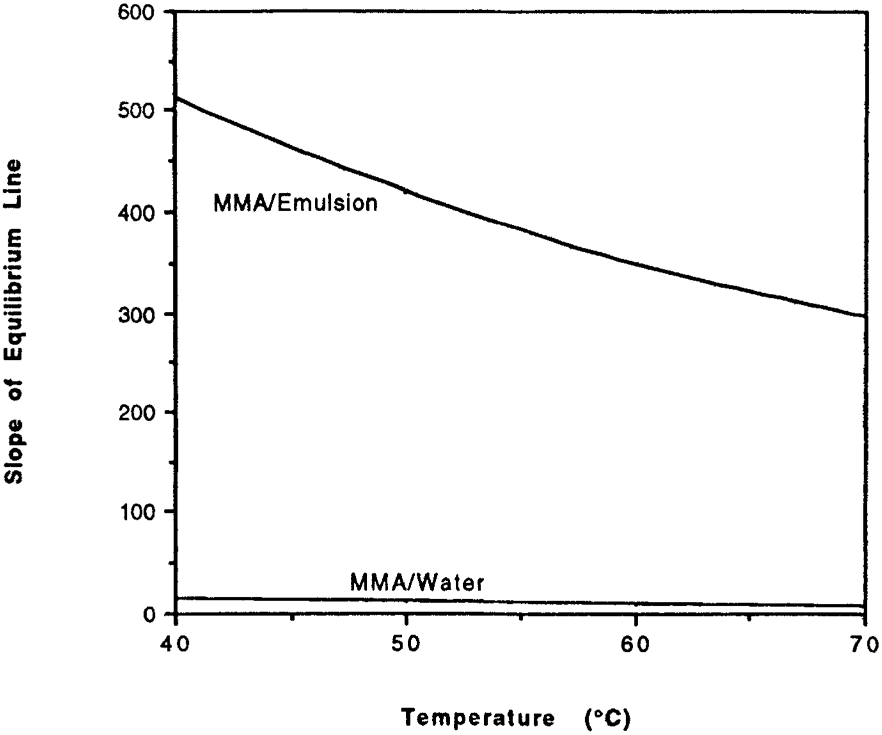

FIG. 4 Phase equilibria of MMA/water/acrylic copolymer.

column which contained the emulsion was jacketed so that water from a constant-temperature bath could be used for temperature control. Steam was sparged into the emulsion through a perforated metal ring at the base of the column. The baffles were constructed of four 12-mm wide strips of stainless-steel metal supported by a Teflon frame. A thermocouple extending into the emulsion measured its temperature during the experiments. A short length of rubber tubing immersed into the emulsion was connected to a sampling assembly which consisted of an evacuated glass bomb affixed with three glass stopcocks used for isolating and venting the assembly.

Outside the column, steam was generated by pulling deionized water through a rotameter and metering valve into a heated copper coil and a heated length of aluminum tubing. The source of heat was electrical heating tape controlled by variable power supplies. Steam flowed through a series of valves which directed the steam either to the steam sparger or

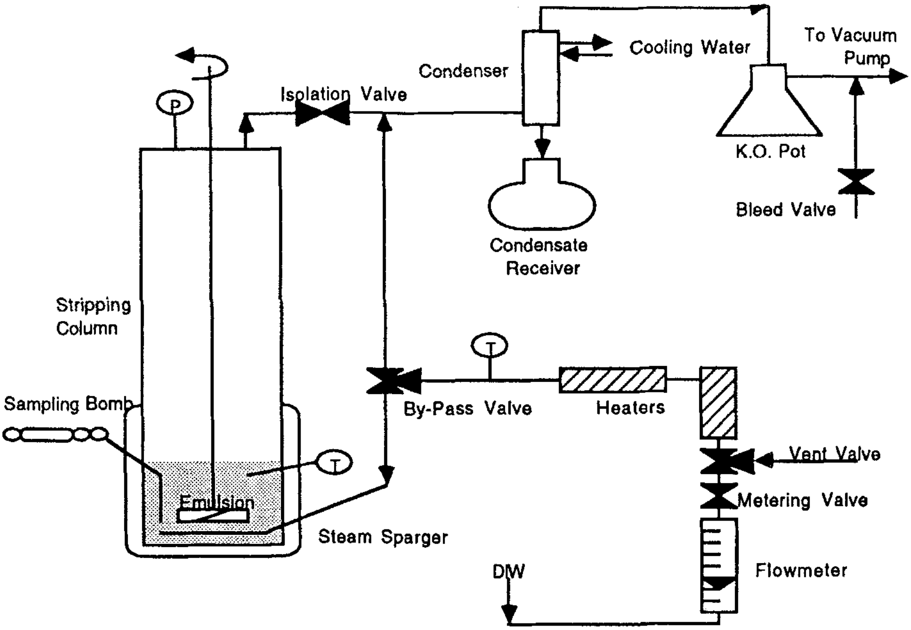

FIG. 5 Batch steam-stripping apparatus.

directly to the condenser. Feeding the steam to the condenser served as a bypass during start-up.

Two necks protruded from the top of the column on either side of the agitator motor. One was connected to the pressure transducer, and the other connected the column to the condenser. The vacuum pump was connected by way of a knock-out pot and bleed valve to the condenser. The bleed valve was used for pressure control.

PROCEDURE

For our experiments, a commercial acrylic copolymer emulsion was used. Experiments were conducted by first diluting the emulsion with deionized water to the desired solids content. Next, 1500 g of the diluted emulsion was transferred to the column. Approximately 3 g silicone emulsion was added to the column contents to minimize foaming during sparging.

To begin the experiment, the bypass valve was opened to allow steam to be generated at the setpoint temperature and flow rate. At the same time, the emulsion was heated to the desired temperature by feeding hot water to the jacket of the column. After the desired temperatures and rates were met, a valve was opened to pull vacuum on the column. Once the initial entrained air was desorbed and the temperature had returned to the setpoint, steam was directed to the sparger, and an initial sample was taken. Samples were obtained by withdrawing 1 g emulsion into an evacuated sampling bomb. Emulsion samples were analyzed for monomer content by capillary headspace gas chromatography.

DISCUSSION

Equation (11) predicts that monomer removal from a polymer latex depends on steam sparge rate and solids content. As suggested by the equilibrium line plotted in Fig. 4, desorption is expected to be nearly independent of temperature. Three sets of experiments were performed to validate the model.

During the first set of experiments, emulsion solids and temperature were kept constant, and the steam sparge rate was varied. During the second set, the sparge rate and temperature were kept the same, and emulsion solids were varied. In the final set of experiments, the sparge rate and solids content were kept constant, and the process temperature was changed. In all experiments the operating pressure was the saturation pressure of the emulsion (i.e., the bubble point of the liquid phase).

In Figs. 6 and 7, MMA and EA emulsion contents (w/w_0), respectively, are plotted against time. Also shown are monomer levels predicted by theory (Eq. 11). The data and theory concur. As expected, the rate at which EA and MMA were removed increased when the steam-sparge rate was increased. When steam is introduced into the emulsion, volatiles are driven into the vapor phase until equilibrium is reached. With higher steam-sparge rates, higher amounts of monomer must transfer to the vapor in order for equilibrium to be attained.

Figures 8 and 9 show the effect of emulsion solids content on devolatilization of MMA and EA, respectively. Plotted are experimental data along with predicted results. As predicted by the model, the desorption rate for monomers from polymer latex increases as the emulsion solids level is lowered. Again, monomers are driven by thermodynamic equilibrium into the vapor phase when steam is introduced. However, the organics also have an affinity for the polymer phase. As the emulsion solids level increases (i.e., contains more polymer), less monomer must transfer to the vapor phase to reach equilibrium. Omi et al. (2) also noted the latex-solids-concentration dependence in their work with styrene-butadiene rubber (SBR) and polystyrene emulsions.

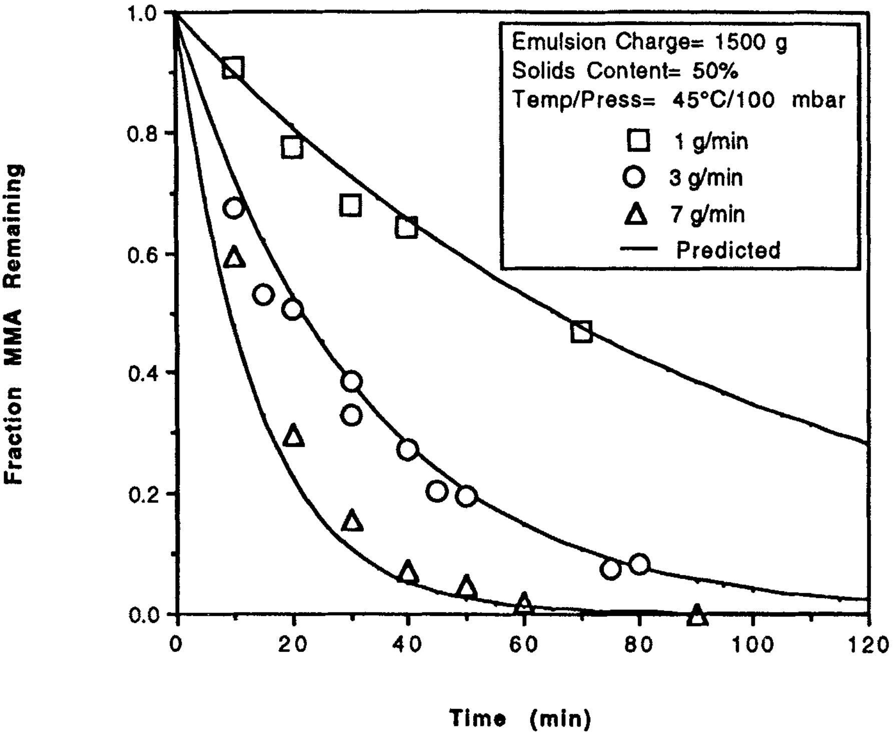

FIG. 6 Effect of steam sparge rate on MMA removal.

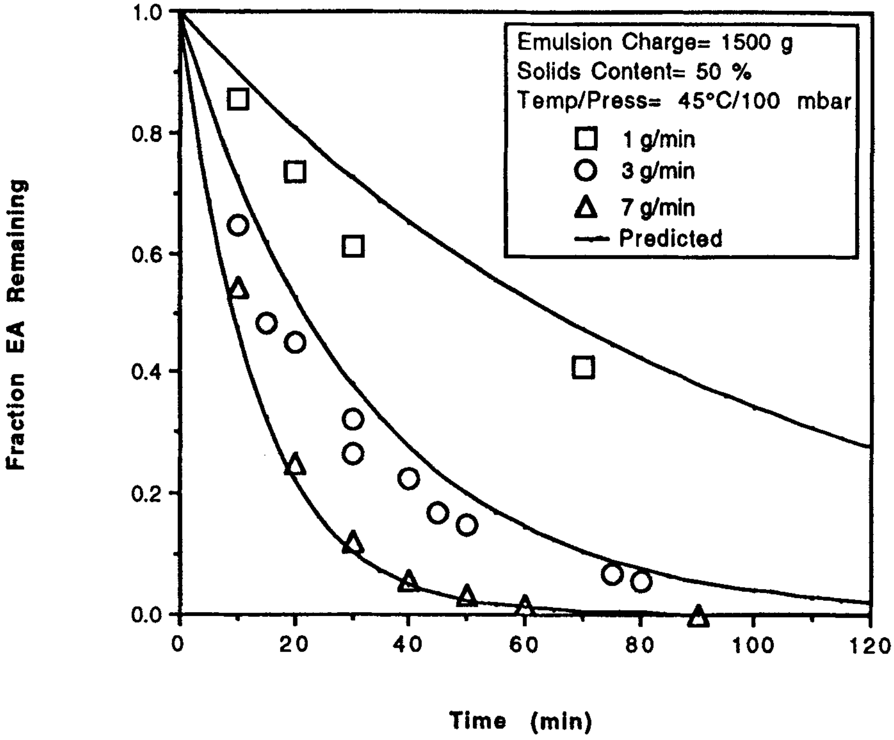

FIG. 7 Effect of steam sparge rate on EA removal.

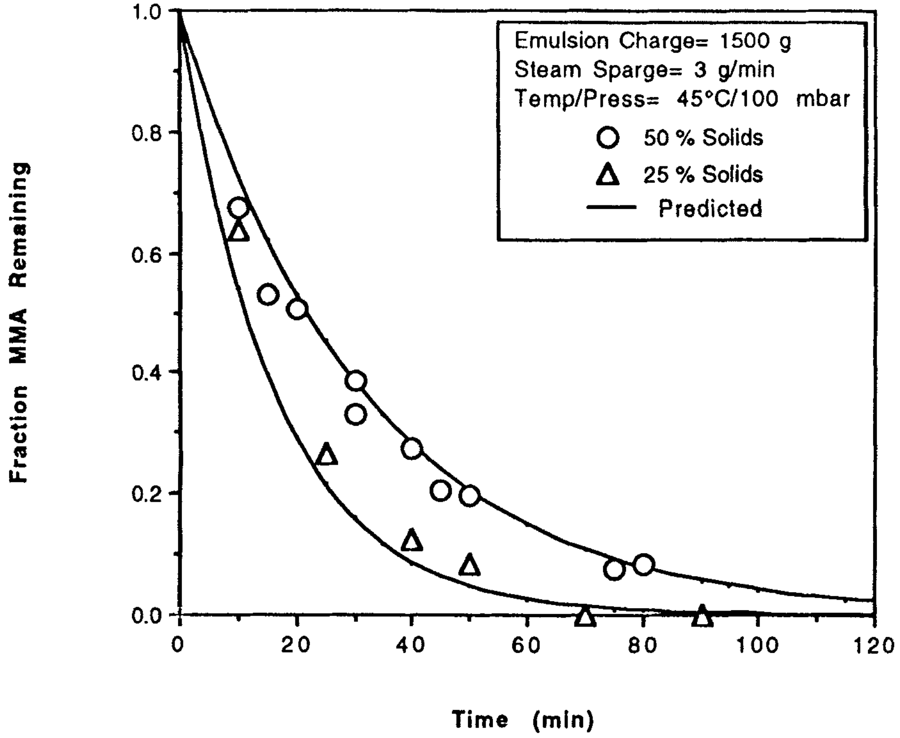

FIG. 8 Effect of solids content on MMA removal.

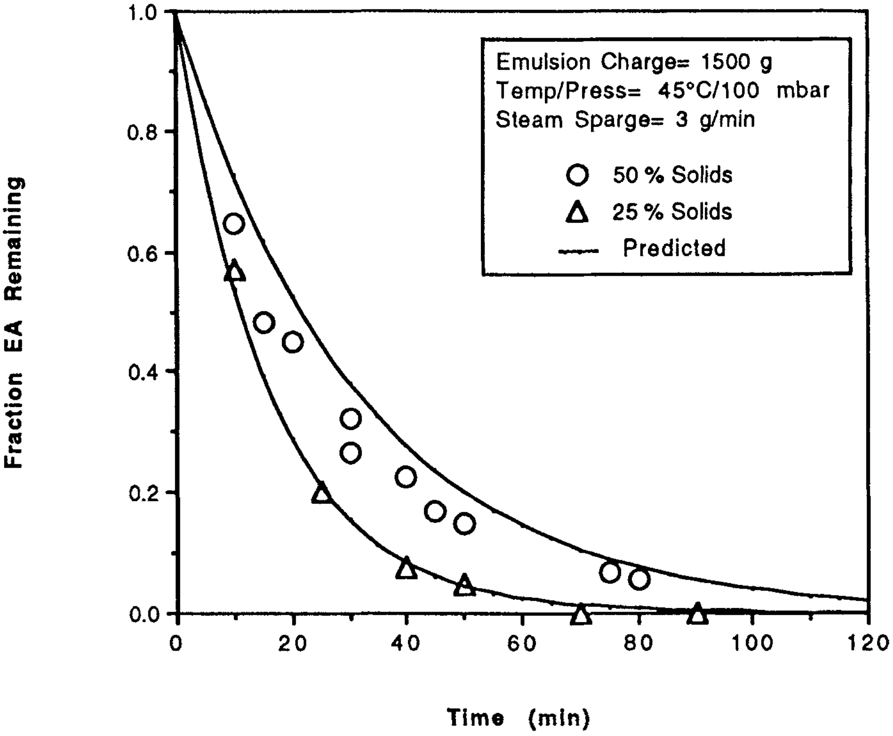

FIG. 9 Effect of solids content on EA removal.

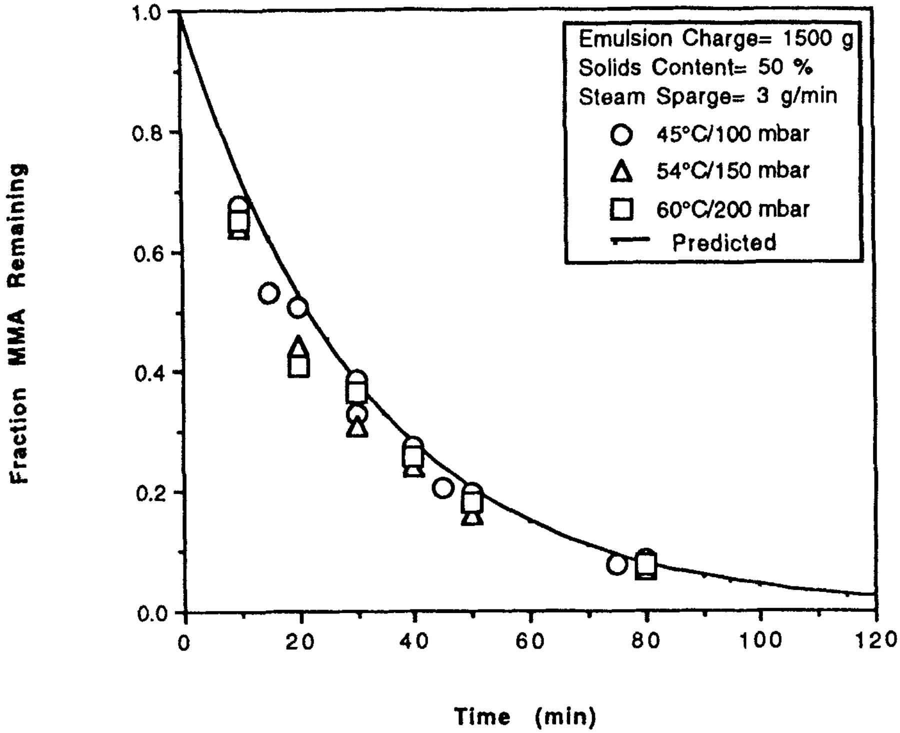

FIG. 10 Effect of temperature on MMA removal.

Figures 10 and 11 compare MMA and EA desorption data, respectively, with predicted results for different operating temperatures. The theory and data both show that temperature has only a negligible effect on monomer removal rate. For systems containing polymer, water, and monomer, the phase behavior is not greatly affected by changes in temperature (see Fig. 3). Hence, changes in temperature have a minimal effect on monomer removal by steam stripping. This was also observed by Englund (1) and Omi et al. (2) for systems containing SBR emulsions.

CONCLUSIONS

Equation (11) predicts monomer removal from polymer emulsions during batch stream stripping. It shows that monomer removal is enhanced

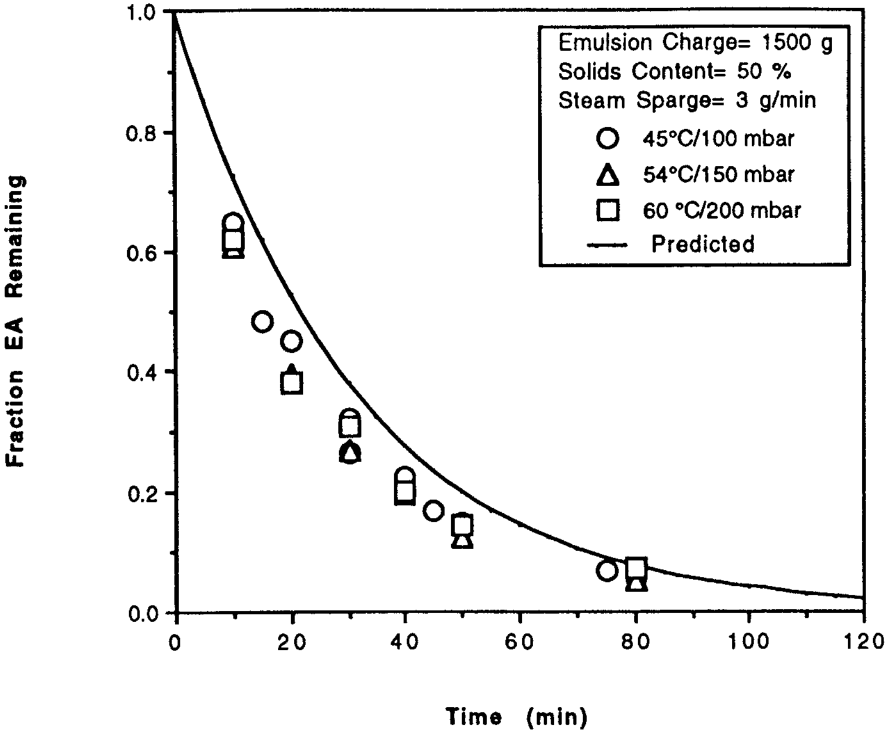

FIG. 11 Effect of temperature on EA removal.

by increasing the steam-sparge rate and becomes more difficult as the solids content is increased. Temperature has little effect.

When designing equipment for batch steam stripping and specifying operating conditions, temperature still must be considered. Higher temperatures allow operation at higher pressure, and a one-stage steam ejector may be all that is needed to provide sufficient vacuum. In addition, higher operating pressures result in higher vapor densities, allowing smaller equipment to be used. Thermal degradation and emulsion instability are more likely at higher temperatures, however. To operate at lower temperatures, steam stripping must take place at lower pressures. At these conditions, vapor density is lower, resulting in larger equipment requirements and increased capital costs. In addition, foaming is a greater problem at low pressures for many polymer emulsions, and chemical or mechanical defoamers must be considered in the design of a low-pressure steam-stripping process.

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