Distribution of Volatile Species in a Refluxing Polymer Colloid

Monomer partitioning between the aqueous and polymer phases in a latex determines many properties of an emulsion polymerization, such as the reaction rate, molecular weight development and, if operated under refluxing conditions, the reaction temperature. A unique two-chamber vapor-liquid equilibrium cell was used during this investigation to obtain an *in situ* separation of the aqueous phase from the latex, thus permitting a direct determination of the compositions of the aqueous, polymer, and vapor phases in a latex, even under refluxing conditions. Thermodynamic analysis of the vapor-liquid equilibrium problem allows the prediction of the composition of all phases from measured values of the temperature and pressure only. These predictions agreed well with data from other investigations under nonrefluxing conditions and with the aqueous and vapor phase compositions from this investigation. The polymer phase composition data for vinyl acetate polymers with average molecular weights in excess of 10^6 showed consistently higher polymer volume fractions than predicted. This latter result may be due to crosslinking or strong entanglements resulting from increased chain branching at these high molecular weights.

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Introduction

In the operation of large-size polymerization reactors the maximum allowable polymerization rate is often determined by the rate of heat transfer. This is especially true for vinyl polymerizations since the heat of polymerization of most of the common vinyl monomers is approximately the same as the heat of combustion of propane. For polymerization reactors cooled entirely by heat transfer to a cooling jacket this problem is further aggravated by the decrease in the surface area to volume ratio as the reactor size is increased.

The most common solutions to this heat transfer problem are either circulating a portion of the reactor contents through an external heat exchanger or operating the reactor under refluxing conditions. Reflux cooling has some very distinct advantages over external heat exchangers for polymerization reactors. The heat exchange areas required for reflux cooling are smaller than those required for external heat exchangers because of the excellent heat transfer obtained for condensing vapors. In addition, the heat exchange surface in a reflux condenser is exposed only to condensing monomer and water vapors. While some fouling of the heat transfer surface may occur under these conditions, via vapor phase polymerization, it is a much smaller problem than the fouling problem on surfaces exposed to liquid polymerizing systems.

While the advantages of reflux cooling are applicable to all types of polymerization processes, reflux cooling of emulsion polymerizations has the further advantage that the escape of the vapors from the reacting mixture is not hampered by high viscosity as in bulk or solution polymerization processes. For emulsion polymerizations two very distinct disadvantages to reflux cooling are usually encountered. From a practical point of view the biggest of these is usually colloidal stability. Under refluxing conditions much of the surfactant added to the system may desorb to form foam, leaving the particles susceptible to coagulation. The refluxing monomer may also pool on top of the latex, offering another site for coagulation.

While these stability problems may be overcome by the selection of the proper surfactant and good mixing, another factor that works against the use of reflux-cooled emulsion polymerization reactors is the lack of data on the vapor-liquid equilibrium of a monomer over a latex. Without such information one cannot relate the boiling point temperature and pressure to the composition of the various phases (vapor, continuous phase, dispersed

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phase). If the composition of the dispersed phase, the polymer particles in an emulsion polymerization, is not known then one can not predict the reaction rate, and hence the rate of heat generation, nor the product quality (molecular weight distribution, MWD).

To date no reports of the necessary vapor-liquid equilibrium data for the design of a reflux-cooled emulsion polymerization reactor have been published, although a few reports of data on a related topic, the distribution of unreacted monomer between the polymer particles and the aqueous phase in a latex, have appeared. This investigation was initiated to fill this need. The experimental phase of this investigation was conducted using a unique vapor-liquid equilibrium cell that allowed an *in situ* separation of the aqueous phase from the whole latex while under refluxing conditions. The data obtained from this modified cell showed the expected trends and agreed very well with the predicted values except for the polymer volume fraction in the polymer phase, which was consistently higher than predicted for high molecular weight ($>10^6$) polymers. This apparent increase in the polymer-solvent interaction parameter may have arisen from crosslinking or severe entanglements within the polymer phase of the latex.

Previous Work

It has been observed that when a latex is treated with a good solvent for the polymer, the particles will swell with the solvent only up to some point beyond which the excess solvent appears as a separate phase. It is this phenomenon that accounts for the disappearance of the separate monomer phase during the early stages of most emulsion polymerizations. The first theoretical description of the phenomena is that by Morton et al. (1954). They suggested that a latex particle would continue to imbibe solvent (monomer) until the free energy decrease caused by the absorption of the solvent was exactly equal to the increase in surface free energy caused by the swelling of the particle. Equating these two free energy changes gave the result

$$-[\ln(1-\phi)+\phi]=\chi\phi^2+\frac{2V_m\sigma}{RTr} \tag{1}$$

Morton went on to observe the distribution of styrene, toluene, and chlorocyclohexane in polystyrene latexes under saturated conditions and found that the results agreed with the predictions of Eq. 1. Similar data, reaching the same conclusions, have also been reported for polystyrene, poly(vinyl acetate) and poly(vinyl hexanoate) latexes in the presence of their own monomers and other solvents (Vanzo et al., 1965; Klein et al., 1973). The theory has also been expanded to allow for multicomponent absorption by the latex particles where the other absorbing component is usually water (Tseng et al., 1982).

While knowledge of the distribution of monomer at saturated conditions is important during the early stages of an emulsion polymerization, the majority of the polymerization time will take place after the disappearance of a separate monomer phase. Gardon (1968) modified Eq. 1 to account for this and obtained the following result

$$\ln\left(\frac{P}{P^o}\right)-\ln(1-\phi)-\phi=\chi\phi^2+\left(\frac{2V_m\sigma}{RTr_o}\right)\phi^{1/3} \tag{2}$$

Gardon also reports a great deal of data, again mostly under saturated conditions, although he does report some data on polystyrene and poly(methyl methacrylate) latexes under less than saturated conditions.

Data on the partitioning of a solvent between the particles and the continuous phase in a polymeric latex under less than saturated conditions are much less plentiful than for saturated conditions. For the vinyl acetate/poly(vinyl acetate) system to be studied during this investigation, Napper and Parts (1962) and Dunn and Taylor (1965) reported data at 313 and 293 K, respectively, obtained by separating the latex particles from the aqueous phase in a high-speed centrifuge and performing a bromometric titration on the clear supernatant. Netschey and Alexander (1970) reported data at both temperatures but obtained their particle/aqueous phase separation by coagulation of the latex using a cationic surfactant and the use of an interferometer to measure the monomer concentration in the supernatant.

The only report of the compositions of the particulate, aqueous, and vapor phases in an emulsion polymerization is an investigation of the emulsion polymerization of vinyl chloride by Chan et al. (1982). The system modeled was operated at 333 K and was not under refluxing conditions. However, since a large amount of the vinyl chloride monomer was in the vapor state for these conditions such an analysis was necessary to adequately model this system. Unfortunately the distribution of the monomer between the various phases is expressed in terms of empirical partition coefficients and so cannot be calculated directly from fundamental properties of the polymerizing system.

For the purposes of modeling a reflux-cooled emulsion polymerization reactor, therefore, all of these prior results are incomplete. No experimental data have been obtained from refluxing systems, most of the data are for saturated conditions, and no temperature greater than 333 K, which is well below the usual temperatures used during reflux cooling, is reported. Since reflux cooling is most easily applied to polymerizations involving low-boiling monomers, the distribution of vinyl acetate in a refluxing poly(vinyl acetate) latex was selected as the system to be studied. Because most latexes are water-borne, we will refer to the continuous phase of the latex as the aqueous phase, although what follows is equally applicable to nonaqueous latexes.

Theoretical Description

At equilibrium the fugacity of any species must be the same in all phases; thus in a latex under refluxing conditions

$$f_i^{aq}=f_i^p=f_i^v \tag{3}$$

Since reflux-cooled reactors are generally operated at high temperatures and low pressures, we will assume that the vapor phase is an ideal gas so that the vapor-phase fugacity of any component is given by

$$f_i^v=y_iP_T \tag{4}$$

The aqueous-phase fugacity can also be given in terms of mole fractions as

$$f_i^{aq}=x_i\gamma_iP_i^o \tag{5}$$

Again assuming an ideal gas vapor phase and equating the fugacity of any species in the vapor and polymer phases, Gardon's expression for the partitioning of a solvent under less than saturated conditions can be rewritten to give

$$f_m^p = P_m^o(1 - \phi) \exp\left(\phi + \chi\phi^2 + \frac{2V_m\sigma}{RTr_o}\phi^{1/3}\right) \tag{6}$$

where it has been assumed that the latex particles do not absorb water.

For reactor modeling purposes, however, we would like these relationships to be expressed in easily observable parameters such as temperature and pressure. Assuming that the polymer is essentially nonvolatile, we can use Eqs. 4 and 5 to get

$$x_m\gamma_m P_m^o + x_w\gamma_w P_w^o = P_T \tag{7}$$

Since the aqueous phase for the system under study consists only of vinyl acetate and water, Eq. 7 allows the composition of the aqueous phase to be calculated knowing only temperature and pressure. This is in agreement with Gibbs' phase rule for this three-component (water, monomer, polymer)–three-phase (aqueous, polymer, vapor) system. (Note that it might be argued that there are four components: water, monomer, polymer, and surfactant. In this case it can also be argued that there are four phases: aqueous, polymer, vapor, and interface, since the effect of the surfactant is felt in the interfacial properties. In either case, Gibbs' phase rule indicates that there are only two degrees of freedom.)

In a typical polymeric latex it is usually easier to observe the total solids, T_s, and the amount of monomer contained in a given amount of the latex as a whole, x_m^*, rather than the compositions of the aqueous and polymer phases. For a water-borne latex the relationship between these factors is given by

$$x_m^* = (1 - T_s^*)\frac{x_m MW_m}{x_m MW_m + 18x_w} + T_s^*\frac{(1 - \phi)\rho_m}{(1 - \phi)\rho_m + \phi\rho_p} \tag{8}$$

The relationship between the usual total solids measurement (T_s) and T_s^* is

$$T_s^* = T_s\left[\frac{\phi\rho_p + (1 - \phi)\rho_m}{\phi\rho_p}\right] \tag{9}$$

One can now use these equations to do either of the following:

1. Given a temperature and pressure, determine the composition of the individual phases and the latex as whole, or
2. Given a measurement of the overall composition of the latex (monomer content and total solids) and the total pressure, determine the boiling point temperature and the compositions of the individual phases.

Experimental Procedures

All four of the latexes used during this investigation were vinyl acetate homopolymer latexes generated either by varying the surfactant used during the polymerization or by varying the manner in which the monomer was added. Two of the latexes were generated by full batch emulsion polymerizations. For these latexes a surfactant solution consisting of 1,803 g water and 20 g active surfactant was formed and added to the polymerization reactor. For one of the latexes the surfactant was sodium dodecyl sulfate (SDS; 95% active) while Aerosol A103 (American Cyanamid Corp., 34% active) was used for the other. Vinyl acetate monomer (614 g) was added and the entire mixture was stirred and heated to 333 K under a nitrogen purge. An initiator solution consisting of 0.25 g potassium persulfate in 25 g water was added to the reactor after the temperature had stabilized. After an induction period of 30–60 min the reaction proceeded smoothly and was virtually complete after 5 h. The resulting latex then was cooled and removed from the reactor for future testing.

The two other latexes were generated using a semibatch process. It was hoped that the particles formed from the polymerization of the initial charge would act as seed particles for the remainder of the process, thus giving fewer but larger latex particles. For these latexes 1,612 g water and 20 g active surfactant were added to the polymerization reactor (again both sodium dodecyl sulfate and Aerosol A103 were used). To this surfactant solution 82 g vinyl acetate was added and the mixture stirred and heated to 343 K under a nitrogen purge. An initiator solution containing 2.2 g potassium persulfate in 25 g water was added to the reactor after the temperature had stabilized. After the reaction mixture turned milky in appearance (usually after 0.5 h) a vinyl acetate feed was started at a rate of 4.4 mL/min. A total of 650 g vinyl acetate was added to the reactor during the feed, requiring 3 h. The reactor was maintained at 343 K for 3 h after completion of the feed to insure complete conversion of the monomer. After this period the latex was cooled and removed from the reactor for future testing.

The monomer used was obtained from Eastman Kodak Co. and contained 10 ppm hydroquinone. No attempts were made to remove the inhibitor. The sodium dodecyl sulfate, Aerosol A103, and potassium persulfate were used as obtained from the various suppliers. The water used during the investigation was the usual deionized water supplied to the lab, which was further treated by passing it through two ion exchange beds, an activated carbon bed, and a submicron filter (resistivity >16.0 MΩ/cm).

The average particle size of the latices ranged from 147 to 235 nm. As described later, this variation in the average particle size had no effect on the vapor-liquid equilibrium results. The average molecular weight of the polymer was determined using dilute solution viscosity measurements in acetone at 303 K. The viscosity data were converted to average molecular weight using the Mark-Houwink-Sakurada equation and the appropriate values of the constants K and a, depending upon the average molecular weight (Brandrup and Immergut, 1975; Friis et al., 1975). Table 1 is a summary of the results from these analyses.

The first apparatus used during this investigation consisted of a round-bottom flask to which a vapor-liquid separator and a

Table 1. Latex Properties

Latex	Synthesis Procedure	Surfactant*	$\overline{d_p}$ nm	$\overline{MW}$ $\times 10^{-6}$
A	Batch	SDS	147	5.2
B	Semibatch	SDS	165	0.35
C	Batch	A103	218	8.3
D	Semibatch	A103	235	2.6

*SDS: sodium dodecyl sulfate
A103: Aerosol A103

reflux condenser were attached. The latex to be studied was placed into the flask, some monomer was added, and the entire assembly placed into a constant-temperature bath and heated until the system started to boil. Samples of the latex and the reflux stream were withdrawn for analysis after equilibrium had been reached. This apparatus was used (by C. T. Chen) for all of the results shown for latexes A and B.

To obtain separate measurements of the aqueous and polymer phases some means for separating the monomer-swollen polymer particles from the continuous phase of the latex, while still under reflux, had to be developed. Centrifugation techniques could not be used since they are limited by the upper operating temperature for the centrifuge (typically no greater than 313 K). Coagulation of the latex may also interfere with the measurements since Eq. 2 indicates that the monomer distribution is affected by changes in the interfacial tension and particle diameter. In fact, any system that requires the removal of a portion of the latex and subsequent separation is likely to encounter severe experimental difficulties because of the volatility of vinyl acetate.

To overcome these problems the vapor-liquid equilibrium apparatus shown in Figure 1 was constructed. The apparatus consists of a double-chamber liquid vessel with each side of the vessel equipped with a separate reflux condenser, but both condensers connected to a common pressure source. The two chambers were separated by a microporous membrane with openings small enough to prevent the passage of the latex particles. Agitation on both sides of the membrane was supplied by magnetic stirrers. This apparatus was used (by D. A. Jones) to obtain the data shown for latexes C and D. This represents a significant improvement over the equipment and procedures used in previous investigations of solvent distribution in that a separation of the particulate phase from the continuous phase may be made within the equilibrium cell, thus minimizing the handling of the samples and the potential for disrupting the equilibrium.

A typical experiment was conducted as follows. The latex to be studied was diluted to the desired total solids level. A portion of this latex was then placed into a high-speed centrifuge to remove all of the particles. The clear serum was used to fill the aqueous side of the apparatus while the remaining whole latex was placed in the other chamber. After immersing the apparatus in a constant-temperature bath, the pressure was adjusted to the desired level (all results reported were obtained at ambient atmospheric pressure, about 92.6 kPa) and a small amount of monomer was added. This monomer injection went principally into the latex chamber, with a small amount added to the aqueous chamber to reduce the time required to reach equilibrium. The temperature in the bath was then raised until a boiling action was noticed. After allowing equilibration the temperature in the latex chamber was recorded and samples were withdrawn from both the latex and aqueous chambers, as well as a liquid sample from the vapor-liquid separator. The constant-temperature bath then was cooled, another injection of monomer was made, and the process described above repeated.

To determine how long a period of time was necessary to insure an equilibrium distribution of the monomer between the two chambers, pure water was placed into both chambers, an injection of vinyl acetate was made into only one chamber, and the composition in both chambers was monitored as a function of time. The results are shown in Figure 2 for testing at room temperature. Figure 2 indicates that the concentrations in the two chambers have effectively equalized after approximately 7 h. Beyond this time there was a steady decrease in the monomer concentration despite efforts to seal the apparatus. Since the escape of the monomer was either equal from both chambers or slow enough so that the equilibrium distribution of the monomer was not upset, this loss of monomer should not affect the results of the subsequent vapor-liquid equilibrium testing. Thus during all of the experiments a period of 8 h was allowed between the time that a fresh monomer injection was made and samples were taken. This should be more than sufficient in view of the results shown in Figure 2, the higher diffusion coefficients at the higher

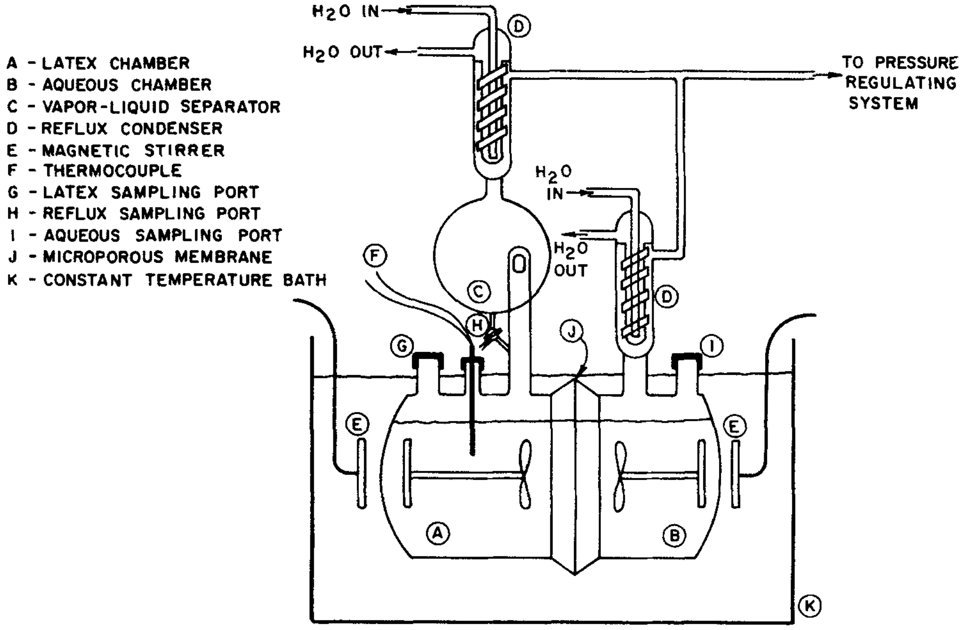

Figure 1. Experimental apparatus.

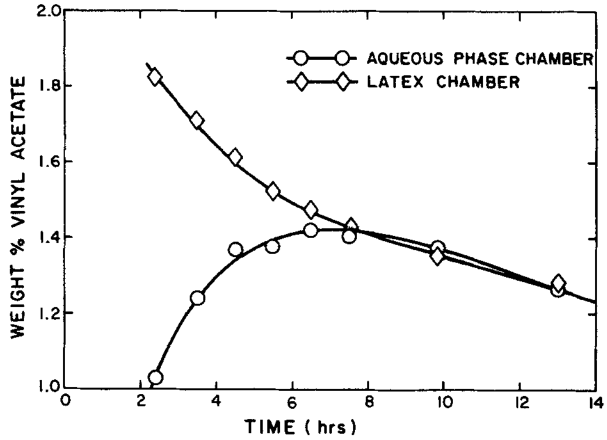

Figure 2. Approach to equilibrium in the experimental apparatus at 298 K.

temperatures used during the testing, and the fact that monomer is added to both chambers. The small size of the latex particles insures that an equilibrium distribution of the monomer between the polymer and aqueous phases was also established during this time.

The three samples taken from the apparatus were immediately chilled to prevent loss of the more volatile components. Each sample was analyzed for composition using a gas chromatograph. Since the apparatus was operated at total reflux, the refluxing stream should have the same composition as the vapors. From the measured values for the monomer content in the whole latex and in the aqueous phase, and knowledge of the solids (polymer) content of the latex, the monomer content of the polymer particles can be calculated.

Results

The observed relationship between the boiling point of the latex and the overall monomer content is shown in Figure 3. As expected, the latexes with the highest solids content showed the highest boiling point for a given overall composition. Since vinyl acetate is preferentially absorbed by its polymer, latexes with higher solids contents will have lower aqueous-phase monomer concentrations than similar latexes with lower solids contents for the same overall monomer level. A lower aqueous-phase monomer content gives a higher boiling point in this case since vinyl acetate is more volatile than water. Note that the monomer content for all experiments was considerably below the saturation value, as is typical in reflux-cooled operations, so that no separate monomer phase existed (stage III of an emulsion polymerization).

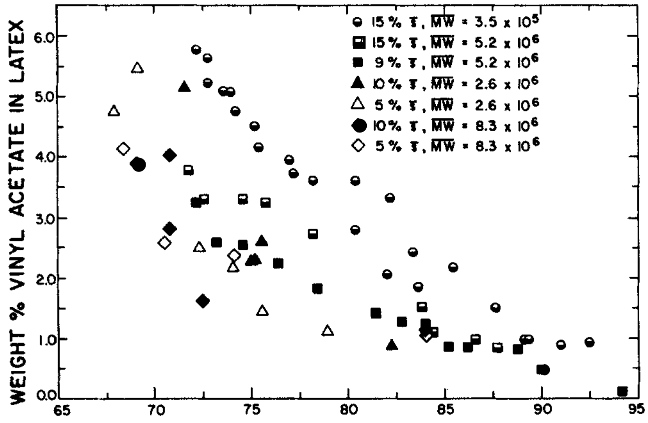

Figure 3. Dependence of latex composition on boiling point temperature.
Pressure – 92.6 kPa

A comparison of the variation in the composition of the three phases with boiling point temperature between the experimentally measured values and the values predicted from the modeling equations is shown in Figures 4, 5, and 6. To use Eq. 7 to predict the aqueous-phase composition we must be able to calculate the activity coefficients as functions of both composition and temperature. Both Casson and Dunn (1967) and Coniglio and Parts (1971) have reported the activity of vinyl acetate in water at 298 K. But while Casson and Dunn report values ranging from 7.3 to 33.8, Coniglio and Parts obtained values from 176 to 185. Data obtained from Union Carbide Corp. (K. Williamson, private communication, 1985) at 283 K indicated a range of values for the activity coefficient of 197 to 180, while researchers at the Shanghai Institute of Petrochemistry (1976) report a value of 187 at 339 K. The data obtained by Casson and Dunn were neglected during the analysis of the results from this investigation because of their lack of agreement with data from these other sources. Since the Union Carbide data were more extensive, the dependence of the activity coefficient on composition was determined using these data. Using the van Laar equation to express the results gives for vinyl acetate at 283 K

$$\ln(\gamma_m) = \frac{A_{12}}{\left(1 + \dfrac{A_{12}\,x_1}{A_{21}\,x_2}\right)^2} \tag{10}$$

where $A_{12} = 5.283$ and $A_{21} = 3.392$. At a constant pressure and composition the effect of temperature on the activity coefficient is given by

$$d(\ln \gamma_i) = -\frac{\overline{\Delta H_i}}{RT^2}\,dT \tag{11}$$

Assuming a constant heat of mixing this equation can be integrated to give

$$\ln\left(\frac{\gamma_{i1}}{\gamma_{i2}}\right) = \frac{\overline{\Delta H_i}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12}$$

Using Eq. 10 to compute the activity coefficient of vinyl acetate at 283 K and the data from Coniglio and Parts at 298 K, the heat of mixing of vinyl acetate is calculated to be 2.35 kJ/mol. Equations 10 and 12 can now be used to predict the activity coefficient for vinyl acetate in water solution for all compositions and temperatures used during this investigation. The activity coefficient of water for the conditions used during this investigation is effectively constant and is unity, to four significant figures.

Figure 4 shows the dependence of the aqueous-phase composition on boiling point temperature. While there is some scatter in the data, the fit between the experimentally measured compositions and the predicted values is especially good when it is

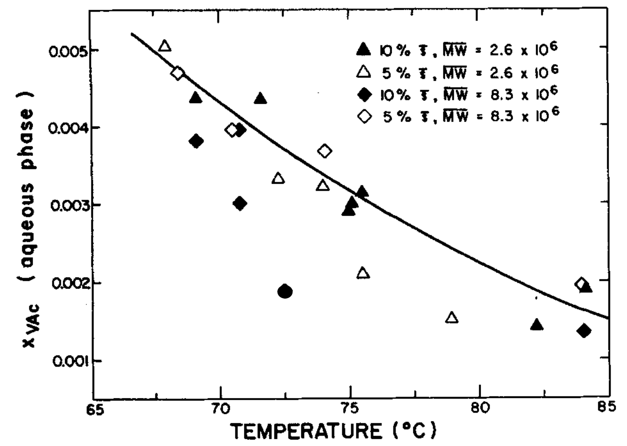

Figure 4. Dependence of aqueous-phase composition on boiling point temperature.
Pressure - 92.6 kPa

remembered that there are no adjustable parameters in the model. This agreement can also be taken as a further indication that the activity data of Coniglio and Parts are more accurate than the data of Casson and Dunn. The aqueous-phase composition is, as expected, independent of the total solids level and the average molecular weight of the polymer.

Equation 4 now can be solved to give the composition of the vapor phase. The comparison between the predicted and the experimentally determined vapor-phase compositions is shown in Figure 5. It is obvious from Figure 5 that the experimental data lie below the predicted values, an offset which may be due to experimental difficulties. The vapor-phase compositions were determined by collecting the reflux stream from the condenser over the latex chamber using the valve located at the bottom of the vapor-liquid separator. This reflux stream was a two-phase stream for even the lowest level of vinyl acetate shown in Figure 5. While we attempted to divert all of the reflux stream through the valve when we sampled, there frequently was pooling at the sampling port. Under such conditions the vinyl-acetate-rich phase, being the less dense, would rise to the top of the liquid in the separator and remain there while the water-rich phase would settle and be pulled out as our sample. This hypothesis is further supported by the fact that the data at the higher temperatures, where the fraction of vinyl acetate which separates to form the water-poor phase is reduced, show a better agreement with the predicted values.

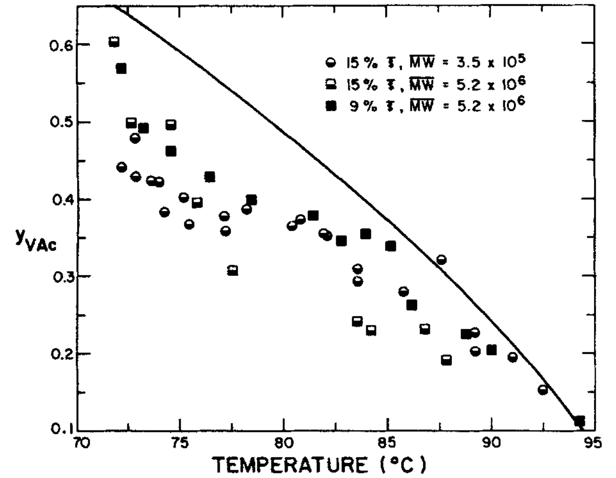

Figure 5. Dependence of vapor-phase composition on boiling point temperature.
Pressure - 92.6 kPa

Equation 6 now can be used to predict the composition of the polymer phase once values for the interfacial tension and the polymer-solvent interaction parameter are known. In previous investigations the value of the interfacial tension was determined by a fitting procedure with the experimental data. Whether using potassium laurate (Morton et al., 1954) or sodium dodecyl sulfate (Vanzo et al., 1965; Klein et al., 1973), the interfacial tension appears to have a value in the range from 3.0×10^{-3} to 25.0×10^{-3} N/m depending upon temperature and the ionic strength of the continuous phase. We observed during this investigation that for boiling points above 343 K the polymer volume fraction in the latex particles was 0.60 or higher. Using 0.3 as the value for the interaction parameter, the magnitude of the terms in the exponential in Eq. 6 can be examined to determine the effect of the uncertainty in the value for the interfacial tension. At $T = 343$ K, $\phi = 0.60$, a large value of the interfacial tension ($\sigma = 25.0 \times 10^{-3}$ N/m), and the lowest value of the particle size ($d_p = 147$ nm), the entire term involving the interfacial tension contributes only 1.3% to the value of the exponential in Eq. 6. For temperatures approaching 373 K, polymer volume fractions approaching 1.0, and the same values of the interfacial tension and the particle size, this term accounts for only 0.84% of the value of the exponential. Neglecting this term completely, even for interfacial tensions twice as large as previously observed ($\sigma = 50.0 \times 10^{-3}$ N/m), alters the calculated value of the fugacity by approximately 1.0%. So, unlike its importance under saturated conditions, the term involving the interfacial tension and the particle size plays only a minor role in determining the polymer phase fugacity under less than saturated conditions. Trying to determine an accurate value for the interfacial tension from the experimental data will not work for this investigation because of this lack of sensitivity between the observable variables and the interfacial tension. Although the term involving the interfacial tension could be ignored, it was retained and a value of $\sigma = 14.0 \times 10^{-3}$ N/m was used, which represents an average value from previous investigators.

This leaves only the polymer-solvent interaction parameter to be determined before we can use Eq. 6 to predict the polymer volume fraction. Using data from Nakajima et al. (1959) and a linear regression the following relationship between the interaction parameter and the polymer volume fraction is obtained:

$$\chi = 0.668 - 0.581\phi \qquad (13)$$

These data were obtained for vinyl acetate in a poly(vinyl acetate) polymer with an average molecular weight of 1.43×10^5 at 303 K. Since the interaction parameter is inversely dependent on the absolute temperature Eq. 13 can be rewritten as

$$\chi = \frac{202 - 176\phi}{T} \qquad (14)$$

to give the interaction parameter as a function of polymer volume fraction and temperature. Using Eqs. 6 and 14 we can now compute the polymer volume fraction as a function of boiling

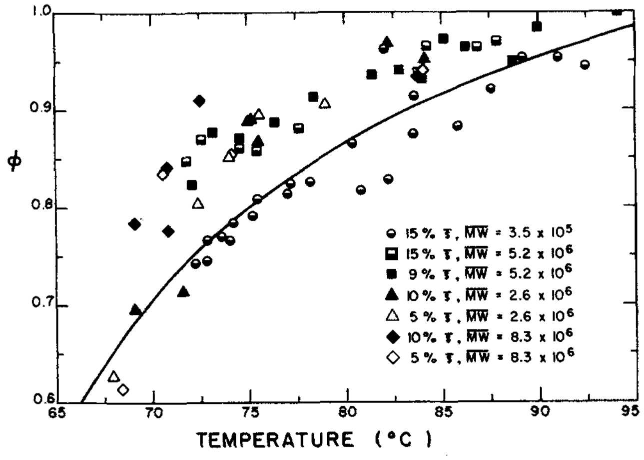

Figure 6. Dependence of polymer-phase composition on boiling point temperature.
Pressure = 92.6 kPa

point temperature and compare this with the experimentally observed values, as shown in Figure 6. Since the experimental runs involving latexes A and B were performed prior to the addition of the second chamber, the polymer phase composition could not be determined directly from the existing experimental data. Instead the results shown in Figure 4 were used to predict what the composition of the aqueous phase should have been and this composition, along with the measured value for the vinyl acetate content of the latex as a whole, was used to determine the polymer phase composition. For the lowest molecular weight polymer investigated the agreement between the predicted curve and the experimental data is good. For the higher molecular weight polymers, however, the data lie consistently above the predicted values.

Discussion

The excellent agreement shown in the figures above, all obtained without adjustable parameters, is encouraging. Unfortunately no similar data have been reported to which the experimental data obtained from this investigation can be compared. Some data under nonrefluxing conditions are available, however, and can be compared with the predictions of Eqs. 4 and 12. Dunn and Taylor (1965) reported that the partitioning of vinyl acetate between the aqueous phase and the polymer phase at 293 K is given by

$$M_p = 13.7\, M_{aq}^2 \tag{15}$$

The predictions using this equation and the equations developed during this investigation (using Nakajima's data for the polymer-solvent interaction parameter) are compared in Figure 7 along with the experimental data of Netschey and Alexander (1970). Netschey and Alexander suggest that the discrepancy between the two sets of data may be due to evaporation of the vinyl acetate monomer during the bromometric titrations used by Dunn and Taylor. The predictions from the modeling equations appear to be more in line with, although somewhat higher than, the data from Netschey and Alexander.

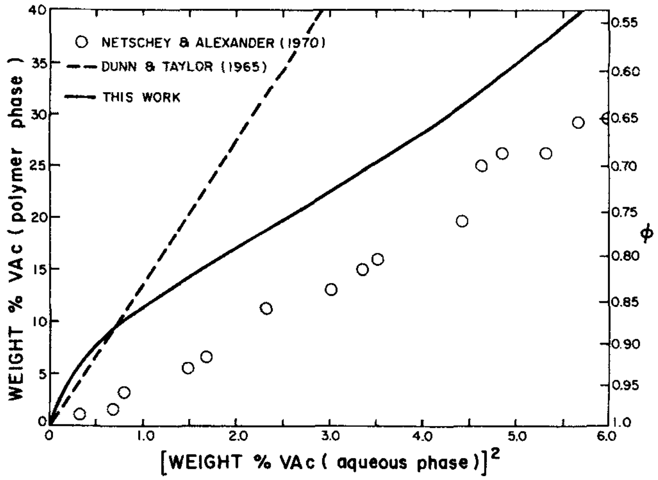

Figure 7. Partitioning of vinyl acetate between aqueous phase and polymer phase at 293 K.
d_p = 54.2 nm

A similar comparison is made in Figure 8 for partitioning at 313 K using data reported by Napper and Parts (1962) as well as Netschey and Alexander. Napper and Parts used the same experimental procedure as Dunn and Taylor and so the offset between their data and those of Netschey and Alexander may again be due to evaporation of the vinyl acetate. At 313 K, however, the agreement between the modeling equations from this work and the data of Netschey and Alexander is excellent. The only significant differences between the two occur for large uptakes of the monomer by the polymer. At this point, however, the interfacial tension term in Eq. 6 becomes increasingly important. Had a smaller value of the interfacial tension been used (and values as low as 3.0×10^{-3} N/m have been reported), the values predicted using the modeling equations would have been greater than the values shown in Figure 8 for ϕ less than 0.6, and more in line with the results from Netschey and Alexander.

The lack of agreement between the data from Netschey and Alexander and the predicted results at 293 K are hard to explain since the values of the activity coefficients and interaction parameter used during this investigation were taken from inves-

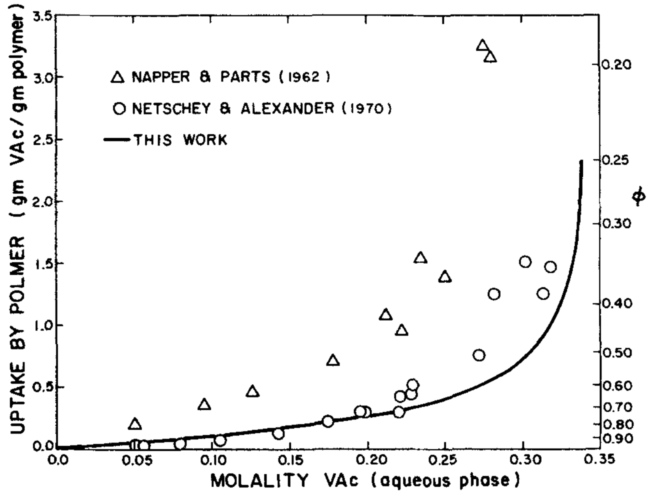

Figure 8. Partitioning of vinyl acetate between aqueous phase and polymer phase at 313 K.
d_p = 54.2 nm

tigations in the temperature range from 283 to 298 K. The differences may lie in factors unreported by Netschey and Alexander, such as the average molecular weight or branching density of their polymers, since these may affect the uptake of monomer. There is also the possibility that the separation of the polymer phase from the aqueous phase using a cationic surfactant may alter the distribution of the monomer. The interfacial tension will be greater at lower temperatures for these systems so that the effect of the addition of the cationic surfactant on the partitioning of the monomer would be more strongly felt for the data collected at 293 K. The agreement between this partitioning data and the modeling equations, coupled with the agreement between the equations and the data from this investigation, is further support for the validity of the data obtained while under refluxing conditions.

Another way of examining the reliability of the data obtained during this investigation is to examine its consistency. Latex B (represented with the symbol ◒ in all of the figures) was used in two trials at the same solids level. No distinction is made between the two repeat trials in any of the figures because of the excellent reproducibility. The other three latexes were all tested at two different solids levels. A test of the internal consistency of the data obtained from the experimental technique developed during this investigation can be performed by adjusting the experimental data for the dependence of the latex composition on boiling point temperature, Figure 3, to a common total solids level. The overall monomer content that any latex would have at the same boiling point but at a total solids level of 10% is given by

$$x_m^*(T_s = 0.1) = \frac{0.1x_m^* + [0.9T_s - 0.1(1 - T_s)]x_{aq}^*}{T_s + \{0.1x_m^* + [0.9T_s - 0.1(1 - T_s)]x_{aq}^*\}} \tag{16}$$

All of the data obtained during this investigation, when so adjusted, are shown in Figure 9. Comparing Figures 3 and 9 it can be seen that for any particular latex the data from different solids levels do indeed yield a common result when adjusted to a common total solids level. It can also be seen that the apparent molecular weight effect seen in Figure 6 carries over to the results in Figure 9 as well.

Because of the apparent effect of molecular weight on the composition of the polymer phase, and the fact that three of the polymers used during this investigation had average molecular weights that were significantly greater than the polymer used by Nakajima et al., the interaction parameter was expressed as a function of composition and temperature of the form

$$\chi = \frac{\alpha + \beta\phi}{T} \tag{17}$$

and a regression analysis was performed on the experimental data to determine the appropriate values of α and β for each of the polymers used. The dependence of the interaction parameter on polymer volume fraction so obtained is shown in Figure 10. These values for the interaction parameter were also used in Eq. 6 to give the predicted curves shown in Figure 9. For the range of polymer volume fractions obtained during this investigation ($\phi \geq 0.6$) the data from the lowest molecular weight polymer agree reasonably well with the data from Nakajima et al., although they show a stronger dependence on the polymer volume fraction. The higher molecular weight polymers all show interaction parameters considerably higher than Nakajima's data and even predict an increase in the interaction parameter with increasing polymer content. While the term in Eqs. 1, 2, and 6 involving ϕ should be correctly written as $[1 - (1/n)]\ \phi$, the molecular weights of the polymers used during this investigation are so high that this correction is insignificant and therefore cannot account for the observed molecular weight effect.

Another phenomenon associated with the molecular weight development of vinyl acetate polymers may be responsible, however. It has been reported that the amount of branching in poly(vinyl acetate) resins increases rapidly with increasing molecular weight for molecular weights greater than 10^6 (Friis et al., 1974). Therefore, the three higher molecular weight polymers used during this investigation are likely to be more highly branched than the lowest molecular weight polymer or the materials used by Nakajima. In fact some solubility problems were observed during the dilute solution viscosity measurements for the three higher molecular weight polymers used in this investigation. The higher branching density, and potential crosslinking, may produce polymer particles in which the ability to

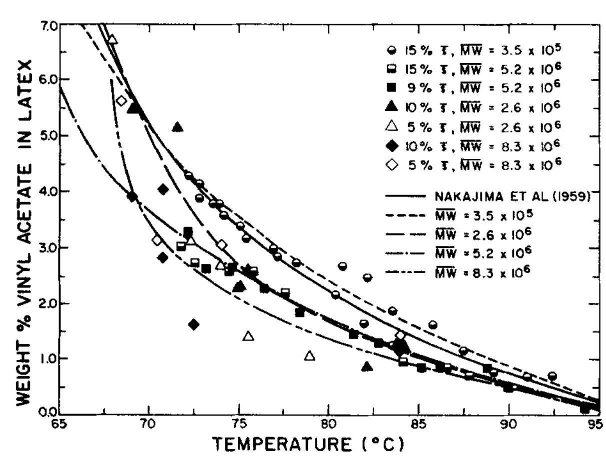

Figure 9. Dependence of latex composition at T_s = 10% on boiling point temperature.

Pressure = 92.6 kPa

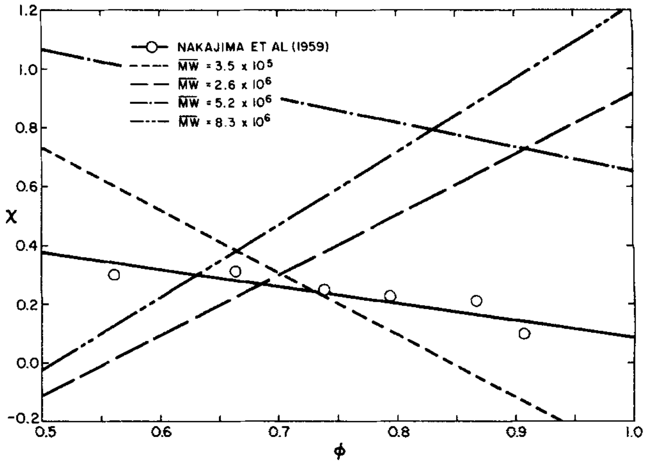

Figure 10. Dependence of polymer-solvent interaction parameter on polymer volume fraction at 303 K.

expand as monomer (solvent) is absorbed is reduced. This in turn should result in a decreased ability of the particle to absorb monomer resulting in the lower than expected monomer uptake observed during this investigation.

It is interesting that the results of this investigation are so sensitive to such apparent changes in the value of the polymer-solvent interaction parameter. It is possible that this technique may be useful as a means of investigating the relationship between the polymer-solvent interaction parameter and such factors as the polymer volume fraction and the polymer molecular structure. This technique would have the advantage of requiring only simple equipment and, because of the small size of the polymer particles, would also eliminate any uncertainty about the failure to establish an equilibrium distribution of the monomer throughout the polymer phase.

Conclusions

An experimental procedure and apparatus have been developed that allow the compositions of all three phases existing in a refluxing latex to be measured simultaneously. The experimental data closely followed the predicted trends with the exception of the polymer phase composition, for which the uptake of monomer for the higher average molecular weight polymers was lower than expected. This result may have been caused by crosslinking or by the formation of irreversible entanglements that restrict the ability of the particle to swell as monomer is absorbed.

Comparisons between data on the partitioning of monomer between the aqueous and polymer phases, but not under refluxing conditions, and the predictions made during this investigation are excellent at 313 K but are not as accurate at 293 K. No clear reason for this difference at the lower temperature is apparent although it may be due to effects of the unreported interfacial tension and molecular weight.

The results from this investigation have shown that it is possible to accurately determine the compositions of all of the phases present in a refluxing homopolymer latex from measured values of the temperature and pressure only. This is of considerable importance for the control of such systems since it indicates that no sophisticated equipment is required in order to accurately determine the instantaneous condition of the reacting mixture.

The results also indicate that the measured polymer volume fractions are sensitive indicators of the interaction parameter. By operating under less than saturated conditions the influence of other hard to obtain parametric values, such as the interfacial tension, is greatly reduced. Thus the experimental procedure developed during this investigation appears to offer another method whereby the dependence of the polymer-solvent interaction parameter on polymer volume fraction and temperature can be studied. This method does not require extensive or expensive equipment and relies only on commonly available instruments for all analyses.

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Notation

A_{12}, A_{21} = van Laar coefficients
f = fugacity
$\overline{\Delta H}$ = heat of mixing
M_{aq} = mass fraction of vinyl acetate in aqueous phase
M_p = mass fraction of vinyl acetate in polymer phase
$\overline{MW}$ = average molecular weight
MW = molecular weight
n = degree of polymerization
P = partial pressure
P^o = vapor pressure
P_T = total pressure
r = particle radius
r_o = unswollen particle radius
R = gas constant
T = temperature
T_s = mass fraction polymer in latex
T_s^* = mass fraction polymeric phase in latex
V = molar volume
x = mole fraction in aqueous phase
x_{aq}^* = mass fraction vinyl acetate in aqueous phase
x_m^* = mass fraction vinyl acetate in latex
y = mole fraction in vapor phase

Greek letters

γ = activity coefficient
ϕ = polymer volume fraction in polymer phase
χ = polymer-solvent interaction parameter
ρ = density
σ = aqueous phase-polymer phase interfacial tension

Subscripts

i = species i
m = solvent (monomer)
p = polymer
w = water

Superscripts

aq = aqueous phase
p = polymer phase
v = vapor phase

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