

Thermodynamic Studies Related to Emulsion Polymerization

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ABSTRACT: Liquid–liquid and vapor–liquid phase equilibria for the binary, ternary, and quaternary systems of vinyl acetate, surfactant, water, and poly(vinyl acetate) (PVAc) were obtained using liquid–liquid equilibria, inverse gas chromatography, and the headspace methods. The Flory–Huggins interaction parameters for the different species in the emulsion polymerization of PVAc latices are reported. These parameters could not be used to predict the phase equilibria because of their strong dependence on concentration. The UNIFAC–vdW–FV model was applied to predict the vapor–liquid equilibria in the binary and ternary systems containing vinyl acetate, 4-nonylphenol polyethoxilate surfactant, and PVAc. The predicted results compare

favorably with the experimental data for all systems. Diffusion coefficients were also measured for the solvents in the PVAc. Analysis confirmed that the diffusion in the latex particles was so fast compared to the reaction that the assumption of uniform monomer composition through the particles was valid. On the other hand, the results indicate that the complex thermodynamic interactions will lead to changes with time in the monomer concentration in the reacting polymer phase. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2092–2099, 2007

Key words: emulsion polymerization; poly(vinyl acetate); vapor–liquid equilibria; latex; UNIFAC–vdW–FV

INTRODUCTION

The process of the formation of latices by emulsion polymerization involves at least four components (water, monomer, surface-active agent, and initiator) and three phases (aqueous, monomer, and polymer). At the end of the polymerization, the product is a stable-emulsion of polymer in water. There are numerous attempts in the literature to model the polymerization kinetics of the emulsion process.^{1–4} In all these models, it is assumed that the monomer mass transfer rates through and between the various phases are fast and the phases are in thermodynamic equilibrium. Furthermore, it is assumed that for a large portion of the polymerization process, the monomer concentration in the polymer phase is constant, i.e., when a separate monomer phase is available to supply monomer to the growing latex particles. Since the surfactant is usually preferentially adsorbed at the water–polymer interface, the availability of the surfactant will depend on the particle growth. Consequently, one would expect the concentration of the surfactant in the three phases to change as the polymer process proceeds. The changing distribution of the surfactant should lead to changes in the concentrations of the water and

monomer in the various phases. One would suspect that the complex interactions between the four species would lead to changes in the monomer concentration in the reacting polymer phase, and thus the polymerization rate would change with time in contrast to the current models that assume constant monomer concentrations in the reacting phase when a monomer phase is present.

To investigate the complex thermodynamics involving the distribution of the four species between the three phases, this study used inverse gas chromatography (IGC), conventional liquid–liquid equilibrium measurements, and the headspace technique for investigating vapor–liquid equilibria over a range of concentrations and temperatures. As a trial, measurements were made for systems related to the emulsion polymerization of vinyl acetate (VAc).

EXPERIMENTAL

Inverse gas chromatography

The inverse gas chromatography (IGC) technique has been used to study the solubility and diffusivity of several solvents in poly(vinyl acetate) (PVAc) with an alkylphenolethoxilates of high and low molecular weight at several concentrations of surfactant.

The capillary columns were coated with PVAc without surfactant and with PVAc with different concentration of high and low molecular weight surfactants

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by the static coating technique.⁵ In this technique, the capillary column is filled with a solution of the polymer and surfactant in a solvent at the required concentration so that when the solvent is removed the remaining polymer/surfactant film will be of the desired thickness. One end of the column is sealed and then the solvent is slowly evaporated by pulling a small vacuum on the other end.

The chromatographic data were analyzed using the model developed by Hadj Romdhane and Danner.^{6,7} In this approach, the evaluation of the CCIGC model parameters is made using the time domain fitting procedure. The transform expression is numerically inverted using the fast Fourier transform algorithm and the deviation between the theoretical profile and the experimental profile is minimized.

The principle of the IGC technique is based on distribution of a volatile solvent between a mobile gas phase and a stationary polymer phase. Because of the mass transfer resistance in the polymer, the volatile substance in the mobile phase is swept forward, while that in the stationary phase lags behind. The net retention time of the peak is related to the solubility, and the spread of the peak to the diffusion coefficient for a given polymer–solvent system.

Pawlisch et al.^{8,9} employed and modified the model developed by Macris¹⁰ for the elution profile in capillary columns. They developed the following expression for the concentration profile at the exit of the column in the Laplace domain.

$$\frac{\bar{C}L}{C_0u} = \exp\left[\frac{1}{2\gamma}\right] \exp\left[-\left(\frac{1}{4\gamma^2} + \frac{s}{\gamma} + \frac{2\sqrt{s}}{\alpha\beta\gamma} \tanh(\beta\sqrt{s})\right)^{1/2}\right] \quad (1)$$

where the three dimensionless parameters are

$$\alpha = \frac{r_c}{K\tau} \quad \beta^2 = \frac{\tau^2u}{D_pL} \quad \gamma = \frac{D_g}{uL} \quad (2)$$

Here \bar{C} is the outlet concentration, C_0 is the strength of the inlet pulse, L is the length of the capillary column, τ is the thickness of polymer coating in the capillary column, r_c is the void cross section radius of the capillary column (radius of capillary column minus the thickness of polymer coating), D_g is the diffusion coefficient of solvent in the carrier gas, u is the velocity of carrier gas, D_p is the mutual diffusion coefficient in the polymer, and K is a dimensionless quantity defined as the concentration in the polymer phase divided by that in the vapor phase.

The systems studied contained PVAc, vinyl acetate (VAc), methanol, methyl acetate (MeAc), toluene, water, and 4-nonylphenol ethoxylates (NPE-9 and NPE-30). The choice of these materials was based upon industrial practice in the emulsion formation of the PVAc polymer.¹

The solvents were of reagent grade (purity > 99.5%), obtained from Aldrich Chemicals (Milwaukee, WI) and were injected as liquids. The PVAc was an amorphous material having a density of 1.191 g/cm³, a weight-average molecular weight of ~ 167,000, and the glass transition temperature of 33–35°C. The 4-nonylphenol ethoxylates (NPE-9, low molecular weight, density 1.07 and NPE-30, high molecular weight, density 1.08) are mixtures of oligomers and several isomers due to the branching of the hydrophobic groups.

The gas chromatograph used in this work was a Varian 3400 (Varian Associates, Walnut Creek, CA) equipped with a thermal conductivity detector (TCD), a split-splitless capillary injector, and an air-circulating oven. The columns were made of fused quartz, were 15 m long, and had an inner diameter of 0.53 mm. The columns prepared were pure PVAc, PVAc with 0.94 and 5.84 wt % low molecular weight surfactant and PVAc with 1 and 5 wt % high molecular weight surfactant. The thicknesses of the polymer coatings were 5 μm as found from SEM analysis. After the columns were installed in the oven, they were conditioned for about 24 h to remove any residual solvents from the polymers. To prove that the polymer and surfactant were miscible at these concentrations, several mixtures of the PVAc, surfactant, and solvent were prepared at the relevant concentrations and then the solvent was removed. The films were completely clear indicating that the polymer–surfactant mixtures form homogeneous phases at these concentrations.

High-purity helium was used as the carrier gas in all experiments. The flow rate of helium through the column was about 1 cm³/min. No appreciable pressure drops were measured across the capillary column. After the gas chromatograph had reached steady state operation, 0.25 μL of methane was injected by a gas tight syringe into the injector block. The mean residence time of the noninteracting methane was used to determine the carrier gas velocity. Pulses of solvents (0.04 μL) were injected through the rubber septum of the injection port into the carrier gas using a variable Hamilton 1 μL syringe. The outlet concentration profiles were monitored by a TCD detector, recorded, and integrated via the data system. In all cases, at least three injections were made: the deviations were less than 1%.

IGC EXPERIMENTAL RESULTS

Although experimental data for VAc and water on PVAc were of primary interest, data were also collected for methyl acetate, methanol, and toluene. Partition coefficients (K) and diffusion coefficients (D_p) for these solvents were measured at infinite dilution of the chemicals. The solubility and diffusivity values were essentially the same regardless of whether a

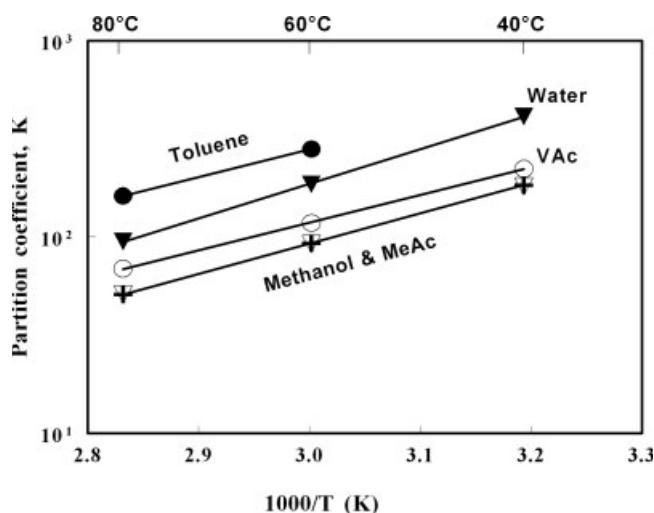


Figure 1 Temperature dependence of the partition coefficients in PVAc containing 5 wt % surfactant.

column containing a low or high molecular weight surfactant was used.

The temperature behavior of the solubility is shown in Figure 1. A typical behavior was observed, i.e., the partition coefficient decreased with increasing temperature. The logarithm of the partition coefficient was a linear function of reciprocal temperature for all systems.

The influence of the surfactant concentration on the partition coefficient, K , at 60°C is depicted in Figure 2. There is no effect of the surfactant concentration at these relatively low concentrations. These studies were conducted without the presence of water. It is possible that the surfactant concentration could alter the concentration of water in the polymer phase and thus influence the solubility of other species such as the monomer. Note that the solubilities of methanol and methyl acetate are the same within experimental error. Essentially identical behavior was observed for the other two temperatures.

Commonly, emulsion polymerization is modeled as a process wherein the monomer has to migrate from the monomer droplet, migrate through the aqueous phase, be absorbed in the latex particle and, finally, diffuse through a reactive medium. Most investigators implicitly assume diffusion is fast and, therefore, all the phases are in their thermodynamic equilibrium state. Henninger et al.¹¹ have shown that mass transfer in the aqueous phase can control the rate of polymerization, but this resistance can be eliminated or greatly reduced by selection of appropriate stirrer type and speed. From a practical point of view, in any industrial application, conditions would be adjusted to minimize the mass transfer resistance and thus increase the production rate.

It is also assumed that there is negligible mass resistance in the polymer. To confirm this assumption,

the continuity equation in spherical coordinates can be written in its dimensionless form:

$$\frac{\partial C}{\partial \bar{t}} = \frac{\partial^2 C}{\partial \bar{r}^2} + \frac{2}{\bar{r}} \frac{\partial C}{\partial \bar{r}} - \left(\frac{k[M^*]R^2}{D_p} \right) C \quad (3)$$

Here C is the monomer concentration in the latex particle, \bar{t} is the time, \bar{r} is the length, all in dimensionless form. The dimensionless group in parentheses, also known as the Damkohler number (Da), compares the diffusion resistance to the reaction rate. As shown in eq. (3), the Da number depends on k , a second order reaction constant, the concentration of radicals on the latex particle $[M^*]$, the radius of the particle R , and on the diffusion coefficient of the monomer in the polymer phase. During emulsion polymerization, a pseudo steady-state is achieved in Stage II and, therefore, the transient part in eq. (3) can be neglected. The steady-state concentration profile in the particle latex is obtained by solving the right hand side of eq. (3), which depends on the Da number. Big Da numbers give sharp gradients inside the latex particle with the monomer being consumed before it reaches the center. Values smaller than 1 lead to flat concentration gradients with the monomer concentration similar to the surface value. An estimation for the Da number was made for the system of interest in this study. k was taken from Rodriguez¹²; $[M^*]$ was assumed to be 1 radical per latex particle during the polymerization process (converted to convenient units); D_p was taken from the diffusivity studies shown in Figure 3. For the typical range of particle sizes, the calculated value of the Da number was less than 0.01, suggesting that mass transfer in the latex particle is fast and the assumption of thermodynamic equilibrium between all the phases during the polymerization kinetics is a reasonable assumption.

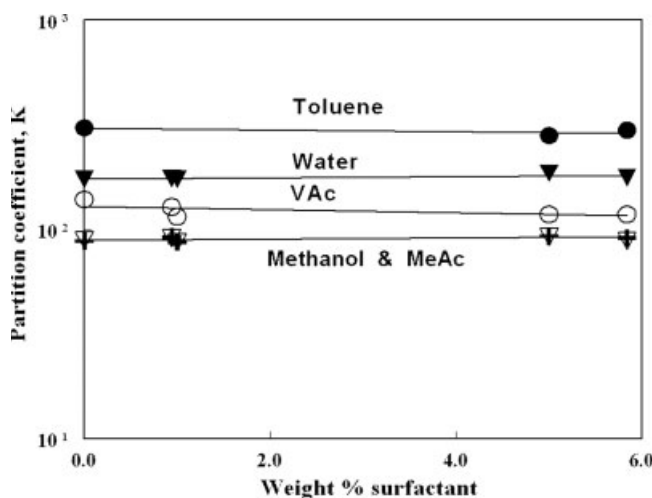


Figure 2 Partition coefficient as a function of surfactant concentration in PVAc at 60°C.

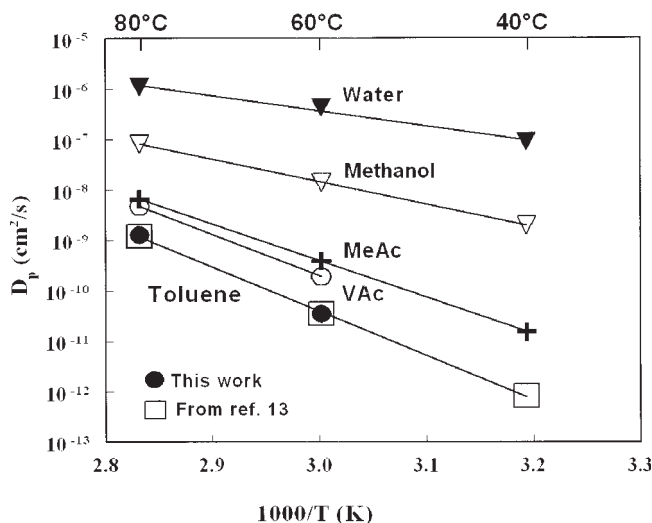


Figure 3 Temperature dependence of diffusion coefficients in PVAc.

The diffusion coefficients for the solvents in PVAc are shown in Figure 3. As expected, the diffusivities increase as the temperature increases following an Arrhenius behavior. The results for D_p appeared to be consistent and in good agreement with the literature data¹³ for toluene. Figure 4 shows how the diffusion coefficients of the compounds changed with the surfactant concentration. As expected, generally the diffusivity increases as the concentration of surfactant increases. This is ascribed to the increase of free volume with the addition of surfactant.¹⁴ However, the diffusivity of water decreases slightly as the surfactant concentration increases. This may be due to the interactions of the water and the surfactant. Figure 4 is for 60°C, but the same basic behavior was found at the other two temperatures. The solubility and diffusion

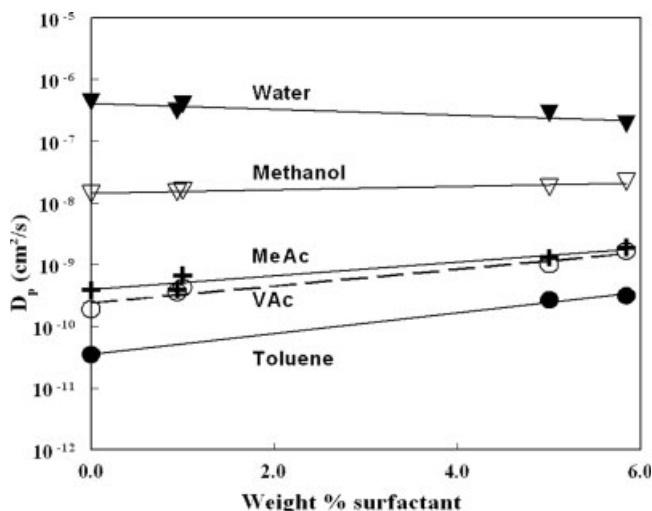


Figure 4 Surfactant concentration effect on solvent diffusivities in PVAc at 60°C.

data on the columns with low molecular weight surfactant in PVAc indicate that the effects of the low molecular weight surfactant are similar to the high molecular weight.

On the basis of the data for the partition coefficients, the weight fraction activity coefficients, Ω_1^∞ , and the Flory–Huggins interaction parameters, χ^∞ , at infinite dilution were calculated.

$$\Omega_1^\infty = \frac{RT}{V_g P_1^s M_1} \exp\left(\frac{-P_1^s (B_{11} - V_1)}{RT}\right) \quad (4)$$

$$\chi^\infty = \ln \Omega_1^\infty - \left(1 - \frac{1}{r}\right) + \ln \frac{\rho_1}{\rho_2} \quad (5)$$

Here $V_g = K/\rho_2$ is the specific retention volume, R is the gas constant, T is temperature, B_{11} is the second virial coefficient of the solvent, P_1^s is the saturation pressure of the solvent, ρ_1 and ρ_2 are the solvent and polymer densities, V_1 is the molar volume of solvent in the liquid phase, M_1 and M_2 are the molecular weight of the solvent and polymer, and $r = \rho_1 M_2 / \rho_2 M_1$ is the ratio of the molar volumes.

The temperature dependence of the infinite dilution activity coefficient of the low molecular weight components in PVAc and the χ^∞ parameter are shown in Figures 5 and 6. The results indicate that Ω_1^∞ and the χ^∞ parameter vary with temperature especially for the hydrogen-bonding solvents (water and methanol). In the PVAc–solvent systems, these parameters decrease as the temperature increases. The relatively large numbers for the infinite dilution activity coefficients of water and methanol in PVAc are indicative of the strong association of these chemicals in pure liquids. Both chemicals are sparingly soluble in the PVAc and, thus, these binary systems, as expected, reveal liquid–liquid miscibility gaps.

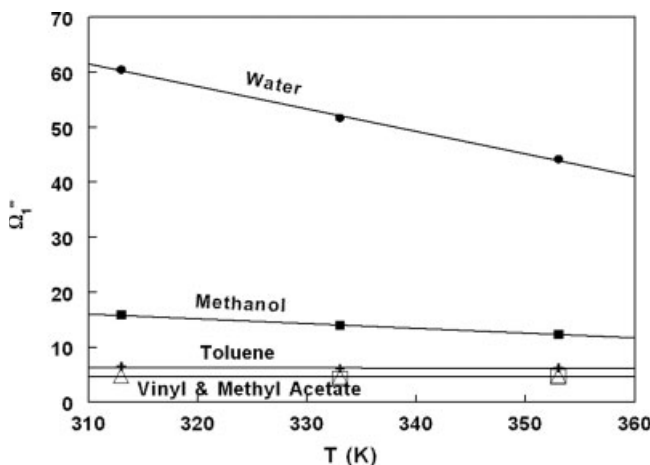


Figure 5 Temperature dependence of Ω_1^∞ for solvents in PVAc–solvent systems.

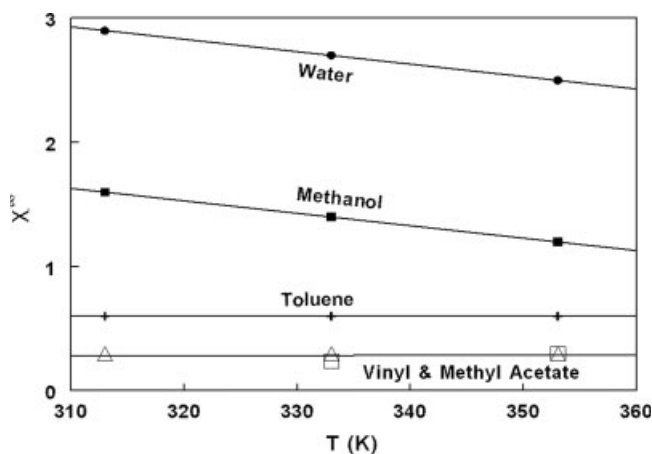


Figure 6 Temperature dependence of χ^∞ for solvents in PVAc-solvent systems.

Liquid-liquid phase diagram in the vinyl acetate-surfactant-water system

Liquid-liquid equilibria data were collected to determine partitioning of the surfactant, water, and VAc between the aqueous phase and the monomer-rich phase at 30°C. These measurements were made at different initial surfactant concentration from 1 to 10 wt % with water to VAc ratios of 50/50 and 90/10.

Various amounts of surfactant, VAc, and water were weighed, and the mixtures were sealed in flasks. After the samples were mixed with a vortex mixer, they were kept in a thermostat at 30°C for a period of 1 to 2 months until the equilibrium was established. The compositions of the equilibrium phases were determined using GC and HPLC.

Figure 7 shows the partitioning of surfactant between the VAc and water phases. It was found that the solubility of surfactant in the monomer-rich phase

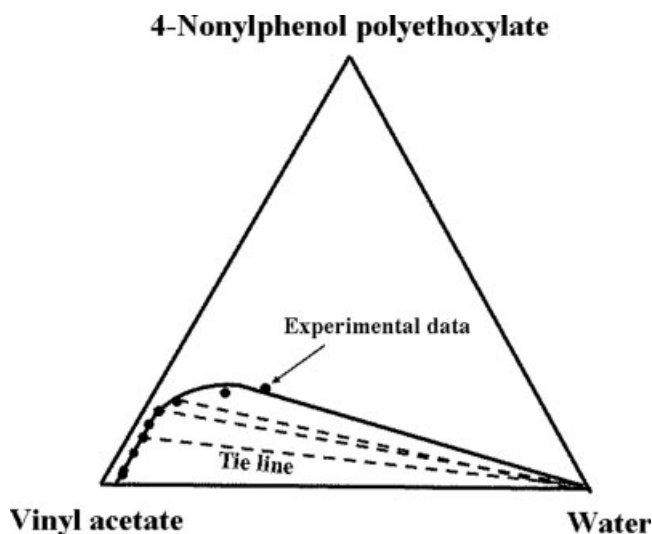


Figure 7 Liquid-liquid phase diagram for the system VAc-water-SF at 30°C.

is much higher than that in the aqueous phase. The concentration of surfactant in the monomer phase is two orders of magnitude higher than that in the water phase. It is known that nonionic surfactants distribute between oils and water and are more soluble in polar oils than in water. Ysambertt et al.¹⁵ demonstrated an increase in the partitioning coefficient (the ratio of the equilibrium organic phase surfactant monomer concentration to the equilibrium aqueous phase surfactant monomer concentration) of octyl phenol ethoxylates with increasing organic phase polarity. VAc is a polar solvent having the same dipole moment as water and some alcohols, and so the same behavior of 4-nonylphenol ethoxylates in the polar organic phase can be expected. Most of the studies in the literature were conducted using surfactant concentrations below the critical micelle concentration (CMC). In this study, the initial concentrations of surfactant are much higher than the very low CMC (10^{-4} M).

The influence of the surfactant concentration and its solubilization effect is especially pronounced at the ratio of water to VAc of 90 to 10. As a result, the solubility of water in the monomer phase increases considerably with increasing weight percent surfactant.

Vapor-liquid equilibria in binary, ternary, and quaternary systems

Experimental procedure

Vapor pressures were measured using a pneumatically driven thermostated head-space sampler (Hewlett-Packard Chromatograph 19395A with Headspace Sampler), which takes 5 mL of the gas phase in equilibrium with the polymer solution and injects the mixture of solvent and helium into the gas chromatograph equipped with a flame ionization detector. A 2-m steel column (inner diameter 1/8) was packed with Porapak Q, 60-80 mesh. The surfactant and polymer

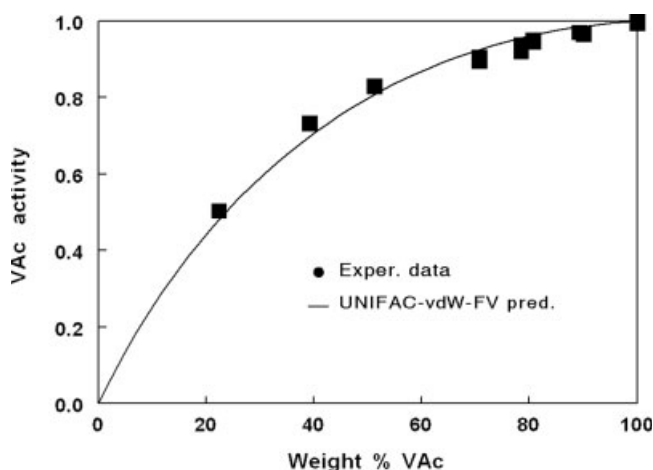


Figure 8 VAc activity as a function of VAc concentration in the VAc-SF system at 40°C.

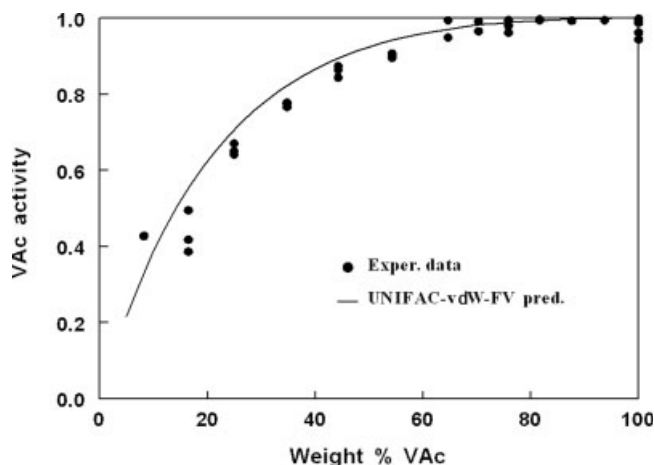


Figure 9 VAc activity as a function of VAc concentration in the VAc-PVAc system at 45°C.

both have negligible vapor pressures. The procedure was the same as described by Balashova and Larina.¹⁶

Vapor-liquid equilibrium results

The results of the measurements of the vapor-liquid equilibria and the concentration dependence of the VAc activity in the VAc-4-nonylphenol polyethoxylate (SF), VAc-PVAc, VAc-SF-PVAc systems at 40°C, and in VAc-PVAc system at 45°C are presented in Figures 8–11. Vapor pressure measurements of VAc in the mixture VAc-SF were made in the concentration range of 20–100 wt % VAc (Fig. 8), in the VAc-PVAc mixture over most of the concentration range of VAc (Fig. 9), and in the ternary system VAc-SF-PVAc in the VAc concentration ranges of 40–100 wt %, with the ratio of surfactant to polymer set to 50 : 50 (Fig. 10). Figure 11 illustrates the activity coefficient of VAc as a function of the surfactant weight fraction in the binary and ternary systems. In both systems, there are

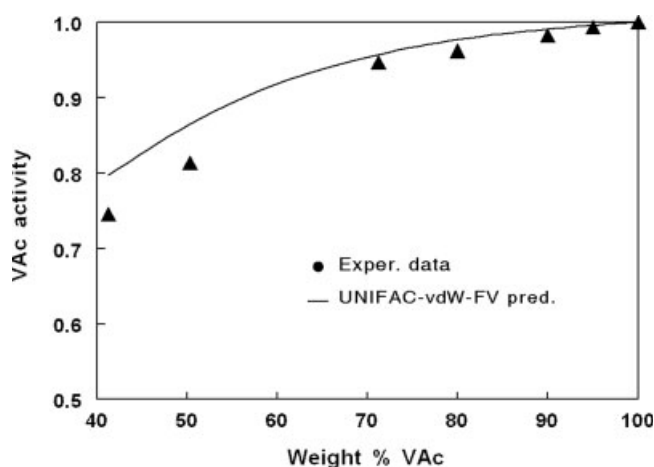


Figure 10 VAc activity as a function of VAc concentration in the VAc-SF-PVAc system at 40°C (PVAc/SF = 50/50).

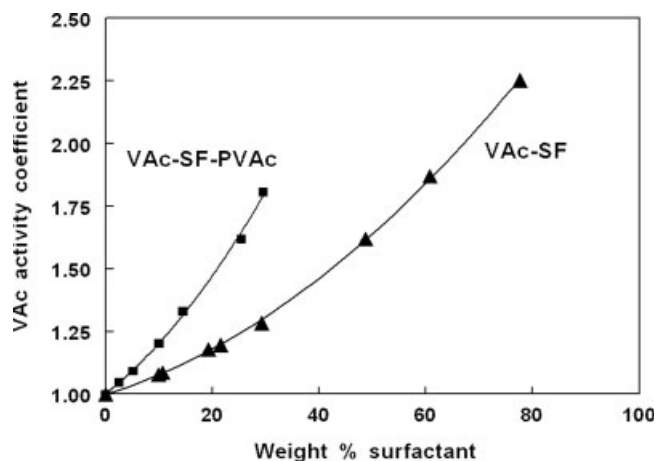


Figure 11 VAc activity coefficient as a function of surfactant concentration in the VAc-SF and VAc-SF-PVAc (PVAc/SF = 50/50) systems at 40°C.

positive deviations from Raoult' law. The VAc activity coefficient in the ternary system is much higher than that in the binary system, particularly at the high concentrations of SF. It has been hypothesized that the surfactant and polymer can form a complex.¹⁷ The ratio of surfactant to polymer in the complex changes with the amount of surfactant and polymer. It may be that formation of such a complex is influencing the VAc behavior at the higher concentrations of surfactant.

To obtain more information about the monomer behavior in the emulsion polymerization process, data have been collected for the quaternary system VAc-latex (the latex contains polymer, monomer, surfactant, and water). The headspace gas chromatography technique was used to investigate the saturation monomer concentration in the latex particles. The latex had an average particle size > 100 nm and was "dead" in the sense that it contained no active initiator and, thus, no further polymerization was pos-

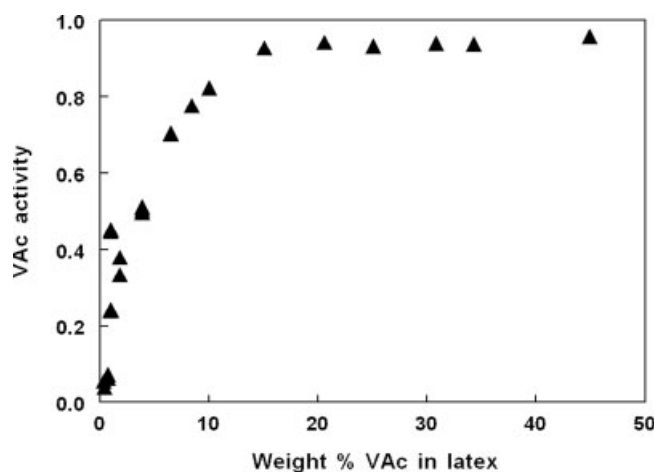


Figure 12 VAc activity as a function of VAc concentration in the VAc-Latex system at 40°C.

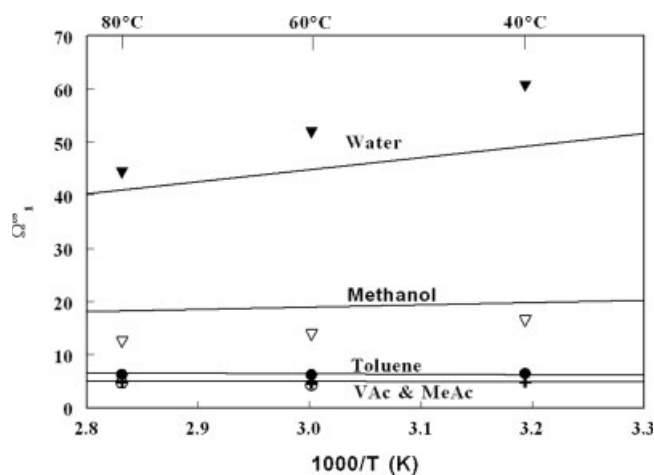


Figure 13 Predictions of the solvent weight fraction activity coefficients, using the UNIFAC-vdW-FV model. Points are experimental data.

sible. Different amounts of VAc were added to this latex and allowed to come to equilibrium at 40°C. The vapor pressure (activity) of monomer over the latex solutions were measured by the headspace technique.

As shown in Figure 12, ~ 15 wt % VAc (based on the latex mass) is enough to saturate the latex particles. The vapor pressure of VAc increases with the monomer concentration up to the saturation limit. Above saturation, the pressure is constant, since the three phases—water, polymer, and monomer—are in equilibrium.

Correlation and prediction of phase equilibrium in the binary and ternary systems

The behavior of the binary, ternary, and quaternary systems is complicated because of the formation of a complex between the surfactant and PVAc, the formation of micelles, and the swelling of the latex particles by water, monomer, and surfactant. We tested different models trying to predict the phase behavior of surfactant, monomer, and water, and how different species partition between the polymer latex phase and the aqueous phase.

The Flory–Huggins theory was examined as a means to characterize the thermodynamics of the latex system. Scott¹⁸ and Tompa¹⁹ were the first to extend the Flory–Huggins theory²⁰ to multicomponent mixtures. The results showed that for the binary and ternary systems, the interaction parameters (x_{ij}) were strong functions of concentration. Even for the binary system VAc–surfactant, when the concentration change was only 1–2 wt %, the change in the interaction parameter was about 30%. Consequently, to use the Flory–Huggins model, extensive experimental work would be required to determine the concentration dependence of the interaction parameters. Also, finding a solution for the nonlinear equations of the quaternary system

when the interaction parameters are concentration-dependent is difficult. This is consistent with Prausnitz et al.²¹ who discuss the difficulty of applying lattice-based theories when the interaction parameters depend on composition.

The UNIFAC-vdW-FV model based on lattice theory of Kannan et al.²² was used for the prediction of phase diagrams in polymer–solvent systems. This model was developed for the predictions in aqueous polymer solutions where the UNIFAC-FV model fails. We have used this model for the prediction of activity coefficients at infinite dilution of different solvents in PVAc–solvent and PVAc–surfactant–solvent systems, and for the prediction of the phase behavior of monomer–solvent–surfactant–polymer systems. The predictions for organic solvents, toluene, VAc, and methyl acetate activity coefficients at infinite dilution were quite good; the predictions for methanol are little bit high (Fig. 13). For water activity coefficient predictions, the deviations from experimental values at the different temperatures were within 7–20%. The predictions of the vapor–liquid equilibrium for the binary and ternary systems are quite good (Figs. 8–10). The deviations in VAc activity from the experimental data are less than 4% for the high concentration of polymer, and 1% in the average range of the concentration.

CONCLUSIONS

Diffusivity and solubility of solvents as a function of surfactant concentration in PVAc were measured by the use of IGC with capillary columns at 40, 60, and 80°C. The data showed that the solubility of all solvents decreases with increasing temperature. There was essentially no effect on the solubility of the surfactant concentration. The diffusivity of the compounds increases as the concentration of surfactant increases due to the additional free volume accompanying the surfactant.

Liquid–liquid and vapor–liquid equilibria for the binary (PVAc–solvents, SF–VAc), ternary (PVAc–solvents–surfactant, VAc–water–SF), and quaternary (PVAc–latex) systems were investigated at 30, 40, and 45°C.

The calculation of the Flory–Huggins interaction parameters showed that they are strong functions of the concentration. Consequently, to use the Flory–Huggins model to characterize the thermodynamics of the latex system, additional extensive experimental work would be required.

Activity coefficients of the solvents at infinite dilution in the polymer–solvent systems and vapor–liquid equilibria in the binary and ternary systems with PVAc, VAc, and surfactant over wide concentration range were predicted successfully using the UNIFAC-vdW-FV model.

Diffusion coefficients were also measured for the solvents in the PVAc. Analysis confirmed that the diffusion in the latex particles was so fast compared to the reaction that the assumption of uniform monomer composition through the particles was valid.

In most analyses of the emulsion polymerization process, it is assumed that the monomer concentration in the particles or polymer phase is constant during the period of the reaction when a separate liquid monomer phase is available. Consequently, during this phase of the reaction, when a free radical is present in the particle, the rate of polymerization is constant. This study shows that the presence of water and surfactant in the polymer phase could influence the monomer solubility. Furthermore, the presence of water and surfactant dissolved in the liquid monomer could influence the monomer activity and consequently its solubility in the polymer phase. Changes of the surfactant concentration in various phases are also influenced by the adsorption of the surfactant on the surface of the latex particles. In conclusion, this study clearly shows that the complex thermodynamic interactions in the multiphase, multicomponent emulsion polymerization process probably will lead to changes with time in the monomer concentration in the reacting polymer phase in contrast to the constant monomer concentration assumption, which is utilized in conventional emulsion polymerization kinetic models.

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