Acrylic Acid/Vinyl Acetate Suspension Copolymerizations. I. Partition Coefficients for Acrylic Acid

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ABSTRACT: During acrylic acid (AA)/vinyl acetate (VAc) suspension copolymerizations, AA is partitioned between the organic phase and the aqueous phase. For this reason, the AA partition coefficient in suspensions of AA/VAc/water is studied here. Partition experiments were performed at different temperatures and AA concentrations. It was observed that the AA partition coefficient ranged from 0.001 to 1.58, depending strongly on the temperature and on the aqueous phase composition. Therefore, the distribution of AA between the continuous phase and the monomer droplets may exert a significant effect upon the observed kinetic behavior during suspension polymerizations. The UNIFAC-LLE model was used to describe the observed liquid–liquid equilibrium of the ternary system AA/VAc/ water and model predictions were compared to the obtained experimental data. It was observed that the UNIFAC-LLE model is able to represent AA partition coefficients qualitatively only when AA dissociation effects are taken into consideration. Additional experiments also indicated that AA partition coefficients may be very sensitive to the presence of polymer in the organic phase and to the presence of salt in the aqueous phase, as usual during actual suspension copolymerizations. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1077–1088, 2004

Key words: copolymerization; miscibility; phase behavior; suspension polymerization

INTRODUCTION

Copolymers of vinyl acetate (VAc) and acrylic acid (AA) are important polymer materials, being used widely for production of paints and stickers of textiles, and of additives used in the mining, agriculture, cosmetics, and paper industries. They can also be used as additives for improvement of the quality of the soil and of the water.[1,2] As these materials are relatively inert, they can be used as thickeners, tampon agents, and polymer supports for applications in biotechnology. AA/VAc copolymers are also being used for covering of medicines and pills.[3]

AA/VAc copolymers can be produced through free radical polymerizations in solution, emulsion, and suspension processes.[3] However, the molecular weight of the final polymer obtained through solution polymerizations is usually much lower than required by most applications. Also, performing AA/VAc copolymerizations in emulsion can be very complex, given the high solubilities of AA and VAc in water and the large number of additives required to stabilize the reaction medium. For all these reasons, development of suspension processes to perform AA/VAc copolymerizations sounds very attractive.

In suspension copolymerizations, if monomers are insoluble in the suspending medium (generally water), the kinetic behavior of the reaction system and the final copolymer properties are essentially equal to those obtained in bulk copolymerizations. However, if monomers have different solubilities in the suspending medium, significant changes of the copolymerization kinetics and of the final properties of the copolymer should be expected, when both suspension and bulk processes are compared.

The AA/VAc suspension copolymerization differs from usual polymerization processes because AA is completely soluble in water (the suspending phase). For that, AA is partitioned between the organic phase, which contains most of the VAc, and the aqueous phase, which contains most of the AA. Due to this particular feature, the determination of the AA partition coefficient between the organic phase and the aqueous phase can be of fundamental importance for proper design of the process operation conditions.

The fundamental point for comprehension of suspension processes when monomer is partially or completely soluble in water is that the amount of monomer available for polymerization within the organic droplets is different from the total amount of monomer within the reactor vessel. The main consequence is that rates of monomer consumption can be strongly affected by monomer partitioning between the twos phases, significantly changing the

kinetic behavior of the process and the final copolymer composition.

Some recent works have focused upon the effects of monomer solubility on the polymer properties during heterogeneous polymerizations as discussed by Fernández-García.[4] Particularly, reactivity ratios can depend strongly on modifications of the chemical composition of the reaction medium, which are expected to occur during heterogeneous polymerization.

Important chemical and kinetic effects induced by partitioning of a monomer between the aqueous phase and the organic phase have been observed in microemulsion polymerizations, especially when the high contents of emulsifier affect the monomer solubility. Sanghvi et al.[5] studied the styrene/acrylonitrile copolymerization in microemulsion. They observed that 56% of the initial load of acrylonitrile were present in the droplets, while the remaining 44% were solubilized in the aqueous phase of the microemulsion system. As a consequence, reactivity ratios, polymerization rates, and copolymer composition were shown to change significantly along the batch. Similar behavior was observed by Xu et al.[6] in styrene/butyl acrylate and styrene/methyl acrylate microemulsion polymerizations. Sanghvi et al.[7] showed that if the monomer concentration in the many phases of the reaction system is not described accurately incorrect description of the kinetic behavior is obtained.

It is interesting to note that Bhawal and Devi[8] showed that ethyl acrylate/methyl methacrylate copolymers synthesized through emulsion polymerization can present two different glass transition temperatures. According to these authors, the polymer obtained by homogeneous nucleation had a greater fraction of the relatively more water-soluble ethyl acrylate, which contributed to the lower glass transition temperature. However, the copolymer obtained through micellar polymerization was rich in methyl methacrylate, which contributed to the higher glass transition temperature. In this case, the different monomer concentrations at the distinct polymerization loci resulted in different copolymer fractions, despite the homogeneous feed composition.

Based on the previous paragraphs, it seems clear that the AA partitioning between the aqueous and organic phases must be characterized, if the AA/VAc suspension copolymerizations are to be performed appropriately. The main objective of this work is presenting monomer partition data for the system AA/VAc/H_2O, at conditions usually required to perform AA/VAc suspension copolymerizations.

EXPERIMENTAL

Polymerization grade VAc and AA monomers were provided by Rhodia, Campinas, Brasil, with a minimum purity of 99.9%. Poly(vinyl alcohol) with a
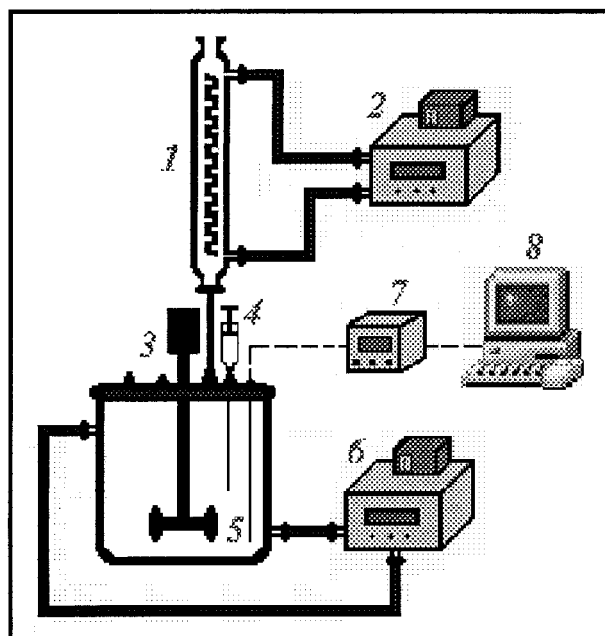

Figure 1 Experimental unit used for partition coefficient determination. (1) Reflux condenser; (2) refrigeration bath; (3) glass reactor; (4) sampling; (5) thermocouple; (6) heating bath; (7) module of signal conditioning; (8) microcomputer for data acquisition.

weight-average molecular weight of 78,000 Da and degree of hydrolysis of 85% was supplied by VETEC Química Fina, Rio de Janeiro, Brasil, and used as a suspending agent. Nitrogen was supplied by AGA S/A, Rio de Janeiro, Brasil, with 99.9% purity. Hydroquinone was supplied by VETEC Química Fina, with minimum purity of 99%. Sodium hydroxide was supplied by VETEC Química Fina, with 97% of purity. Phenolphthalein was supplied by VETEC Química Fina, Sodium chloride was supplied by Química Fina, with minimum purity of 99%. All reagents were used as received, without additional purification. Distilled water was used as suspension medium for partition experiments.

Partition experiments were carried out in a 300-mL jacketed glass reactor. Experiments were performed at 60, 70, and 80°C (except for partition experiments with sodium chloride, which were carried out at 70°C), with 30% in weight of organic phase, and with 100–200 ppm of hydroquinone, to guarantee that polymerization would not take place during the experiments. The scheme of the experimental unit is presented in Figure 1. The overall concentration of AA in the organic phase was varied within the range of 2.5–20% in weight. The reactor was equipped with a reflux condenser, connected to a refrigeration bath (PolyScience KR30-TO). A tachometer (Takotron TD2004-C) was used to measure and control the speed of agitation. A heating bath (Haake DC-3) was used to maintain the temperature of the reaction medium at the desired set

point value. The mechanical agitator (Fisaton 713-T) was equipped with a blade-type impeller and the speed of agitation ranged from 90 to 6000 rpm. J-type thermocouples were used to monitor and control the reactor temperature. The temperature of the reaction medium and the agitation speed were monitored and controlled in line through a microcomputer equipped with a data acquisition system AD/DA (analog-digital/digital-analog model LabView PC, National Instruments).

After addition of the chemical constituents into the reactor flask, the agitator was turned on. Agitation speed was then kept constant for 60 min. Afterwards, the agitator was turned off and the system was allowed to rest for additional 60 min. After that, thermodynamic equilibrium conditions were assumed to exist. Samples of 30 mL of each phase were then collected by slow draining through the bottom of the reactor flask. Aqueous phase samples were used to evaluate the AA and VAc aqueous content. AA and VAc contents in the organic phase were obtained with the help of the overall mass balances.

Partition coefficients of AA between the organic phase and the aqueous phase were determined through potentiometric titration with 0.1 M solutions of NaOH in water. The analyses were performed with the help of high precision burettes with capacity of 50 mL, also using 3 droplets of a 0.03 M phenolphthalein solution (prepared in ethanol 60% v/v) as a visual indicator of the neutralization point. About 5 mL of the aqueous phase sample was utilized for analysis. To guarantee the reproducibility of the experimental measurements, titrations were performed three times at each particular experimental condition. After titration, the AA concentration in the aqueous phase can be determined with the following equation

$$[AA]^{II} = \frac{\eta_T V_T PM_2}{V_S} \tag{1}$$

where $[AA]^{II}$ is the AA molar concentration in the aqueous phase, η_T is the molar concentration of NaOH in the reference NaOH solution, V_T is the volume of the NaOH solution required for neutralization of the AA aqueous sample, PM_2 is the molecular weight of AA, and V_S is the volume of the analyzed sample of the aqueous phase.

As the total mass of AA added into the reactor is known (m_2), the masses of AA in the organic phase (m_2^I) and in the aqueous phase (m_2^{II}) satisfy the following mass balance constraint

$$m_2 = m_2^I + m_2^{II} \tag{2}$$

The concentrations of AA in the aqueous and organic phases can also be given by:

TABLE I
Density Values Used for Numerical Computations

Component	Density (g/mL)	Reference
VAc	$\rho_1 = 0.9584 - 1.3276 \cdot 10^{-3} (T - 273.15)$	19
AA	$\rho_2 = 1.0821 - 1.1969 \cdot 10^{-3} (T - 273.15)$	20
H_2O	$\rho_w = 1.00066 - 7.35 \cdot 10^{-5}(T - 273.15) - 3.5 \cdot 10^{-6} (T - 273.15)$	21

$$[AA]^I = \frac{m_2^I/PM_2}{V^I} \tag{3}$$

$$[AA]^{II} = \frac{m_2^{II}/PM_2}{V^{II}} \tag{4}$$

The volumes of the overall aqueous and organic phases can be given by:

$$V^I = \frac{m_1}{\rho_1} + \frac{m_2^I}{\rho_2} \tag{5}$$

$$V^{II} = \frac{m_w}{\rho_w} + \frac{m_2^{II}}{\rho_2} \tag{6}$$

where m_1 and m_W are the masses of VAc and H_2O; and ρ_1, ρ_2, and ρ_W are the densities of VAc, AA, and H_2O, respectively. It is implicitly assumed that volume additivity holds, and that the amounts of water in the organic phase and of VAc in the aqueous phase can be neglected. Equations (1)–(6) are used to compute the mass distribution of all chemical species between the two phases. The overall volumes and masses computed for each phase were compared to experimental values, to avoid gross errors. Density values used for computation are presented in Table I. The partition coefficient of AA can finally be defined as the ratio between the molar concentrations in the two phases and can be represented by:

$$K = \frac{[AA]^I}{[AA]^{II}} \tag{7}$$

Gas chromatography was used to determine the solubility of VAc in water in the presence of AA. A standard gas chromatograph (Varian 3350) equipped with a flame ionization detector and with capillary GSQ columns (J&S Scientific) was used for analyses. Acetone was used as an internal calibration standard. Figure 2 shows the obtained calibration curve. Volumes of 1 mL of aqueous phase were diluted 10 times in a 0.1% wt solution of acetone. To avoid the saturation of the capillary column, approximately 1 μL of the sample was injected into the chromatograph. Analyses were repeated three times at each particular experimental condition to guarantee the reproducibility of
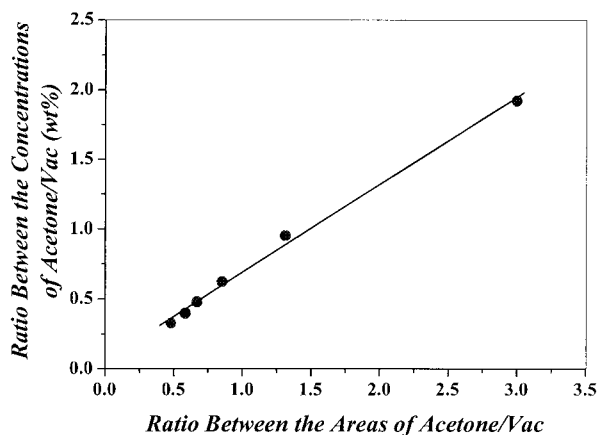
Figure 2 Calibration curve for chromatography.

the experimental value. The chromatograph was operated with the following conditions: injector, column, and detector were maintained constant at 180, 200, and 250°C, respectively; volumetric flow of nitrogen, hydrogen, and compressed air were kept constant at 30, 30, and 300 mL/min, respectively; column pressure was maintained constant at 12 psig; volumetric flow into the column was kept constant at 9 mL/min and a nitrogen makeup of 21 mL/min was used.

A conductivity meter (Tecnopon mCA-150) was also employed for indirect evaluation of the AA concentration in the aqueous phase. Conductivity measurements were performed in a glass flask of 100 mL. Conductivity values were determined for suspensions containing different concentrations of VAc, AA, and AA/VAc copolymer.

MODELING OF LIQUID–LIQUID EQUILIBRIUM

Activity coefficient

There is a relatively large number of models used to describe activity coefficients in multicomponent mixtures. Among them, models based on the concept of local composition (e.g., WILSON, MARGULES, VAN LAAR, NRTL) and models based on the concept of group contribution (e.g., ASOG, UNIQUAC, UNIFAC) are the most well known.[9]

Particularly, the use of group contribution methods is quite attractive, mainly when experimental data for the system of interest are not available or are scarce. Such models are believed to generate satisfactory results, even when little is known about the liquid–liquid equilibrium (LLE) of the studied process.

The UNIFAC model originally developed by Frendenslund et al.[10] is used here to describe the ternary system AA/VAc/H_2O. The UNIFAC model assumes that the liquid mixture can be treated as a solution of structural chemical groups (e.g., —CH_3, —CH_2O—,

—CH_2NO_2, H_2O, etc.). It is assumed that the size and shape of the groups and the interactions between the different groups determine the properties of the liquid mixtures.[11]

The activity coefficient (γ_i) of a component in the mixture can then be described as the sum of a configurational contribution that is due to differences of the molecular size of the different groups and the spatial distribution of the groups in the liquid phase, and a residual contribution, due to the interaction forces among the many groups that constitute the phase.

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^R \qquad (8)$$

where $\ln\gamma_i^C$ represents the configurational or combinatorial contribution, and $\ln\gamma_i^R$ is the residual contribution.

The UNIQUAC model supplies the *combinatorial* portion for the UNIFAC group contribution method as:

$$\ln\gamma_i^c = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i\ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{NC}x_jl_j \qquad (9)$$

with

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - l) \qquad (10)$$

In eqs. (9) and (10), z is the coordination number and represents the number of molecules within the coordination sphere of any particular molecule considered (normally assumed to be equal to 10). NC is the number of constituents of the chemical mixture.

The area (θ_i) and volume (Φ_i) fractions are given as:

$$\theta_i = \frac{r_ix_i}{\sum\limits_{j=1}^{NC}r_jx_j} \qquad (11)$$

$$\Phi_i = \frac{q_ix_i}{\sum\limits_{j=1}^{NC}q_jx_j} \qquad (12)$$

where x_i stands for the molar fraction of the ith component of the mixture. The parameters r_i and q_i represent the superficial area and the Van der Waals molecular volume, respectively, and can be calculated as:

$$r_i = \sum_{k=1}^{NG}\upsilon_k^{(i)}R_k \qquad (13)$$

$$q_i = \sum_{k=1}^{NG} v_k^{(i)} Q_k \qquad (14)$$

where $v_k^{(i)}$ is the number of groups of type k in molecule i, and NG is the number of distinct chemical groups in the mixture. The parameters R_k and Q_k are the parameters that characterize the area and volume contributions of the functional groups.

The ASOG model supplies the *residual* part of the activity coefficient of the UNIFAC model as:

$$\ln \gamma_i^R = \sum_{k=1}^{NG} v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (15)$$

where Γ_k is the residual activity coefficient of the group k in the solution, and $\Gamma_k^{(i)}$ is the residual activity coefficient of the group k in a reference solution that contains molecules of the component i only.

The activity coefficient Γ_k is given by:

$$\ln \Gamma_k = Q_k \left[l - \ln\left(\sum_{m=1}^{NG} \Theta_m \Psi_{mk} \right) - \sum_{m=1}^{NG} \frac{\Theta_m \Psi_{km}}{\sum_{n=1}^{NG} \Theta_n \Psi_{nm}} \right] \qquad (16)$$

which can also be used for computation of $\Gamma_k^{(i)}$ as:

$$\ln \Gamma_k^{(i)} = Q_k \left[1 - \ln\left(\sum_{m=1}^{NG} \Theta_m^{(i)} \Psi_{mk} \right) - \sum_{m=1}^{NG} \frac{\Theta_m^{(i)} \Psi_{km}}{\sum_{n=1}^{NG} \Theta_n^{(i)} \Psi_{nm}} \right] \qquad (17)$$

The area fraction of the group m (Θ_m) is given by:

$$\Theta_m = \frac{Q_m X_m}{\sum_{n=1}^{NG} Q_n X_n} \qquad (18)$$

where X_m represents the molar fraction of the group m in the mixture as:

$$X_m = \frac{\sum_{j=1}^{NC} v_m^{(j)} x_j}{\sum_{j=1}^{NC} \sum_{k=1}^{NG} v_k^{(j)} x_j} \qquad (19)$$

The interaction parameters Ψ_{mn} are given by:

$$\Psi_{mn} = \exp\left[-\left(\frac{U_{mn} - U_{nn}}{RT} \right) \right] = \exp\left(-\frac{\alpha_{mn}}{T} \right) \qquad (20)$$

TABLE II
Number of Groups of Type k in Molecule i

	$v_k^{(i)}$			
	CH$_2$=CH (1)	CH$_3$COO (2)	H$_2$O (3)	COOH (4)
VAc (1)	1	1	0	0
H$_2$O (2)	0	0	1	0
AA (3)	1	0	0	1

where U_{mn} is a measure of the interaction energy between the functional groups m and n. The interaction parameters a_{mn} and a_{nm} ($a_{mn} \neq a_{mn}$) are normally obtained from experimental phase equilibrium data. Magnussen et al.[12] present parameters of interaction a_{mn} for 32 distinct functional groups, based on experimental liquid–liquid equilibrium data.

Equilibrium compositions

The composition of the distinct liquid phases at liquid–liquid equilibrium can be determined through solution of the following system of equations:

$$y_i^{\mathrm{I}} \gamma_i^{\mathrm{I}} = y_i^{\mathrm{II}} \gamma_i^{\mathrm{II}} \quad i = 1,2,3 \qquad (21)$$

$$n_i = y_i^{\mathrm{I}} N^{\mathrm{I}} + y_i^{\mathrm{II}} N^{\mathrm{II}} \quad i = 1,2,3 \qquad (22)$$

$$\sum_{j=1}^{NC} y_j^i = 1 \quad i = \mathrm{I,II} \qquad (23)$$

where n_i is the total number of moles of component i in the mixture (which is known), y_i^j is the mol fraction of the component i in the phase j, N_i^j is the number of mol of component i in the phase j, and γ_i^j is the activity coefficient of the component i in the phase j (computed with the activity model).

This set of equations was solved numerically, using the modified method of Levenberg-Marquardt.[13,14] The standard numerical procedure DUNLSF, obtained from the IMSL™ library,[15] was used for implementation of the computer code. Numerical solutions were obtained with absolute tolerance of 10^{-8}. The parameters used for calculation of the activity coefficients are listed in Tables II–IV.

RESULTS AND DISCUSSION

AA partition coefficients

The AA partition coefficient can be defined as the ratio between the AA molar concentration in the organic phase and the AA molar concentration in the aqueous phase, as shown in eq. (7). Figure 3 shows the partition coefficient (K) as a function of the AA concentration in the aqueous phase at 60, 70, and 80°C. It can be ob-

TABLE III
Interaction Group Parameters[12]

	α_{mn}			
	CH$_2$=CH (1)	CH$_3$COO (2)	H$_2$O (3)	COOH (4)
CH$_2$=CH (1)	0	−577.50	896.0	1647.0
CH$_3$COO (2)	485.60	0	385.9	1417.0
H$_2$O (3)	220.60	−6.32	0	−465.7
COOH (4)	−48.52	−117.60	652.3	0

served that the temperature exerts significant influence upon the partition coefficient. The higher the temperature, the higher the partition coefficient, which indicates a decrease of the relative solubility in water when temperature increases. Therefore, the rate of AA incorporation in the copolymer should be expected to increase at higher temperatures during suspension AA/VAc copolymerizations. However, Figure 3 also shows remarkable changes of the AA partition coefficient as the AA concentration decreases, as it happens during polymerization. Particularly, as the AA concentration decreases, AA molecules tend to remain in the aqueous phase. This may exert a profound effect during batch copolymerizations, as the rate of AA incorporation in the copolymer may be expected to decrease dramatically as reaction proceeds, leading to larger composition drifts when compared to usual solution copolymerizations.

The variation of AA partition coefficients can be understood qualitatively if the ionic equilibrium of AA in water is considered. For example,

$$K_I = \frac{[AA^-][H^+]}{[AA]} = \frac{\alpha^2[AA]_0^2}{(1-\alpha)[AA]_0} \qquad (24)$$

where α is the degree of dissociation of AA in water. According to eq. (24) the larger the concentration of AA in the aqueous phase, the smaller the degree of dissociation of AA molecules and the larger the AA affinity for the organic phase, as it is believed that AA molecules are not dissociated in the organic phase. An important piece of information that can be obtained from Figure 3 is the existence of a minimum AA concentration limit (0.13 mol/L), below which AA remains almost completely in the aqueous phase, so that effective AA/VAc copolymerizations cannot be

TABLE IV
Surface and Volume Group Parameters[12]

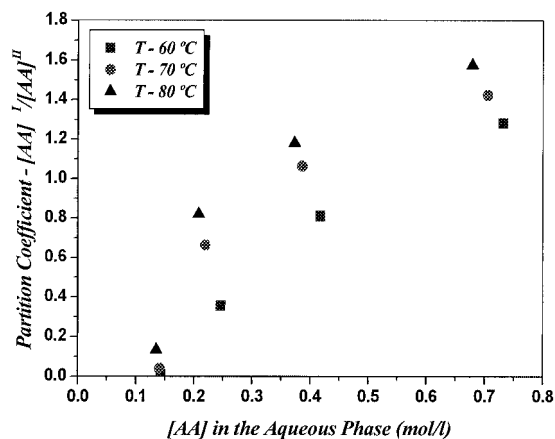|	R_k	Q_k
CH$_2$=CH (1)	1.3454	1.1760
CH$_3$COO (2)	1.9031	1.7280
H$_2$O (3)	0.9200	1.4000
COOH (4)	1.3013	1.2240

Figure 3 AA partition coefficient at different temperatures and concentrations.

performed below this AA concentration limit. Therefore, operation procedures should be developed either to recover unreacted AA or to increase partition coefficients during actual copolymerizations, to avoid waste of AA monomer.

Influence of AA concentration on VAc solubility in water

The influence of AA concentration on the solubility of VAc in water is shown in Figure 4. According to Figure 4, it can be observed that the presence of AA exerts a strong influence on the solubility of the VAc in water, and that this effect becomes more pronounced as the amount of AA increases. The larger the amount of AA in the feed, the lower the VAc solubility in water, probably because of AA dissociation in the aqueous phase. The remarkable influence of AA becomes evident when one compares the data in Figure 4 with solubility data obtained for pure VAc. Kalfas et
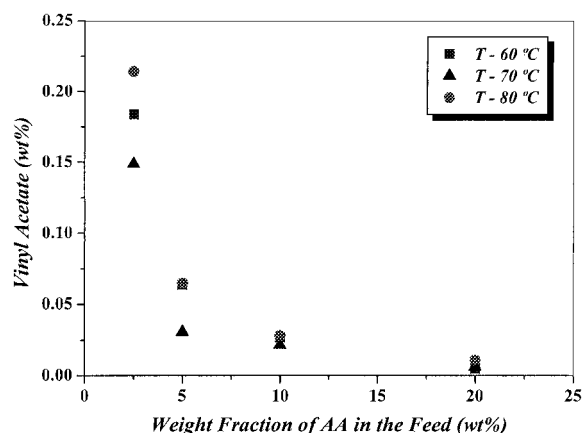

Figure 4 Influence of AA concentration on VAc solubility in water.

al.[16,17] found that solubility of the VAc in water is equal to 3% at 70°C, as confirmed independently in this work. This value is about 20 times larger than the one obtained in presence of only 2.5% of AA at the same temperature. Therefore, for most practical reasons, the total amount of VAc in the aqueous phase can be neglected during AA/VAc suspension copolymerizations.

Liquid–liquid equilibrium

Simulation studies were performed to evaluate whether the available experimental data could be interpreted in terms of the popular UNIFAC group contribution model. Figure 5 shows simulation results obtained for the binary system AA/VAc. It can be observed that the system behavior is strongly nonideal [see Fig. 5(A)], and that significant variations of the activity coefficient occur when the composition changes, especially for AA low concentrations. The complete miscibility of VAc and AA can be verified in Figure 5(C), as inflection points are not formed in the diagram when the AA concentration changes. It is interesting to observe, that the activity of AA remains approximately constant in a wide range of concentration values ($0.8 < y_{VAc} < 0.95$), which probably explains why AA remains almost completely in the aqueous phase of low AA concentrations, providing independent simulation support for the obtained experimental data. It is interesting to observe that activities are not sensitive to temperatures variations in the range analyzed.

Simulation results obtained for the binary system VAc/H_2O are presented in Figure 6. According to Figure 6(A), the system is highly nonideal, showing appreciable variations of the activity coefficients as concentrations change. Figure 6(B) and (C) shows that the system exhibits phase split phenomena, as two local minima can be observed in the diagram that describes how the Gibbs free energy of mixture changes with the system composition. The points of minimum are placed approximately at 2% of VAc in water and 5% of H_2O in VAc. Once again, activity coefficients are not very sensitive to temperature changes.

For the binary system AA/H_2O, the obtained simulation results are presented in Figure 7(A)–(C). As shown in Figure 7(A), the nonideal behavior of the mixture seems to be less pronounced, when compared to the binaries AA/VAc and VAc/H_2O. In this system, the water presents the characteristic behavior of an almost ideal solution, as its activity coefficient is close to 1 in the whole range of compositions. According to Figure 7(B) and (C), phase separation does not occur demonstrating the complete solubility of AA in water.
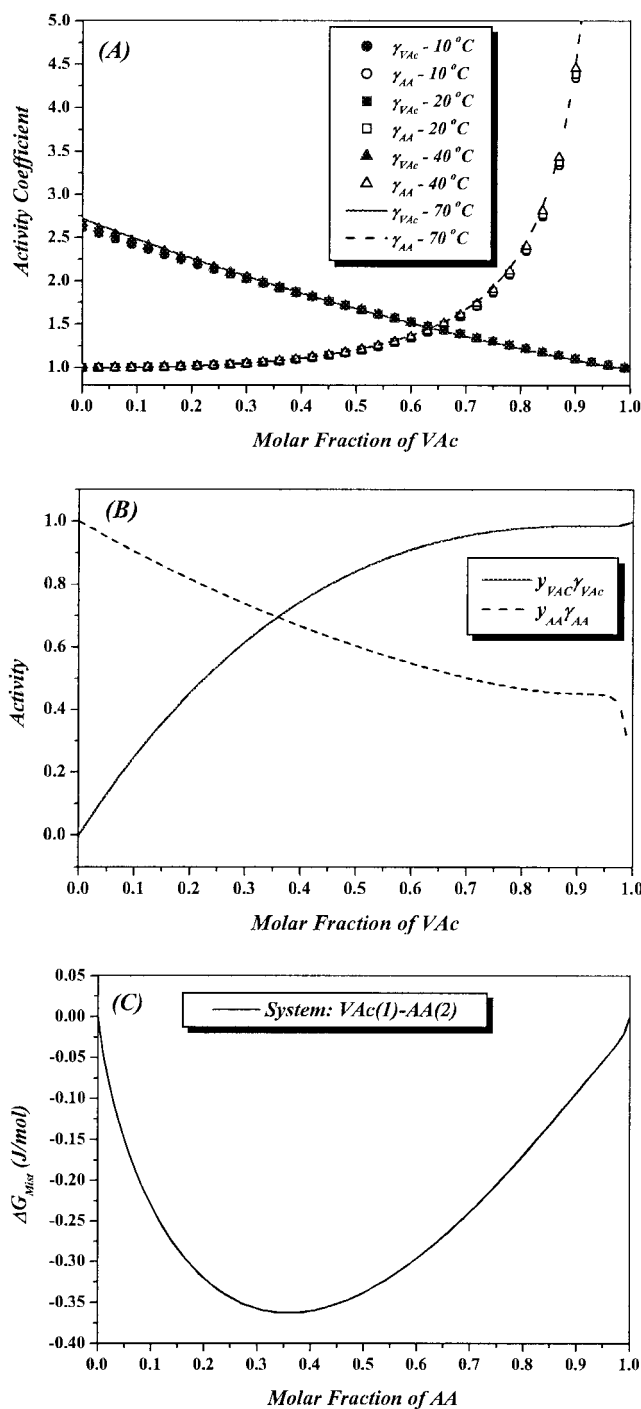

Figure 5 Binary system VAc(1)–AA(2): (A) activity coefficient; (B) activity ($T − 70°C$); (C) Gibbs free energy of mixing ($T − 70°C$).

Experimental solubility data for VAc in water and AA partition coefficients between the organic phase and aqueous phase at different temperatures are compared with model predictions in Figures 8 and 9. Figure 8 shows that although model predictions do not describe exactly the solubility of VAc in water, the qualitative behavior is captured appropriately. The
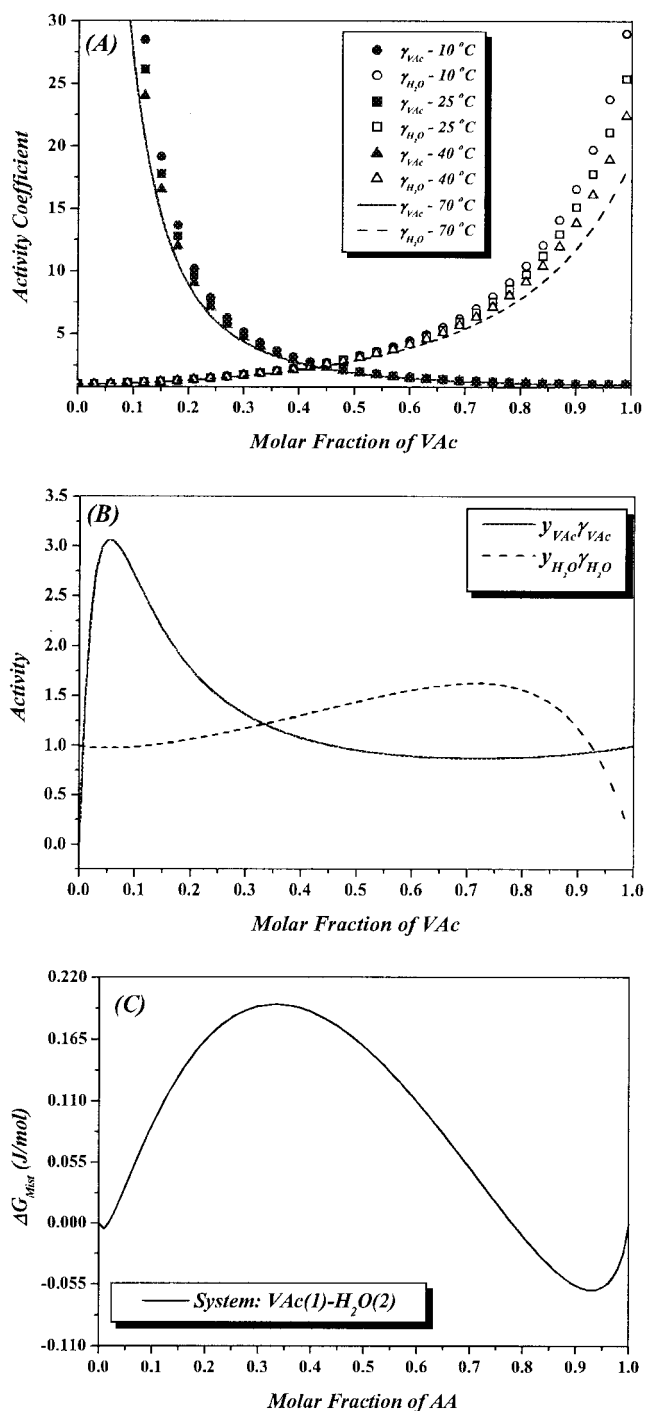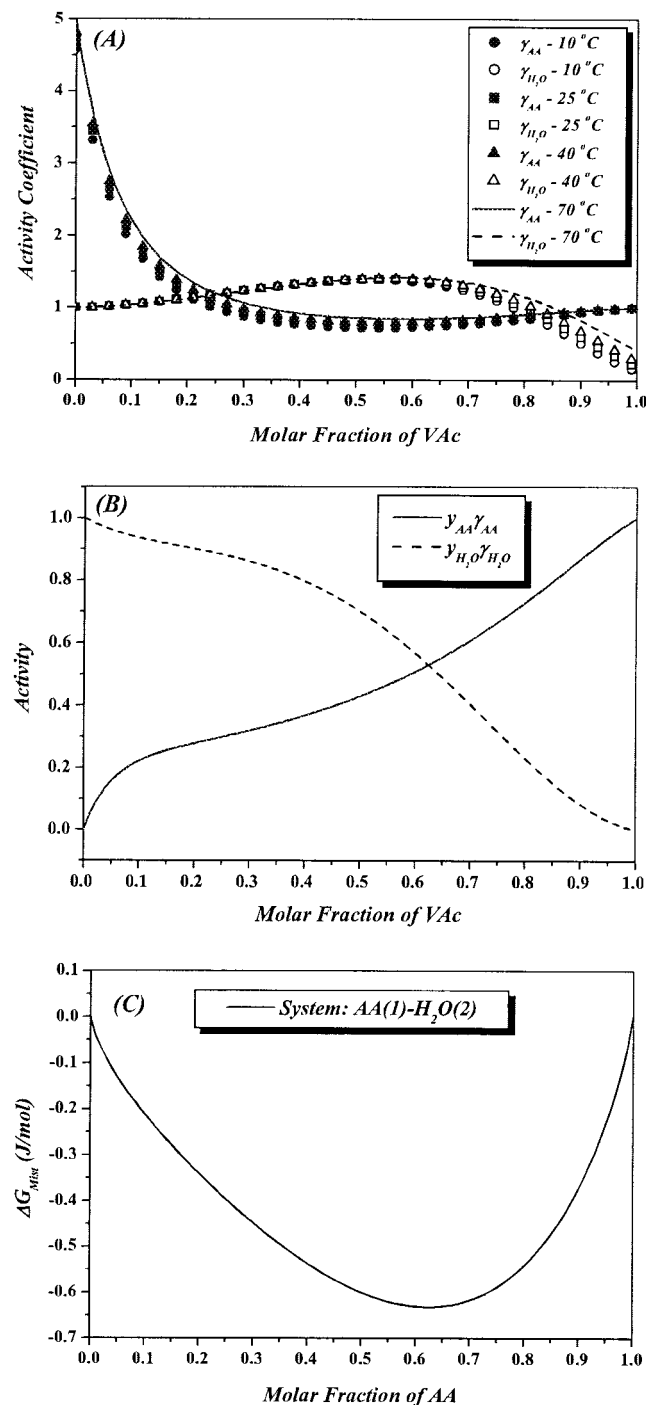
Figure 6 Binary system VAc(1)–H$_2$O(2): (A) activity coefficient; (B) activity ($T - 70°C$); (C) Gibbs free energy of mixing ($T - 70°C$).

the UNIFAC-LLE model for different ternary systems containing acids and observed the inefficacy of the model in many cases. Also, according to Magnussen et al.,[11] a group of contribution models usually describe well the binodal curve, but can present appreciable errors for low concentrations.

To illustrate how modeling of the ionic nature of the medium can allow for significant improvement of the

Figure 7 Binary system AA(1)–H$_2$O(2): (A) activity coefficient; (B) activity (T-70°C); (C) Gibbs free energy of mixing ($T - 70°C$).

results supplied by the UNIFAC-LLE model for the AA partition coefficient are presented in Figure 9 and compared to the experiment data. The model is unable to predict the enormous sensitivity of the partition coefficient to variations of the composition of the medium. This fact can probably be attributed to the ionic nature of the AA/H$_2$O solution. Tochigi et al.[18] tested
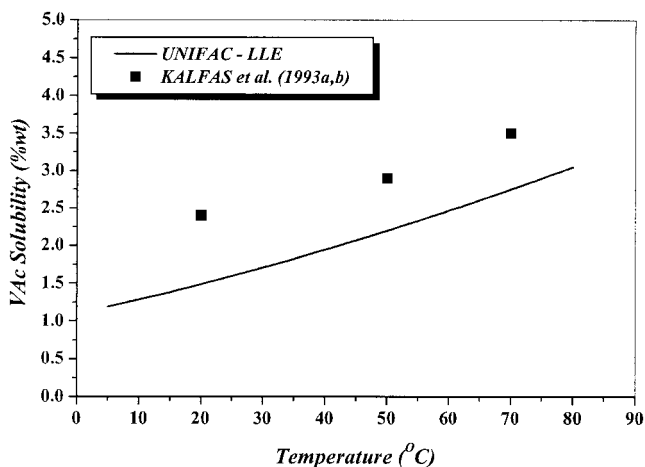
Figure 8 VAc solubility in water.

simulation results, the equilibrium equations are rewritten below. It is assumed that there are four different chemical species in the medium: $VAc^{(1)}$, $AA^{(2)}$, $AA^{-(3)}$, and $H_2O^{(4)}$. Based on the results presented previously, it is assumed, that only AA is distributed between the phases. Then

$$n_1^I = N_{VAc} \qquad n_1^{II} = 0$$
$$n_2^I = x \qquad n_2^{II} = y$$
$$n_3^I = 0 \qquad n_3^{II} = N_{AA} - x - y$$
$$n_4^I = 0 \qquad n_4^{II} = N_{H_2O} \qquad (25)$$

$$K^{ionic} = \frac{[N_{AA} - x - y]^2}{[y]} \qquad (26)$$

$$\gamma_2^I x_2^I = \gamma_2^{II} x_2^{II} \qquad (27)$$

Figure 10 illustrates how simulation results change when the ionic character of the medium is taken into consideration. Although quantitative results cannot be regarded as good yet, qualitative results are improved very significantly when it is assumed that part of the AA present in the medium is dissociated in the aqueous phase. Particularly, it is shown that the extremely large variations of the AA partition coefficient can be explained in terms of the ionic equilibrium of AA in water, which seems to indicate that the sensitivity of the AA partition coefficients to temperature variations is mainly due to the ionic equilibrium of AA in water. Therefore, the key factor for comprehension of the AA partition coefficient in the $AA/VAc/H_2O$ system is the ionic equilibrium of AA in water.

Based on the performed simulations the ionic equilibrium constant (K^{ionic}) can be described as:

$$K^{ionic} = \exp\left(-54.394 + \frac{18583.3}{T_2}\right) \qquad (28)$$

Modeling and simulating the liquid–liquid equilibrium in the presence of electrolytes is beyond the scope of this text, given the much more complex structure of required thermodynamic models and the much larger number of model parameters. For this reason, to
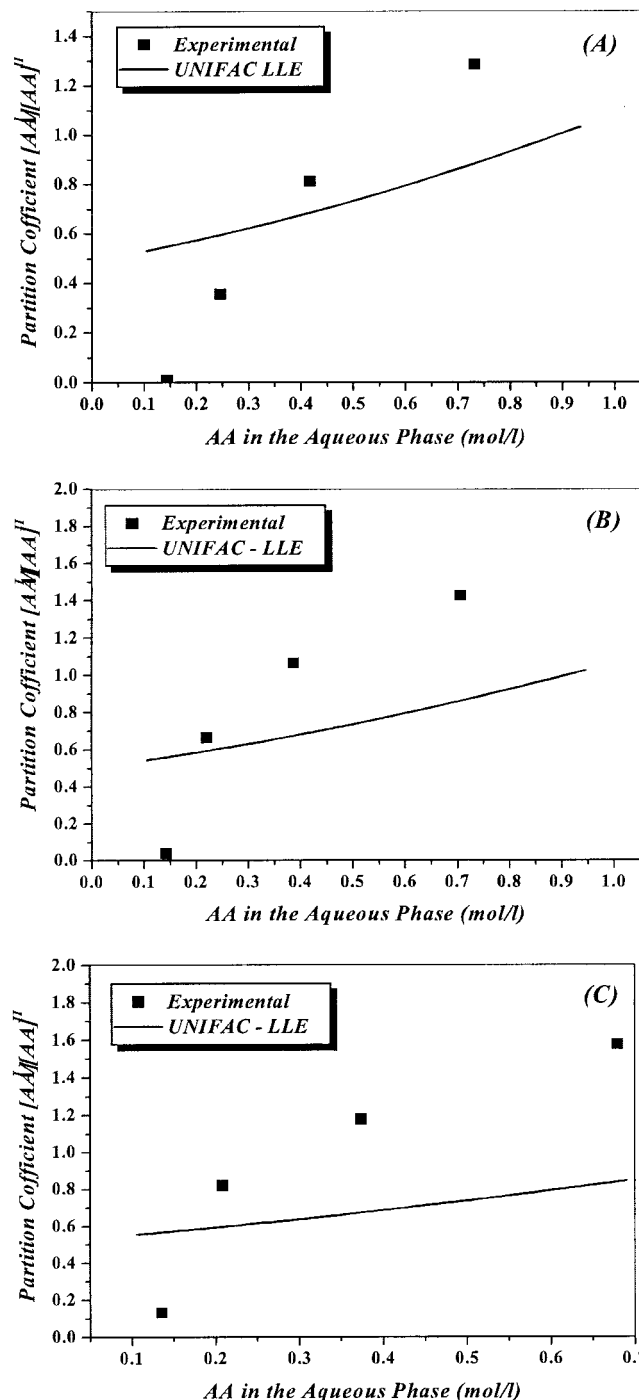
Figure 9 AA partition coefficients: (A) $T - 60°C$; (B) $T - 70°C$; (C) $T - 80°C$.

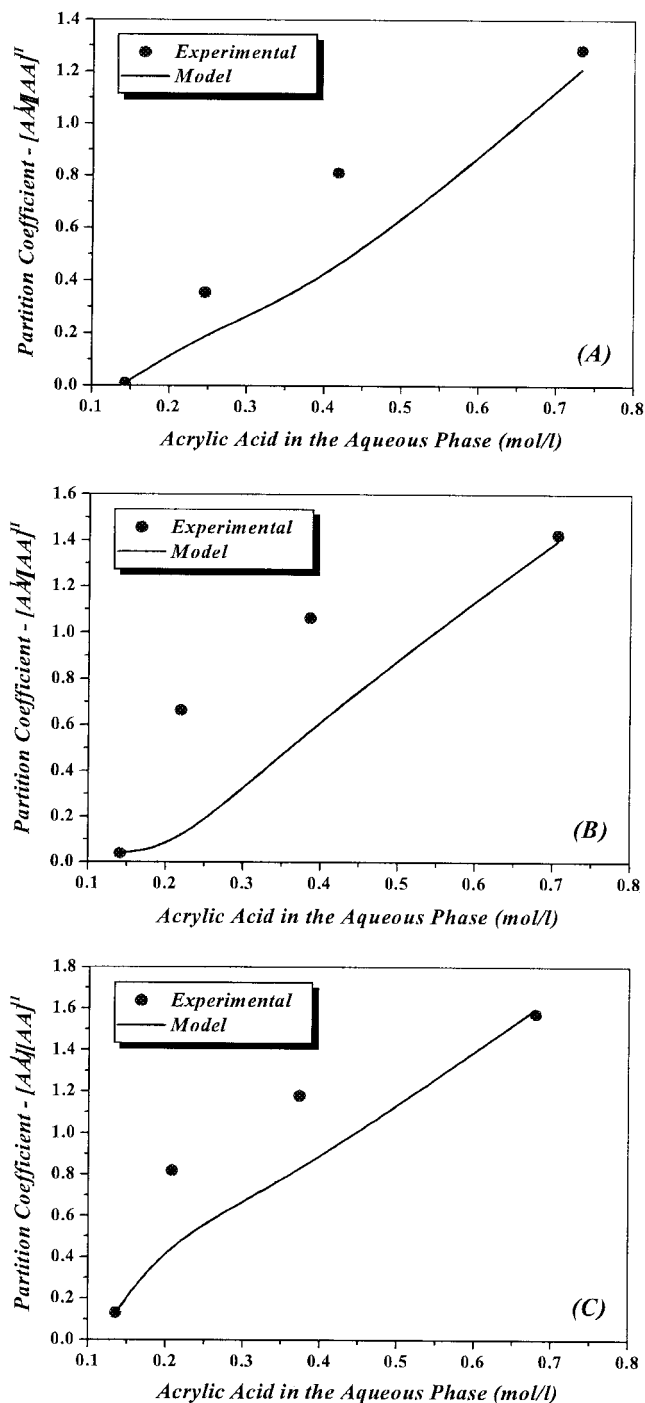**Figure 10** AA partition coefficients. Simulation includes ionic equilibrium. (A) $T - 60°C$, $K^{ionic} = 4.0$; (B) $T - 70°C$, $K^{ionic} = 0.80$; (C) $T - 80°C$, $K^{ionic} = 0.14$.

allow for the design of suspension copolymerization processes, a more straightforward procedure is used here. The following functional form can be proposed for the partition coefficient

$$K(T,[M_2]^{II}) = \left[A + B[M_2]^{II} + \frac{C}{([M_2]^{II})^2} \right] \quad (29)$$

where the coefficients A, B, and C are adjustable parameters that are assumed to depend on the reactor temperature, as presented in eqs. (30)–(32). Figure 11 illustrates the quality of the obtained results and shows that the empirical equation can be used effectively to interpolate the partition coefficients in the analyzed experimental range.

$$A = -16.67 + 0.455(T - 273.15)$$
$$- 2.92 \cdot 10^{-3}(T - 273.15)^2 \quad (30)$$

$$B = 23.02 - 0.594(T - 273.15)$$
$$+ 3.96 \cdot 10^{-3}(T - 273.15)^2 \quad (31)$$

$$C = 0.317 - 9.02 \cdot 10^{-3}(T - 273.15)$$
$$+ 6.04 \cdot 10^{-5}(T - 273.15)^2 \quad (32)$$

Influence of suspension composition upon AA partition coefficients

During actual suspension copolymerizations, the polymer concentration inside the organic phase increases steadily along the reaction course. Therefore, it is important to analyze whether the polymer concentration exerts any significant effect on the AA partition coefficient. Also, the aqueous phase can also contain additional components, such as the suspending agent, which can also influence the AA partition coefficient. To evaluate how sensitive K can be to modifications of the system composition, conductivity measurements were performed at different experimental conditions.

Figures 12 to 14 show how the conductivity of the suspension medium is affected by variations of the system composition in different situations. First, Figure 12 shows that the VAc does not influence the conductivity measurements in the whole range of studied VAc mass concentrations (0.9–30% wt). Conductivity values are very close to 4.3 $\mu S/cm$, which is

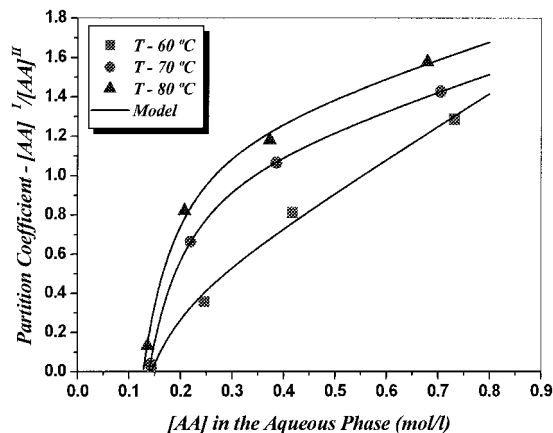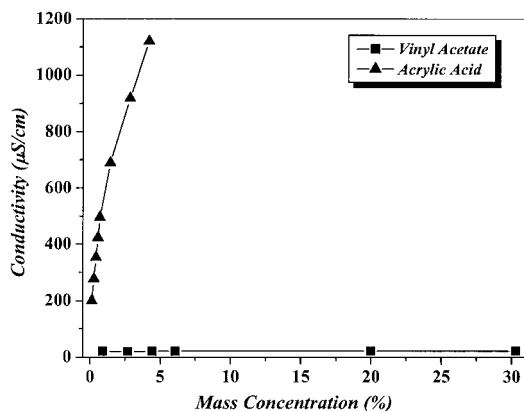**Figure 11** AA partition coefficients—empirical model.

Figure 12 Influence of VAc and AA concentration on the conductivity of medium.

Figure 14 Conductivity of medium obtained at different concentrations of VAc.

the conductivity of pure water at ambient temperature. As expected, this indicates that conductivity values depend mostly on the characteristics of the continuous phase. When small amounts of AA are poured into distilled water, however, very significant changes of conductivity values can be observed. The conductivity of the AA/H$_2$O solutions grow from 4.3 to 1100 μS/cm when the AA concentration increases from 0 to 4.2% wt. As shown in Figures 13 and 14, conductivity values do not change much when small amounts of VAc (0–30% wt) are added into AA/water solutions that contain small AA concentrations, indicating that AA remains in the aqueous phase, as observed previously during partition experiments. This also confirms that conductivity values are not sensitive to the presence of the organic phase and depend mostly on the characteristics of the continuous aqueous phase. It is also interesting to observe that conductivity values are not sensitive to addition of the suspending agent poly-(vinyl alcohol), which indicates that the suspending
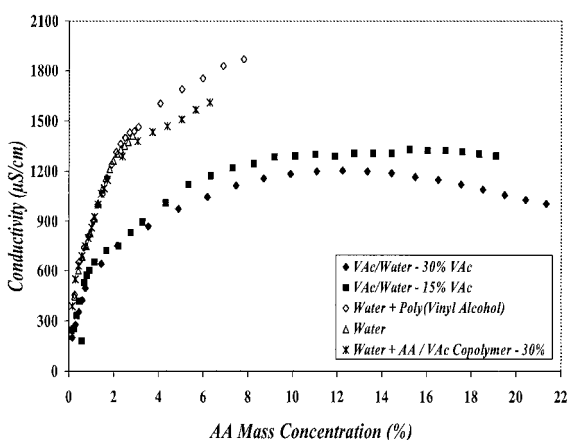

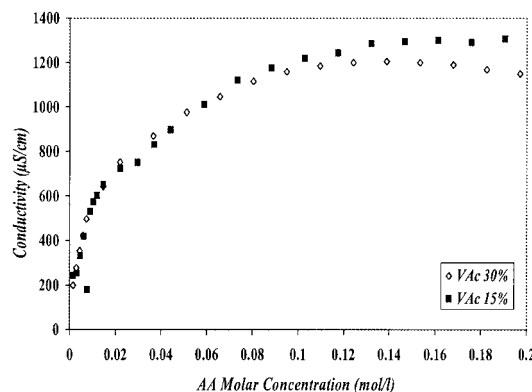**Figure 13** Behavior of conductivity for different concentrations of medium.

agent does not exert any significant influence on the AA partition coefficient.

Figure 13 illustrates conductivity values for different system compositions. It is interesting to observe that two distinct groups of curves are present. The first group includes data obtained without the addition of VAc, and the second group includes data obtained when different amounts of VAc were added to the system. In the first group conductivity values were much larger than observed in the second group, indicating that the aqueous AA concentration was larger in the first group. It is very important to observe that conductivity values obtained for suspensions of AA/VAc copolymers (10% wt of AA) in water (30% wt of copolymer) were extremely similar to conductivity values obtained for pure water. This is a clear indication that the AA partition coefficient between the organic phase and the aqueous phase decreases when the copolymer concentration increases in the organic phase. Therefore, the AA partition coefficient should be expected to decrease even further during actual suspension copolymerizations, which tends to magnify the composition drifts during the copolymerization if proper operation procedures are not developed. It is clear, though, that part of the available AA is captured by the copolymer phase when the AA mass concentrations are above 2.5%, as conductivity values obtained for copolymer suspensions were smaller than those obtained for pure water in those cases. For the curves in the second group, it can be observed that conductivity values were smaller when larger amounts of VAc were added, indicating the removal of additional amounts of AA from the aqueous phase, as it should be already expected. However, for low AA concentrations, as already explained and shown in Figure 14, conductivity values were essentially the same, indicating the extremely low partition coefficients in these cases. This is an independent indication of the likely existence of a minimum AA concentration limit, below which AA remains almost completely in
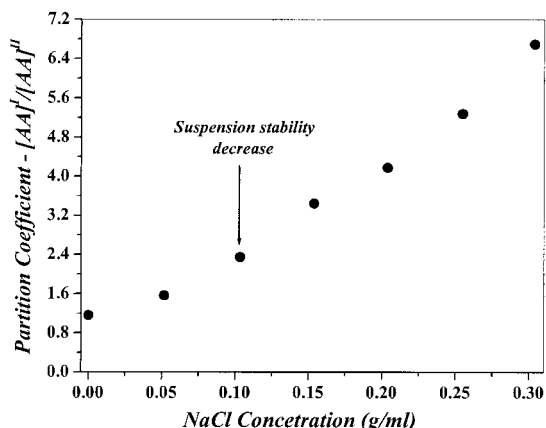
Figure 15 Effect of sodium chloride on AA partition coefficients (concentration of NaCl in relation to water content).

the aqueous phase, and the partition coefficient is very close to zero.

Salt effect on AA partition coefficients

To increase the AA partition coefficient during the reaction course, one possible strategy would be the addition of salts to the water phase. To evaluate the influence of salt (NaCl) concentrations on AA partition coefficients, several experiments were performed using salty water with different salt concentrations as suspending medium. This analysis is also interesting because suspension recipes commonly contain small amounts of salts to adjust the pH, density, and viscosity of the continuous phase, and to prevent polymer incrustation on the reactor walls. Figure 15 shows that the increase of the salt concentration can indeed increase AA partition coefficients. However, observed variations are small, and require too large amounts of salt for most practical situations. Also, it is important to notice that high contents of salt can decrease the suspension stability and cause massive agglomeration of the suspended droplets, if the agitation speed and suspending agent concentration are kept constant. For this reason, addition of salt to the aqueous phase does not seem to be of much use during AA/VAc suspension copolymerizations.

CONCLUSIONS

AA partitioning between the organic and the aqueous phases in suspensions of AA/VAc in water was studied. It was observed that partition coefficients of AA between the organic phase and the aqueous phase range from 0.001 to 1.58 at conditions normally used to carry out suspension copolymerizations. Also, it was shown that AA partition coefficients vary significantly with the composition of the aqueous phase and is very sensitive to temperature variations. It was also

observed that the presence of AA exerts a strong influence on the VAc solubility in water and that this effect becomes more pronounced as the amount of AA increases, causing significant decrease of the solubility of VAc in water. Finally, it was shown that the AA partition coefficient is expected to decrease during actual suspension copolymerizations, as these coefficients are smaller for copolymer suspensions than for VAc suspensions, and are not much sensitive to variations of the salt concentration in the water phase.

It was shown that the popular UNIFAC-LLE model does not describe the liquid–liquid equilibrium of the ternary system AA/VAc/H_2O properly, probably due to the AA ionic nature. However, when dissociation effects are included in the model, it is able to supply appropriate qualitative information about the behavior of the VAc solubility and the liquid–liquid equilibrium of the ternary system AA/VAc/H_2O.

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