

Measurements of Monomer Partitioning in Emulsion Copolymerization Systems

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SYNOPSIS

A new apparatus to measure the equilibrium solvent activity in a multiphase system containing a particulated polymer is presented. An experimental procedure to determine the monomer partitioning in typical emulsion copolymerization systems is developed; the method is devised in a way that no phase separation between water and swollen polymer particles is required in order to determine the monomer content in each phase. The analytical technique used is quantitative gas chromatography, either of the vapor or of the liquid phases. Different monomers (styrene, methyl methacrylate, and vinyl acetate) and polymeric matrices (polystyrene and methyl methacrylate–vinyl acetate copolymer) are examined both above and below saturation conditions (corresponding to intervals II and III of an emulsion polymerization process). The experimental results are compared with predictions of a literature model. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The swelling of polymeric latex particles by monomers is a key aspect in the emulsion polymerization processes. Rate of polymerization, molecular weight of the polymer, and composition of the copolymer are directly related to the concentrations of the monomeric species in all the coexisting phases, i.e., the aqueous solution, the polymer particles, and the oil droplets.

The experimental evaluation of monomer partitioning in such systems has been a subject of interest for long time. A comprehensive review of experimental techniques up to 1968 may be found in the paper by Gardon.¹ As reported in this work, the experimental methods used are classified as follows: (1) static centrifugation, (2) static vapor pressure, (3) disappearance of monomer droplets, and (4) maximum in conversion rate. While the last two methods are operated during the polymerization reaction and give saturation informations only, methods 1 and 2 can be applied as direct partitioning measurements to nonreacting latices. Moreover, the

second method only may be applied below the saturation condition, during the so-called interval III of polymerization.

From those years up to 1990, a moderate experimental activity in this field appeared in the literature (cf. Ugelstad et al.,²⁻⁴ Guillot,⁵ Tseng et al.,⁶ Nomura et al.,⁷ and Alonso et al.⁸). In all of the referred papers, measurements were performed with reference to both homo- and copolymers but below saturation only; moreover, the adopted experimental approach was essentially the same, i.e., analyses of the condensed phases, sometimes combined with phase separation. A noticeable exception is the last paper referred to, in which gas chromatography (GC) analyses of the gas phase in equilibrium with the liquid mixture have been performed along the reaction. The aim of this work was to estimate the evolution of copolymer composition from the measured monomer composition in the gas phase through a fully predictive partitioning model; therefore, analyses of the monomers in all condensed phases were not necessary.

Recently, a significant series of papers has been published by Maxwell et al.,^{9,10} Noël,¹¹ and Schoonbrood et al.¹² Large amounts of experimental data of monomer partitioning both at and below satu-

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ration and with homo- and copolymeric matrices are reported; monomers with limited water solubility are examined, and the experimental approach is based on phase separation between polymer particles, aqueous solution, and oil droplets by means of ultracentrifugation, followed by GC analysis of each phase. Problems related to incomplete water-particle separation are reported. One of the main results is the elucidation of the limited role of the "colloidal" term (related to the negligible monomer solubility in particles due to its small size¹³), at least below saturation, together with a simplified expression of the correction term that accounts for it.

In this work, an original apparatus for measuring monomer partitioning in polymer latices is presented. Direct estimation of the solvent activity is allowed by a GC measure of its partial pressure in the gas phase at equilibrium with the latex; at the same time, concentrations in all condensed phases are evaluated by GC of the pertinent phase through a procedure that overcomes phase separation between water and particles. The capability of measuring solvent activity in latex systems is believed to be the qualifying aspect of the proposed apparatus and technique; note that the selection between competing thermodynamic models applied to multiphase systems may be performed more reliably when activity versus concentration data are available for each one of the phases involved. Different monomeric species (styrene, methyl methacrylate, and vinyl acetate) and polymeric matrices (polystyrene and methyl methacrylate-vinyl acetate copolymer) are examined both at and below saturation. Experimental results are compared with those predicted by the monomer partitioning relationships proposed by Maxwell et al.⁹ and Noël et al.¹¹ and the reliability of this theoretical approach is confirmed only when using monomers with limited water solubility.

EXPERIMENTAL

Apparatus

The basic idea underlying the technique presently developed is the direct measurement of component activities in a liquid mixture by analysis of the gas phase in equilibrium with it. The adopted operating procedure was selected among three possible alternatives: (1) head-space chromatography, (2) open-loop saturator, and (3) vapor recirculation apparatus. The first case is a classical static approach, whose main difficulties are the accurate measurement of the equilibrium pressure inside the vial,

needed to calculate activity correctly, and the long equilibration time required. In the second and third cases, a dynamic apparatus is needed. An inert gas phase is bubbled through the liquid mixture and saturates with the component present in there. The difference between cases (2) and (3) is determined by the gas flow, which may be operated in a one-through way (case 2) or may be recycled (case 3). In both cases, a good mixing of the liquid mixture is ensured by gas bubbling. The recirculation mode has been preferred so as to avoid composition changes in the liquid due to stripping of components by the gas, when repeated measurements have to be performed according to configuration (2).

A scheme of the equipment is shown in Figure 1. Essentially, it consists of a thermostatic oven (HERAEUS, model UT 6120), where the recirculation apparatus is located, and a gas chromatograph equipped with a vapor sampling device. In the oven, two bottles, referred to as equilibrators (volume \approx 200 cc), are arranged in a parallel manner so as to perform all measurements in a relative mode (i.e., taking as a standard-state reference, the pure solvent at the same temperature and pressure of the mixture). Thus, the pure solvent (monomer) is loaded in one equilibrator, and the mixture under examination in the other one. A small diaphragm compressor with TeflonTM membrane (KNF, model N 06 AT.18) ensures the circulation of the gas phase in equilibrium with the liquid ones throughout the circuit, made entirely by stainless steel tubes, where the loop of a six-way sampling valve (VALCO) is also located. Two manometers measure the pressures in two positions of the circuit, namely inside the equilibrators and as close as possible to the sampling loop. They are piezoelectric membrane manometers and display the absolute pressure in bars, provided by a previous calibration with a reference manometer. The gas chromatograph used for activity and condensed phase composition analyses is a Shimadzu GC-8A equipped with a packed column with 10% SP-1000 on SUPELCOPORT 80/100.

The operating procedure is now summarized with reference to Figure 2, where the relative positions of the four- and six-way valves are displayed. Normally, they are as in position 1, so that the gas phase is free to circulate through the whole circuit, including the sampling loop. By switching the six-way valve from the load to the injection position 2, the content of the loop is discharged into the chromatographic column, and its analysis can be carried out. Subsequently, the four-way valve is actuated to isolate the part of the circuit between the two valves (position 3), and the six-way valve is switched again

back to the load position. By doing this, both the loop and the in-between part of the circuit are vented to the atmosphere (position 4). This is done because the GC column operates at a pressure of nearly 3 bar, while the equilibrators are close to the atmospheric pressure; and we preferred to be sure to eliminate any possible sources of error between subsequent analyses, caused by such a pressure difference.

Estimation of Activity

If the symmetric convention is assumed as a reference state for activity, and the gas phase is supposed to be ideal, the vapor-liquid equilibrium condition in the reference equilibrator (the one containing pure monomer) may be written as

$$P_{eq}y_i = P_i^o(T_{eq}) \quad (1)$$

where P_{eq} and T_{eq} are the total pressure and the temperature in the equilibrator, y_i is the mole fraction of component i in the vapor phase, and P_i^o is its vapor pressure. Thus, the moles number of i in the gas phase, n_{is} , can be evaluated as

$$n_{is}^* = \frac{P_s^* V_s P_i^o(T_{eq})}{RT_s P_{eq}^*} \quad (2)$$

where V_s , P_s , and T_s indicate the volume, pressure, and temperature of the sampling loop, and R is the universal gas constant. Note that asterisk stands for values referring to the equilibrator filled with pure monomer. When the equilibrium condition is written for the equilibrator containing the multi-phase mixture, it can be obtained as follows:

$$P_{eq}y_i = P_i^o(T_{eq})\gamma_i x_i \quad (3)$$

where γ_i and x_i are the activity coefficient and liquid mole fraction of component i . Accordingly, the moles of i in the gas phase are given by

$$n_{is} = \frac{P_s V_s P_i^o(T_{eq})\gamma_i x_i}{RT_s P_{eq}} \quad (4)$$

By taking the ratio of eq. (4) to (2) and rearranging, we obtain

$$a_i = \gamma_i x_i = \frac{n_{is} P_{eq} P_s^*}{n_{is}^* P_{eq}^* P_s} \quad (5)$$

which allows to evaluate the activity of component i in the mixture, if the mole numbers, n , and the

pressure values, P_s , are available. Note that n can be replaced by the chromatographic peak area if the linearity of the calibration curve over the examined concentration range is verified. The advantage of operating in a relative mode rather than using a single equilibrator is clear by looking at eq. (5), which contains only experimentally measured quantities.

Preliminary Test

In order to validate the proposed apparatus, a series of experimental runs was performed, with reference to the model system vinylacetate (VAC)-water at two different monomer-to-water ratios, identified by subscripts 1 and 2 in Table I. The quantity

$$\frac{m_{is} P_{eq}}{P_s} = \frac{V_s P_{eq} y_i P M_i}{RT_s} \quad (6)$$

was measured both for pure component (asterisk) and for components in the mixture. In eq. (6), m_{is} and $P M_i$ are the mass and molecular weight of i , respectively. Some results are summarized in Table I at different values of the recirculating gas flow rate, i.e., at different pressure profiles along the circuit. Note that higher ΔP (i.e. $P_{eq} - P_s$) values reported in the first column of Table I indicate larger gas flow rates in the experimental run. In the pure component case, the quantity given by eq. (6) is proportional to its vapor pressure, whose value can be estimated from the literature.¹⁴ For this reason, the quantities shown in columns 2, 3, and 5 of the table, which are defined as

$$z_i = \frac{\frac{m_{is} P_{eq}}{P_s}}{\frac{V_s P_i^o P M_i}{RT_s}} \quad (7)$$

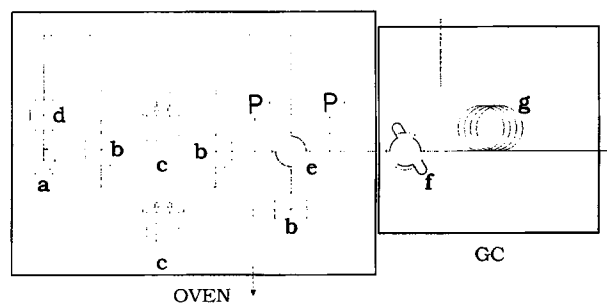


Figure 1 Scheme of the experimental apparatus: (a), pump; (b), three-way valve; (c), equilibrator; (d), regulating valve; (e), four-way valve; (f), six-way valve; (g), chromatographic column.

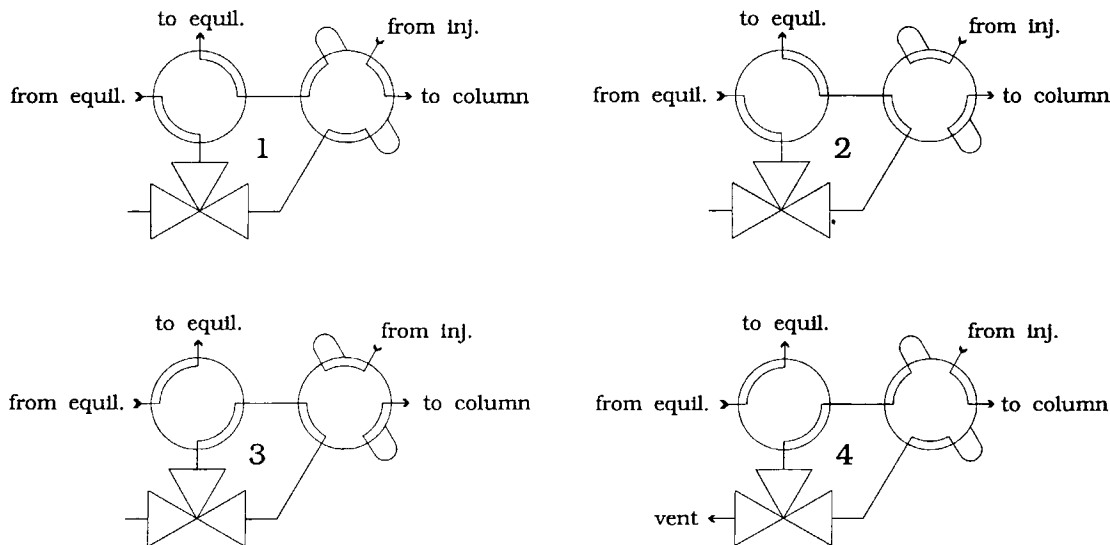


Figure 2 Operating scheme of the four- and six-way valves (see text for details).

are not exactly equal but only proportional to the lefthand side term in eq. (6).

By inspection of the results reported in the table for the pure component (z_i^*), an unexpected drift of the measured quantity is verified at increasing ΔP values. The positive deviations may be understood if we notice that the pressure difference mentioned above is directly related to the gas flow inside the circuit. Due to the pressure drop in the six-way valve, the measured pressure P_s is smaller than the one actually experienced by the gas in the sampling loop, and this discrepancy increases as the flow gets higher.

The effect reported above is an intrinsic limitation of the apparatus; however, its impact has to be verified with reference to the quantity of present interest, i.e., the monomer activity. Let us focus on the last four columns in Table I, corresponding to two different monomer to water ratios, both close

to one half of the saturation value. While the quantity given by eq. (6) exhibits the same behavior as for the pure component, activity values are clearly independent of the pressure difference and, hence, of the flow rate. From this result, we concluded that, although operating with a single equilibrator allows accurate activity determination in a limited range of (low) ΔP values only, this range can be largely extended by working in a relative mode. From a practical viewpoint, it was convenient to perform all measurements at a pressure difference greater than 0.3 bar, since data obtained under these conditions were highly reproducible and much less scattered. All measurements reported in this work were performed with ΔP between 0.3 and 0.4 bar, corresponding to an operating gas flow rate of about 150 cm³/min. These conditions guaranteed measurement accuracy and good mixing of the condensed phases by gas bubbling; in all cases, pure monomers were used as reference system for activity evaluations.

Table I z_i and Activity Values at Different Pressure Drops, $\Delta P = P_{eq} - P_s$

ΔP (bar)	z_i^*	z_{i1}	a_{i1}	z_{i2}	a_{i2}
0.1	0.940	0.467	0.497	—	—
0.2	1.001	0.502	0.501	—	—
0.3	1.032	0.521	0.505	—	—
0.4	1.099	0.547	0.498	0.500	0.455
0.5	1.188	—	—	0.552	0.465
0.6	1.360	—	—	0.609	0.448
0.7	1.451	—	—	0.675	0.465

Refer to eq. (7).

Experimental Procedure

In the case of single monomer systems, the relationship between gas phase activity and aqueous phase monomer concentration was first obtained from measurements on water–monomer mixtures spanning from highly diluted to saturation conditions. After each set of activity measurements, the analyses of the aqueous phase were performed by GC of the residual condensed phase inside the equilibrator. Secondly, an analogous series of experi-

Table II Recipes and Final Polymer Characterization for the Polymerization Reactions

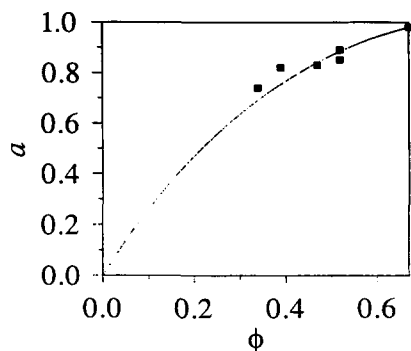
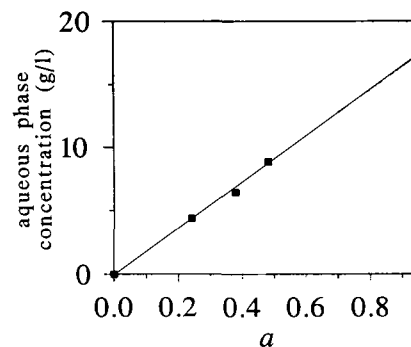
	Water (g)	Monomer 1 (g)	Monomer 2 (g)	Emulsifer (g)	Initiator (g)
polySTY 1	1002	100	—	10	0.99
polySTY 2	1010	496	—	25	1.50
MMA-VAC copolymer	1000	21	70	4	1.50

	Solid Content (%)	Particle Diameter (nm)
polySTY 1	8.1	62
polySTY 2	26.6	104
MMA-VAC copolymer	6.8	49

ments was performed with the latex, i.e., in the additional presence of the polymeric phase. Below saturation, activity and overall monomer concentration in both of the condensed phases (aqueous and polymeric) were measured exactly as for the polymer-free mixtures. The monomer concentration in the two separate phases could be determined by taking advantage of the relation between activity and monomer concentration in aqueous phase, as evaluated without the polymer. As a matter of fact, at thermodynamic equilibrium with given T and P , the activity value is independent of the number of coexisting phases, and the aqueous phase monomer concentration can be accurately derived from monomer activity in the gas phase. Finally, monomer concentration in the polymer particles is calculated as the difference between the overall amount in the condensed phases and the one in the aqueous phase. Being the overall amounts of water, monomer and polymer known from the initial conditions, the determination of all desired concentrations is a matter of simple material balance equations. Note that the same approach was applied also at satu-

ration conditions, i.e., in the presence of the additional solvent-rich condensed phase. The separation between oil droplets and water + particles phases is readily obtained by stopping gas bubbling and allowing for phase separation by segregation. Usually, few minutes were required to complete this step so that the sampling and the GC analysis of the water + particles phases could be easily performed.

When two monomers are present in the emulsion, a rigorous extension of this treatment would require the analysis of several aqueous solutions of binary monomeric mixtures (without polymer particles) at different relative concentrations in order to cover the whole range examined. However, it is possible to simplify the problem by assuming that the dependence of monomeric activity on its concentration in the aqueous phase is not affected by the second monomer. Due to the limited water solubility of the monomeric species under examination, this assumption is reasonable; moreover, it has also been verified experimentally. Therefore, the same approach previously detailed in the case of monocom-

**Figure 3** Activity versus volume fraction in particle phase for STY in polystyrene.**Figure 4** Aqueous phase concentration versus activity for MMA; the straight line equation is $y = -0.0208 + 18.2x$.

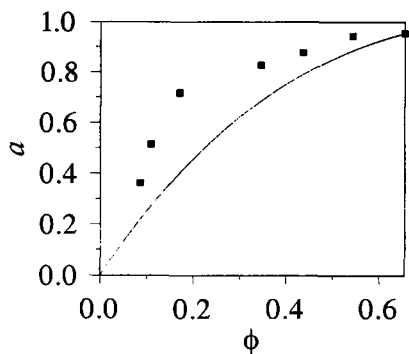


Figure 5 Activity versus volume fraction in the particle phase for MMA in poly(MMA-VAC).

ponent systems was then applied to all binary systems considered. The only additional point is that, below saturation conditions, GC analyses are required for both condensed phases (water particles and oil droplets); however, due to their good separability, these analyses could be easily carried out.

Materials and Latex Preparation

Three monomeric species were considered: styrene (STY) (99%, Janssen), methyl methacrylate (MMA) (99%, Janssen) and vinyl acetate (VAC) (99+%, Janssen). Potassium persulphate (98%, Carlo Erba) was used as initiator and sodium lauryl sulphate (Carlo Erba) as emulsifier. All monomers were distilled under reduced nitrogen pressure just before use, while the other reagents were used without further purification.

The seed latices used for equilibrium determinations were prepared in a batch well-mixed glass reactor ($T = 50^\circ\text{C}$; stirring speed = 400 rpm) according to the recipes detailed in Table II, where the overall masses of all components initially charged to the reactor are reported. In all cases, bi-

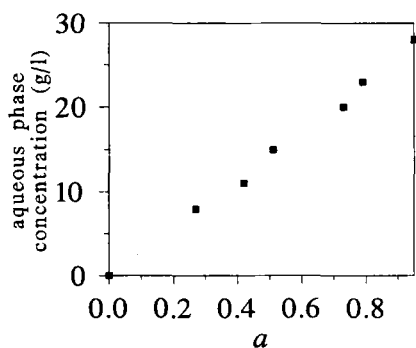


Figure 6 Aqueous phase concentration versus activity for VAC; the straight line equation is $y = -0.0387 + 28.8x$.

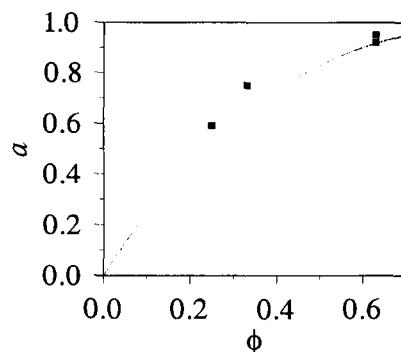


Figure 7 Activity versus volume fraction in the particle phase for VAC in polystyrene.

distilled water was used. Note that for the copolymer, a constant composition reaction was carried out by properly adding one monomer to the reactor. This approach, detailed elsewhere,¹⁵ resulted in a nearly constant composition polymer, as verified by monitoring the monomer mixture inside the reactor during the reaction.

The characterization of the polymeric latices produced was performed by evaluating the solid content gravimetrically and the average particle size (d_p) by dynamic light scattering (Coulter Counter, model N4S). The obtained results are also reported in Table II.

RESULTS

Results of the experimental runs are summarized in terms of activity, or particle phase volume fraction, as a function of a suitable composition; the order in which they are displayed agrees with increasing monomer solubility in water and number of components. All data were obtained at an equilibrium temperature of 50°C .

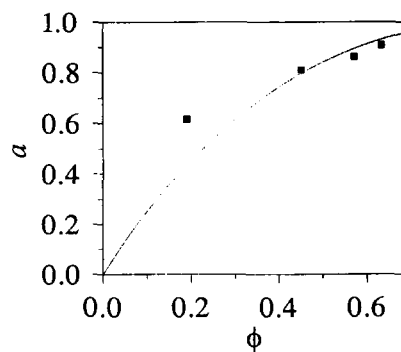


Figure 8 Activity versus volume fraction in the particle phase for VAC in poly(MMA-VAC).

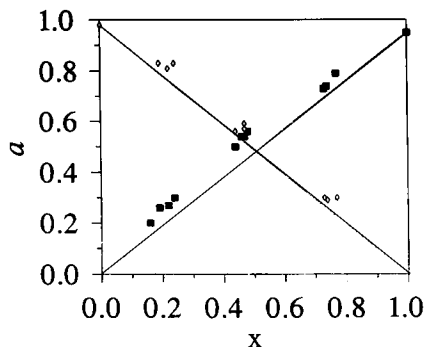


Figure 9 Activity versus VAC molar fraction in the drop phase for the mixture VAC(■)/STY(◇).

Before discussing the experimental data, it is worth mentioning that, in all cases, they are compared to the corresponding values calculated by the model proposed by Maxwell et al.⁹ and Noël.¹¹ Namely, the activity in both organic phases (droplets and particles) has been calculated as a function of the relevant volume fraction by the Flory-Huggins equation, but by introducing the following assumptions:

1. The colloidal term is neglected for the oil droplets;
2. The colloidal contribution and the monomer-polymer interaction parameters are lumped into a constant term, which is evaluated by fitting the maximum swelling at saturation;
3. The monomer-monomer interaction parameters are neglected;
4. The size of the monomer unit is negligible with respect to that of the polymer chains.

The resulting expressions of monomer activity in oil droplets and in particles are reported in the

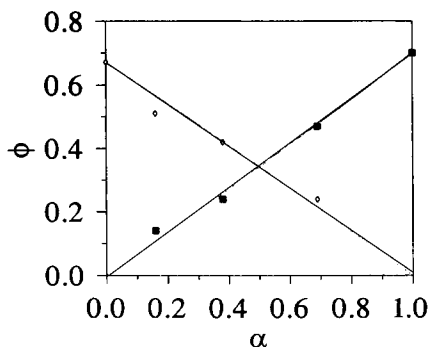


Figure 10 Volume fraction in the particle phase versus VAC volume fraction in the drop phase for the mixture VAC(■)/STY(◇) in polystyrene.

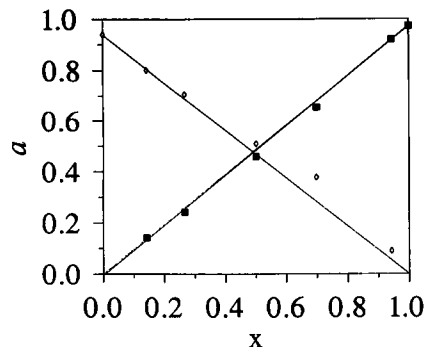


Figure 11 Activity versus VAC mole fraction in the drop phase for the mixture VAC(■)/MMA(◇).

quoted papers; note that the only model parameters needed are the lumped terms [cf. assumption (2)], being the monomer unit size ratios evaluated by the ratios of the corresponding molar volumes.

The system examined first is STY in polystyrene. Due to its extremely low solubility in water, the relationship between activity and aqueous concentration is not required for this monomer since neglecting the mass of the monomer dissolved in aqueous phase would not affect the calculation. Data of activities versus compositions in polymer particles are shown in Figure 3. As expected,^{12,16} activities show an asymptotic behavior at large values of concentration; moreover, the saturation activity is very close to one (0.98), thus confirming weak interaction between water and STY. The calculated behavior is in good agreement with experimental results, thus verifying the model applicability to this system. Note also that, due to the high boiling temperature of STY, no measurements were performed at a volume fraction less than 0.3.

In contrast with the previous case, MMA and VAC show an appreciable solubility in the aqueous phase, which has to be accounted for properly. For

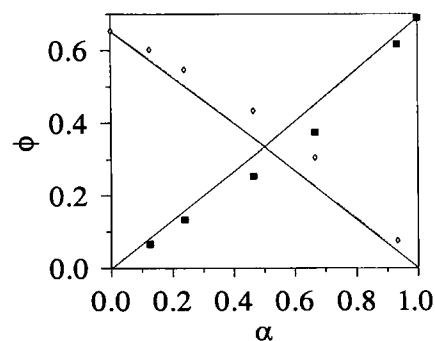


Figure 12 Volume fraction in the particle phase versus VAC volume fraction in the drop phase for the mixture VAC(■)/MMA(◇) in poly(MMA-VAC).

Table III Data of the Mixture VAC/MMA in Poly(MMA-VAC) Below Saturation

$\phi_{\text{VAC}}^{\text{pseudobinary}}$	$\phi_{\text{MMA}}^{\text{pseudobinary}}$	a_{VAC}	a_{MMA}	ϕ_p
0.410	0.590	0.457	0.508	0.471
0.322	0.678	0.317	0.433	0.760
0.348	0.652	0.195	0.299	0.827
0.410	0.590	0.101	0.180	0.891
0.531	0.469	0.506	0.379	0.575
0.405	0.595	0.360	0.281	0.802
0.487	0.513	0.169	0.151	0.847
0.262	0.738	0.284	0.650	0.466
0.231	0.769	0.225	0.592	0.658
0.277	0.723	0.158	0.519	0.790

MMA, this is displayed in Figure 4; a linear behavior is evidenced, as expected due to the adopted diluted conditions. Data of MMA activity vs particle composition are shown in Figure 5 with reference to a MMA-VAC copolymeric matrix. As readily verified, the trend is the same as for STY, but the lower activity saturation value (0.95) reflects the greater solubility in water. In this case, the agreement between model predictions and experimental results is poor; this reflects a higher interaction between monomer and polymer, not properly accounted for by the adopted activity model. Similar considerations apply to VAC, whose curve of activity concentration in water, once more linear, is reported in Figure 6. This monomer shows the usual activity vs particle volume fraction behavior both in polystyrene (Fig. 7) and in the MMA-VAC copolymer (Fig. 8), with similar saturation compositions in the particle phase and reasonable agreements with model predictions. Again, the value of activity at saturation (0.96) is affected by the increased interaction with water with respect to styrene.

Let us then focus on the two-component system STY-VAC in a polystyrenic latex above saturation. As previously observed, the activity of VAC as a function of its concentration in the aqueous phase (Fig. 6) can be used in this context too, if its applicability in the presence of a second monomer is experimentally checked. As a matter of fact, in Figure 6, both single monomer and mixture experimental values have been reported; within experimental accuracy, they lead to a single curve, so that mixture effects can be neglected. In Figure 9, the activity values of both monomer species are shown vs mole fractions in oil droplets; in the same figure, the calculated curves are reported. Both experimental and calculated activities exhibit an almost linear behavior, thus indicating a slight deviation from ideality

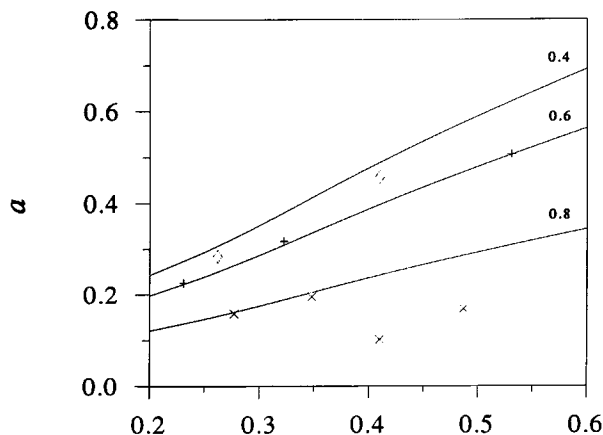


Figure 13 Activity versus pseudobinary volume fraction in the particle phase for VAC in poly(MMA-VAC) and MMA as a function of polymer volume fraction ϕ_p (full lines). Experimental data: $0.45 < \phi_p < 0.47$ (\diamond); $0.57 < \phi_p < 0.76$ (+); $0.79 < \phi_p < 0.89$ (\times).

for the organic phase. In Figure 10, the behavior of monomer volume fraction in the polymeric phase vs the oil droplet phase composition is shown and compared with the calculated curves. Neglecting small deviations within the experimental error, we can conclude that the simple equipartition rule is a satisfactory approximation for this system.

Finally, the mixture MMA/VAC in its copolymer latex both above and below the saturation point is considered. In this case two correction curves are needed, one for each monomer; as discussed just above, any mixture effect is neglected, and the pure component curves (as reported in Figs. 4 and 6)

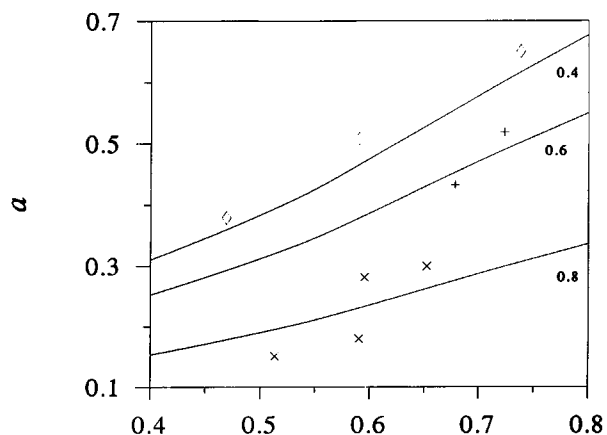


Figure 14 Activity versus pseudobinary volume fraction in the particle phase for MMA in poly(MMA-VAC) and VAC as a function of polymer volume fraction ϕ_p (full lines). Experimental data: $0.46 < \phi_p < 0.57$ (\diamond); $0.65 < \phi_p < 0.79$ (+); $0.80 < \phi_p < 0.89$ (\times).

have been adopted. The behavior of activity with respect to drop phase composition (above saturation) is shown in Figure 11, together with the corresponding theoretical curves. The quasilinearity observed for the previous two-monomer system is verified also in this case. The situation with respect to monomer solubility in the particle phase is presented in Figure 12 for conditions above saturation. It is evident from the reported graph that the previously observed equipartition between drop and particle phases is no more applicable here, and that significant deviations from this rule (and from the calculated curves) appear, both positive (for MMA) and negative (for VAC). Experimental results for the same system but below saturation are summarized in Table III. These data may be reordered in terms of activity vs a pseudobinary monomer composition at different amounts of polymer, as shown in Figures 13 and 14. Here, the measured activities of VAC and MMA have been reported as a function of the quantity $\phi_1/(\phi_1 + \phi_2)$; they are compared with calculated curves at constant polymer volume fractions. In general, the agreement between model and experiment is reasonable but not sufficient from the quantitative viewpoint. However, two main features can be pointed out: at constant pseudobinary monomer volume fraction, the activity decreases with increasing polymer concentration; at constant polymer volume fraction, the activity increases with increasing monomer concentration.

CONCLUSIONS

In this work, an apparatus for measuring monomer partitioning in emulsion copolymerization has been designed and built up. A convenient experimental procedure was proposed and tested; it allows to avoid phase separations and to handle systems with more than one monomer, and it can be applied either above and below saturation. A unique feature is the capability of a direct measurement of the solvent activity, with the most relevant variable to check thermodynamic models.

Several systems were studied, involving one and two monomer species and homo- and copolymeric matrices, both above and below saturation. The re-

sults obtained validated the adopted experimental apparatus and procedure.

Experimental data were compared with those calculated by a literature model,^{9,11} whose applicability is partially confirmed.

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REFERENCES

1. J. L. Gardon, *J. Polym. Sci., Part A-1*, **6**, 2859 (1968).
2. J. Ugelstad, P. C. Mork, K. Herder Kaggerud, T. Ellingsen, A. Berge, *Adv. Colloid Interface Sci.*, **13**, 101 (1980).
3. J. Ugelstad, P. C. Mork, A. Berge, T. Ellingsen, A. A. Khan, in *Emulsion Polymerization*, I. Piirma, Ed., Academic Press, New York, 1982, p. 383.
4. J. Ugelstad, P. C. Mork, I. Nordhuus, H. Mfutakamba, E. Soleimany, *Makromol. Chem. Suppl.*, **10/11**, 215 (1985).
5. J. Guillot, *Acta Polymerica*, **32**, 593 (1981).
6. C. M. Tseng, M. S. El-Aasser, J. M. Vanderhoff, *Org. Coat. Plast. Chem.*, **45**, 373 (1981).
7. M. Nomura, K. Yamamoto, I. Horie, K. Fujita, *J. Appl. Polym. Sci.*, **27**, 2483 (1982).
8. M. Alonso, M. Oliveres, L. Puigjaner, F. Recasens, *Ind. Eng. Chem. Res.*, **26**, 65 (1987).
9. I. A. Maxwell, J. Kurja, G. H. J. Van Doremaele, and A. L. German, *Makromol. Chem.*, **193**, 2049 (1992).
10. I. A. Maxwell, J. Kurja, G. H. J. Van Doremaele, A. L. German, *Makromol. Chem.*, **193**, 2065 (1992).
11. L. F. J. Noël, I. A. Maxwell, and A. L. German, *Macromolecules*, **26**, 2911 (1993).
12. H. A. S. Schoonbrood, M. A. T. Van den Boom, A. L. German, J. Hutovic, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 2311 (1994).
13. C. A. Johnson, *Surf. Sci.*, **3**, 429 (1965).
14. R. C. Reid, J. M. Prausnitz, T. K. Sherwood, in *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1977.
15. P. Canu, S. Canegallo, M. Morbidelli, G. Storti, *J. Appl. Polym. Sci.*, **54**, 1899 (1994).
16. P. J. Flory, in *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 496.

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