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ORIGINAL CONTRIBUTION

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Polymerisation of vinyl acetate in microemulsions with methanol

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Abstract The homogeneity domains for the system vinyl acetate – methanol – monomaleate of nonylphenol ethoxylated with 25 mol ethylene oxide as an aqueous solution (MEMNPEO25) (33%) have been studied; it has been shown that, due to the shorter chain of methanol, these domains are more reduced than in the case of ethanol. The changes in refractive indexes and electrical conductivities have shown the formation of microemulsions with different structures (water-in-oil, bicontinuous or oil-in-water). Ammonium persulphate is soluble only in oil-in-water or in bicontinuous microemulsions. The initial polymerisation rates as well as the decomposition rates for the initiator are apparently affected when the microemulsion structure is modified. The polymerisation rate of vinyl acetate is higher in the presence of methanol than in the presence of ethanol for similar compositions; this fact may be attributed to a higher degree of ionisation of the initiator in the presence of methanol. Also, in polymerisations initiated by benzoyl peroxide, the conversions are influenced by the microstructure; thus, the maximum corresponds to water-in-oil microemulsions. By measuring the amount of unreacted MEMNPEO25 (gel permeation chromatography) we were able to show that the copolymer formed consisted of vinyl acetate and reactive surfactant.

Key words Microemulsions · Vinyl acetate · Methanol

Introduction

Microemulsions, as stable structured systems, spontaneously formed in mixtures consisting of short-chain cosurfactants (SCC), such as C_2-C_4 alcohols and water, have been extensively studied in recent years [1–5]. The formation of these microemulsions is due to hydrophobic demixtion, induced by the short hydrophobic chain of the alcohol [6]. According to Refs. [6–9], this phenomenon may occur in the SCC–water systems, even in the case of a hydrophobic chain containing only one carbon atom. Starting from these observations, the present work describes the formation of microemulsions of vinyl acetate (VAc) in the presence of methanol (MeOH) and compares the results with those obtained for VAc in the presence of ethanol (EtOH).

Using the results already obtained in the presence of EtOH [1], we further studied the properties of homogeneous samples in the presence of MeOH; the change in some physical properties may be a useful tool to appreciate microemulsion structure.

The persulphate initiator decomposition and, in general, the kinetics of VAc polymerisation depend on the microemulsion structure in the presence of either EtOH or MeOH; the corresponding phenomena illustrated.

Experimental

Materials

VAc, MeOH, EtOH and ethyl acetate were purified conventionally by distillation. Ammonium persulphate (APS) (Riedel de Haen) and benzoyl peroxide (Bz_2O_2) (Chimopar) were used without further purification. MEMNPEO25 was synthesised from maleic anhydride and nonylphenol ethoxylated with 25 mol ethylene oxide, according to a previously reported procedure [1].

Obtaining the domain of homogeneous compositions

MeOH and EtOH were used as SCC. For each alcohol, we prepared five mixtures VAc/alcohol = 10/90, 30/70, 50/50, 70/30, 90/10 (weight ratios); these mixtures are labelled as "o" (the organic phase). In all circumstances, the aqueous phase ("w") consisted of a solution of 33% (w/w) of MEMNPEO25 in water. In order to cover all the composition domain, nine o/w mixtures were prepared in the following weight ratios: 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10. After vigorous stirring, the systems were kept for 24 h at room temperature to reach equilibrium.

The mixtures that remained homogeneous after reaching equilibrium are designed by an o in the ternary diagram. Figure 1 corresponds to the systems where the SCC is MeOH; the number of homogeneous systems is mentioned on the ternary diagram.

Polymerisations for homogeneous mixtures

Polymerisations were carried out at 63 °C only for the homogeneous samples; APS and Bz_2O_2 were used as initiators.

In the case of APS we chose mixtures VAc/SCC: 30/70, 10/90 (weight ratios), where SCC was either MeOH or EtOH. The tests were carried out in two different ways:

1. Without stirring. Homogeneous samples (containing 1 g APS for each 400 g microemulsion) were introduced into glass vials, sealed off and kept in the thermostatic bath for 24 h.
2. With stirring. Microemulsion (400 g) was prepared in a glass reactor under vigorous stirring (150 rpm); APS was only introduced after reaching the desired polymerisation temperature. At suitable times, samples were saved to measure the conversions for monomer and initiator, respectively; the total reaction time was 3 h.

When we used Bz_2O_2, MeOH alone was chosen as the SCC. All polymerisations were carried out with homogeneous mixtures characterised by the weight ratios VAc/MeOH: 30/70, 10/90. The samples were prepared by mixing the organic and aqueous (33% MEMNPEO25 in water) phases in weight ratios from 10/90 up to 90/10. Polymerisations were carried out in sealed-off vials at 63 °C for 24 h. Bz_2O_2, was previously dissolved (2% and 4% respectively) in VAc; subsequently, the volatile products were removed (in a vacuum) from the reaction mixture.

Measurements on homogeneous systems

Refractive indexes were measured with an Abbe refractometer, while the conductivities were obtained with a Radelkis OK 102/1 instruments. All measurements were carried out at 25 °C. To observe the effect produced in the presence of initiator, the conductivities were also measured after introducing APS into the microemulsion (1 g APS for 400 g microemulsion).

Analyses

The monomer conversion was obtained gravimetrically, while the initiator conversion was established by cerimetry [10].

The molecular-weight distribution as well as the consumption of the reactive surfactant were determined by gel permeation chromatography with a Waters model 510 apparatus endowed with an RI model 410 detector. The set of columns used covered the domain between 100 and 4×10^6. All calculations were made based on polystyrene standards.

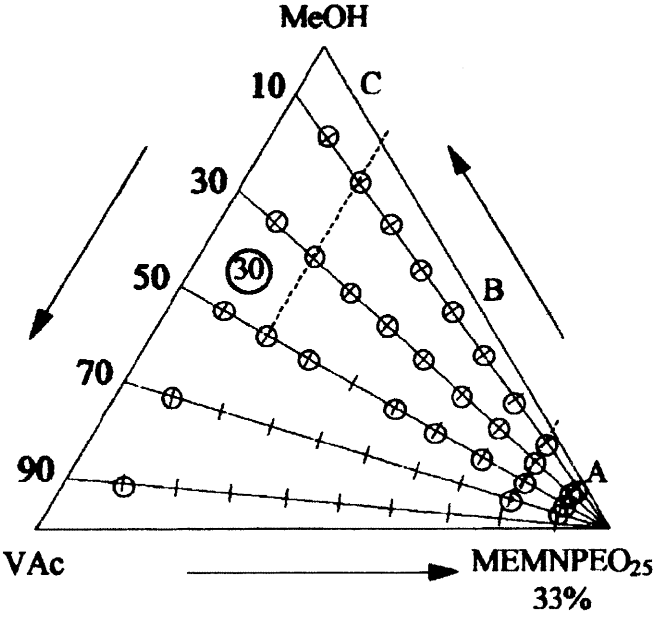


Fig. 1 Homogeneous systems obtained for the mixture vinyl acetate (*VAc*) methanol (*MeOH*) monomaleate of nonylphenol ethoxylated with 25 mol ethylene oxide (*MEMNPEO25*) (33%)

Results and discussion

From the total of 45 compositions of samples, 32 are homogeneous in the case of EtOH (used as the SCC); when replacing EtOH with MeOH only 30 systems were homogeneous. The difference arises in the domains characterised by high concentrations of VAc and low concentrations of surfactant. Indeed, MeOH, with its shorter hydrophobic chain, may induce hydrophobic demixtion in the presence of water [6–9]; its short chain offers a small zone for nonpolar compounds [8]. Accordingly, the effect of chain length (reducing the domain of homogeneous systems) becomes obvious in the area where MeOH and MEMNPEO25 (that produce the solubility of nonpolar compounds) are at low concentrations. The phenomenon of nanostructuration of the SCC is also manifest in the presence of surfactants [11].

The fact that in the presence of MeOH the number of microemulsions obtained is lower than in the case when other alcohols with longer chains were used has also been reported for styrene [3]. Fluorescence studies carried out on aqueous solutions of MeOH, EtOH or propanol [8] have shown peculiar behaviour for the short-chain alcohol; thus, methanolic solutions do not offer a solubility zone for styrene, as in the case of propanol [8].

The effect of temperature on the stability of the homogeneous systems was studied by maintaining these systems for 5 h at a constant polymerisation temperature. In order to avoid thermal polymerisation, VAc was replaced with ethyl acetate. In these conditions all 40 homogeneous systems remained stable.

Information regarding the structural changes due to composition was obtained for those VAc/SCC systems which are homogeneous for all o/w ratios. Some results are presented in Figs. 2 and 3 (for EtOH and MeOH); $x = w/(w+o)$ represents the weight fraction of the aqueous phase. All systems exhibit nonlinear changes in conductivity or refractive indexes as a function of x; moreover, for the corresponding derivatives, the nonlinear relationship becomes more apparent. These results are in good agreement with our previous communications [1–5] as well as with data reported by other authors [12–16].

The results illustrated in Figs. 2 and 3 were compared with those systems where the SCC was acrylic acid [13], methacrylic acid [14] or hydroxyethyl methacrylate [15, 16]; thus, it may be said that the three distinct regions noted on the graphs (Figs. 2, 3) represent the changes in the structure of the microemulsions formed.

In the literature [12–16] conductometric measurements together with viscometric, light-scattering and electron microscopy measurements are described. In our own work [1–5, 18, 19] conductometric measurements were carried out together with viscometric, refractometric or fluorimetric determinations. The similarities of the results in the two sets of work allow us to find the zones where the microstructure of the systems obtained has been modified.

Consequently, we considered zone A (x = 0.8–1) as corresponding to an o/w microemulsion, zone *B* (x = 0.2–0.8) would coincide with a bicontinuous structure, while zone C (x = 0–0.2) represents a w/o system. It may be noted that the three domains may be also be found in Fig. 1. There is satisfactory agreement between the data presented in the ternary diagrams for EtOH and MeOH (Fig. 1) and those corresponding to other SCCs [12–16].

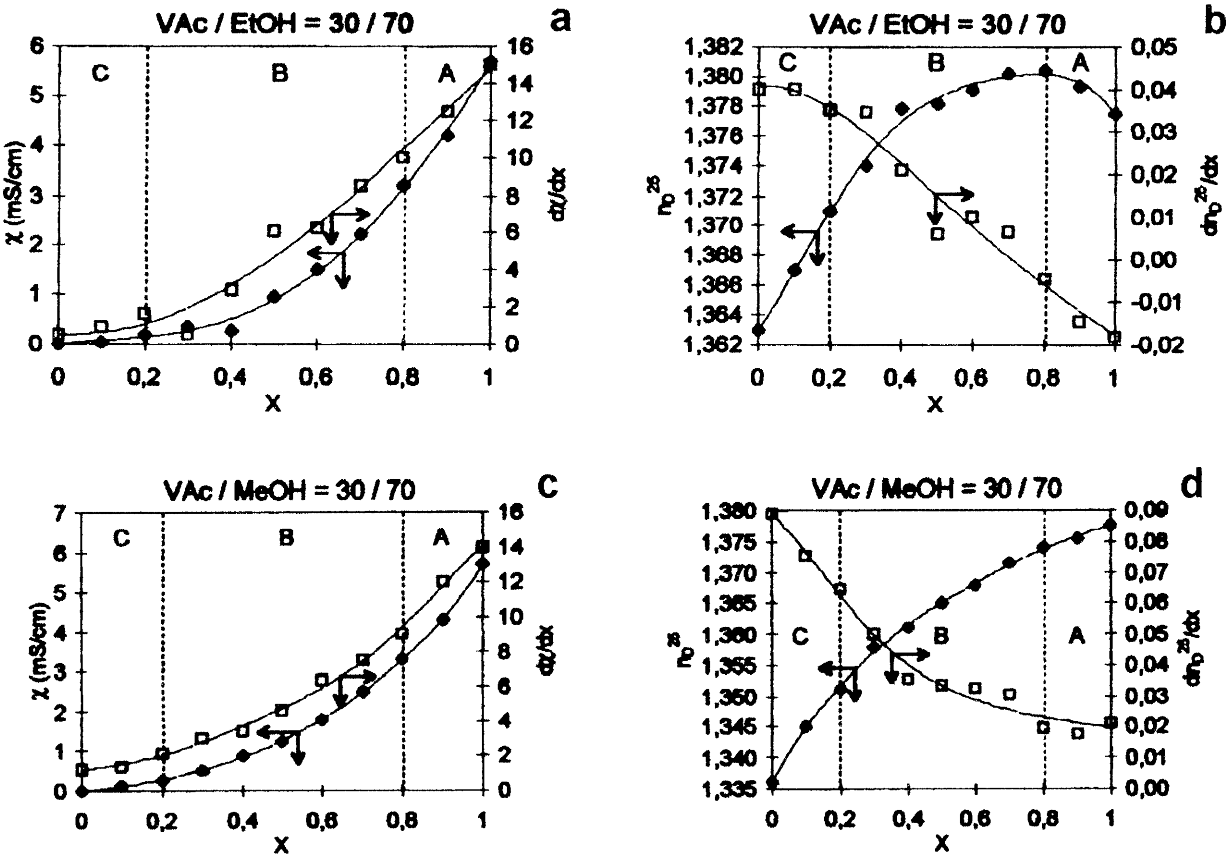


Fig. 2 The change in conductivity (**a**, **c**) and refractive indexes (**b**, **d**) for the systems where the organic phase is **a**, **b** VAc/ethanol (EtOH) and **c**, **d** VAc/MeOH = 30/70

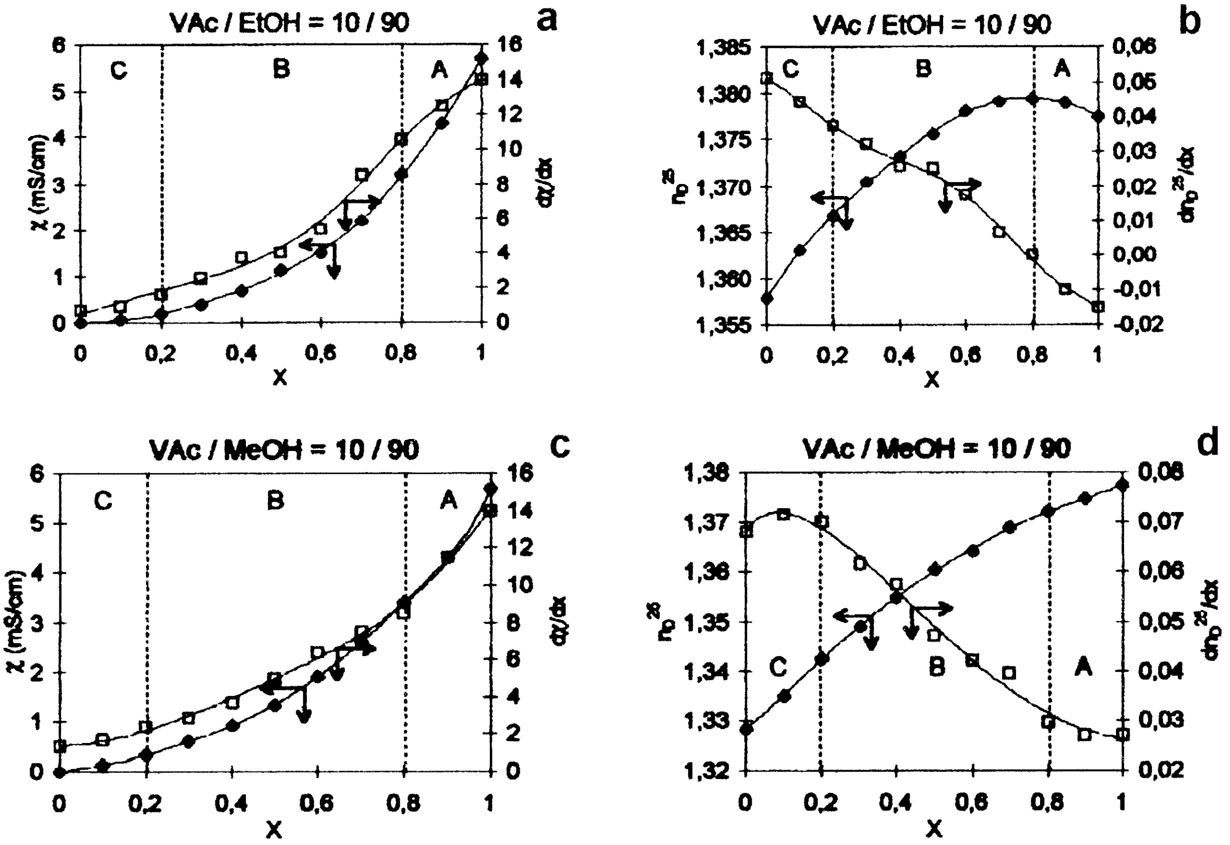


Fig. 3 The change in conductivity (**a**, **c**) and refractive indexes (**b**, **d**) for the systems where the organic phase is **a**, **b** VAc/EtOH and **c**, **d** VAc/MeOH = 10/90

To observe such phenomena we measured the variation of the refractive index for the simplest binary system of the components described previously, namely MeOH–water (Fig. 4); such refractometric results are in excellent agreement with previously reported viscometric data [9].

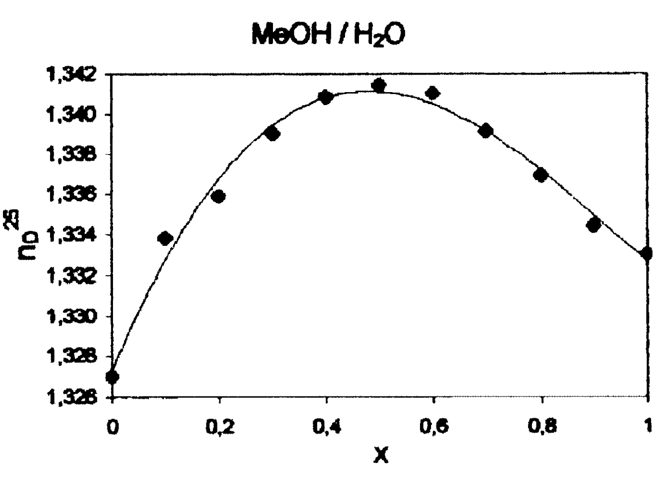


Fig. 4 Refractive indexes versus the composition of the mixture water/MeOH

A possible explanation for the shape of the curve presented in Fig. 4 might be the existence of a critical concentration [7], namely 1 mol MeOH for 5 mol H_2O ($y = 0.737$). When y is higher than this value, MeOH is not associated; in contrast, when $y < 0.737$ CH_3 groups may be associated [17], thus producing a nanostructuration of apparently homogeneous solutions. Due to such associations, the viscosity of the mixture reaches a maximum for the critical concentration. Likewise, the same effect may explain the behaviour of the refractive index. Forming of a zone with a local concentration of the hydrocarbon chain higher than the average may produce a positive shift of the refractive index with regard to the average value.

Starting from these observations for the MeOH/water mixture, as well as from the coincidence between the critical concentration and the boundary value of y (from zone A to B), one may consider that the apparently homogeneous mixtures studied in this work are in fact structured microemulsions.

The homogeneous systems obtained with ethyl acetate revealed the conductivity modification and the refractive index variation as for VAc at 25 °C. These properties could not be determined at the polymerisation temperature due to the high volatility of the organic compounds used.

On examining the graphs of conductivity versus composition (Figs. 2, 3) it is apparent that when replacing MeOH with EtOH the conductivities of the microemulsions decrease; this comportment shows a lower ionisation of COOH groups in the presence of a less polar SCC. Next, we measured the system conductivity in the presence of APS using the same experimental sets as in Figs. 2 and 3, but by adding 1 g APS for 400 g microemulsion; the results are presented in Fig. 5.

It must be underlined that APS was not soluble in all the samples studied; the solubility is lower in EtOH than in the presence of MeOH. Thus, for VAc/EtOH = 30/70 APS is soluble for $x \geq 0.5$, while for VAc/EtOH = 10/90, APS is soluble for $x \geq 0.4$. In the case of the VAc/MeOH systems, APS is soluble in all cases when $x \geq 0.2$. An immediate explanation arises from zone C (consisting of w/o structures), that comes into view at $x = 0.2$; water molecules are dispersed in the SCC, so APS cannot find suitable aqueous solubility zones. Although APS was not totally soluble in zone C, we nevertheless measured the conductivity even for $0.2 \geq x$ for MeOH-containing samples; even in these circumstances one may notice the three different structures (A, B and C) for the microemulsions.

The conductivities of the microemulsions, both in the absence of APS (χ^1) or in its presence (χ^2), show higher values when using MeOH instead of EtOH. The conductivity of the system in the presence of APS for the four VAc/SCC compositions previously studied is shown in Fig. 6; the ratio was w/o = 50/50 ($x = 0.5$). The higher conductivity in the presence of MeOH may be explained by a more advanced ionisation of the initiator in the presence of a polar SCC; it may be expected, as previously reported [18], that the higher the degree of ionisation of APS, the higher its decomposition rate.

We measured the initial decomposition rate of the initiator, as well as its conversion after 3 h, as a function of microemulsion composition; the results regarding the set of tests characterised by a ratio VAc/MeOH = 30/70 are given in Fig. 7a.

By comparing the decomposition of APS in the presence of an aqueous phase ($x = 1$) with that measured when adding a small amount of an organic phase ($x = 0.9$), we found an increase in the decomposition rate in the second case; however, a further increase in the organic phase ($x = 0.9$–0.6) leads to a smaller value for the initial decomposition rate, probably due to a lower degree of ionisation. So, a minimal value was

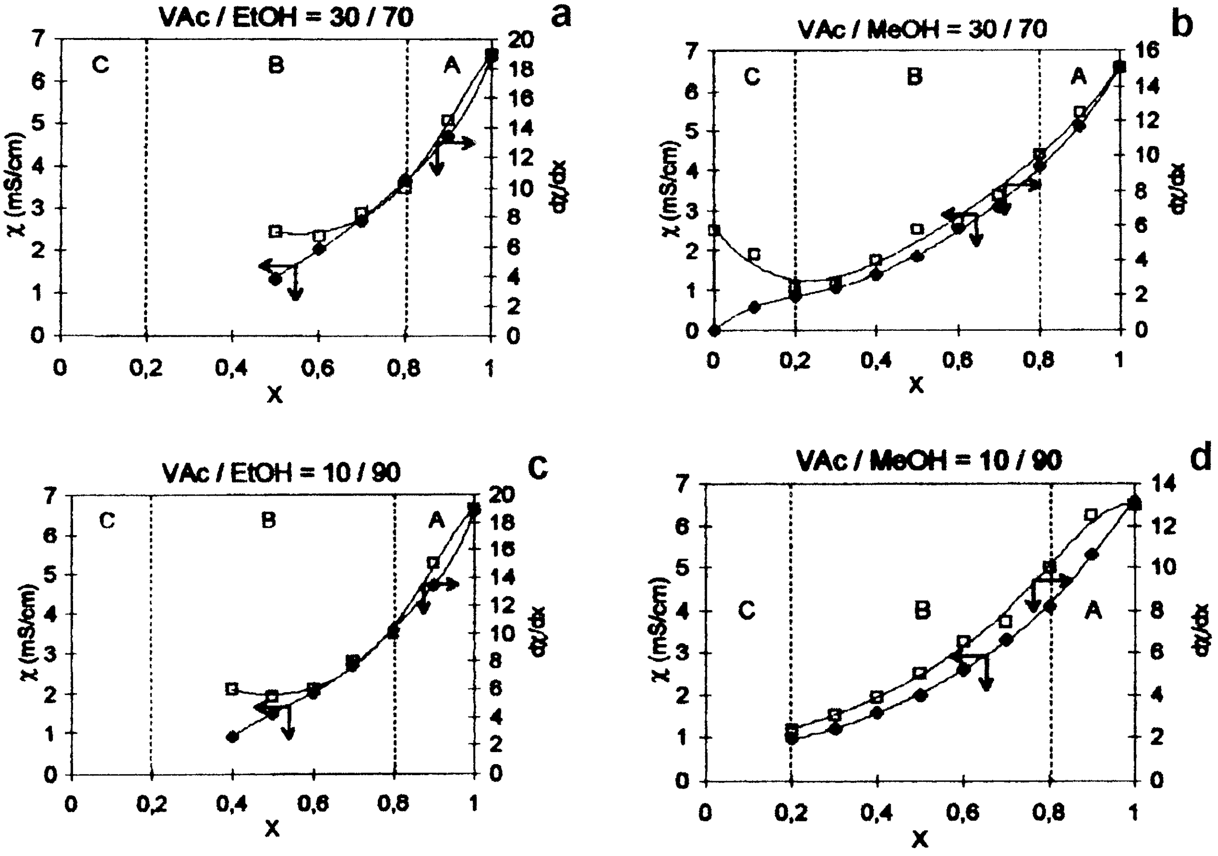


Fig. 5 Conductivity against composition for the microemulsion containing ammonium persulphate (*APS*). The organic phase was **a** VAc/EtOH = 30/70; **b** VAc/EtOH = 10/90; **c** VAc/MeOH = 30/70; **d** VAc/MeOH = 10/90

recorded for $x = 0.6$. Moreover, the formation of a polymer induces a phase separation in the range $x = 0.6–0.7$; in turn, the phase separation results in an increase in the concentration of the organic phase, thus giving rise to the local concentration of APS.

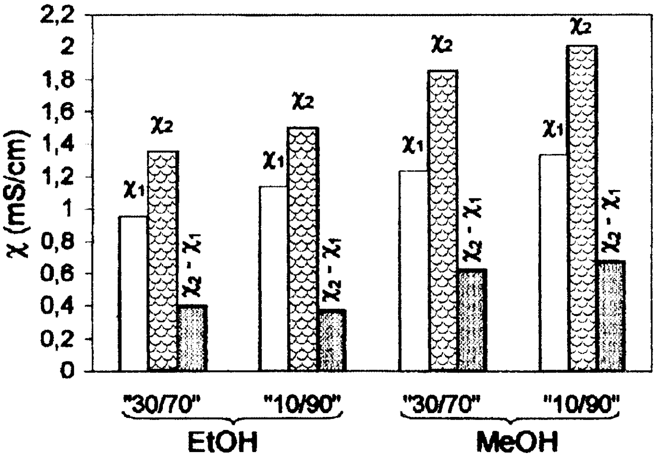


Fig. 6 The conductivities of microemulsions for $x = 0.5$ in the absence of APS (χ^1) and in the presence of APS (χ^2)

When the concentration of the aqueous phase is further diminished ($x = 0.6–0.2$), although the total conductivity of the microemulsion decreases, we recorded a rise in the initial decomposition rate of APS. It might be presumed that in this domain the effect of redox reactions between APS and organic reactants becomes manifest; conversion of APS (measured after 3 h) increases when x is reduced [2, 5].

The results for the polymerisation of VAc carried out at a ratio VAc/MeOH = 30/70 are presented in Fig. 7b and show the effect of microemulsion structure corresponding to different compositions.

Both, the initial polymerisation rate and VAc conversion (after 3 h) increase with the raising of the monomer concentration in the system. The polymerisation rate depends on the monomer concentration and the decomposition rate of the initiator. The increase in the polymerisation rate in zone A is more important than in zone B at $x = 0.8–0.4$. Although the monomer concentration increases, the decrease in the decomposition rate of the initiator as well as the phase separation result in a lower polymerisation rate for the monomer. In domain B ($x = 0.4–0.2$), where the decomposition rate increases again (Fig. 7a), both the polymerisation

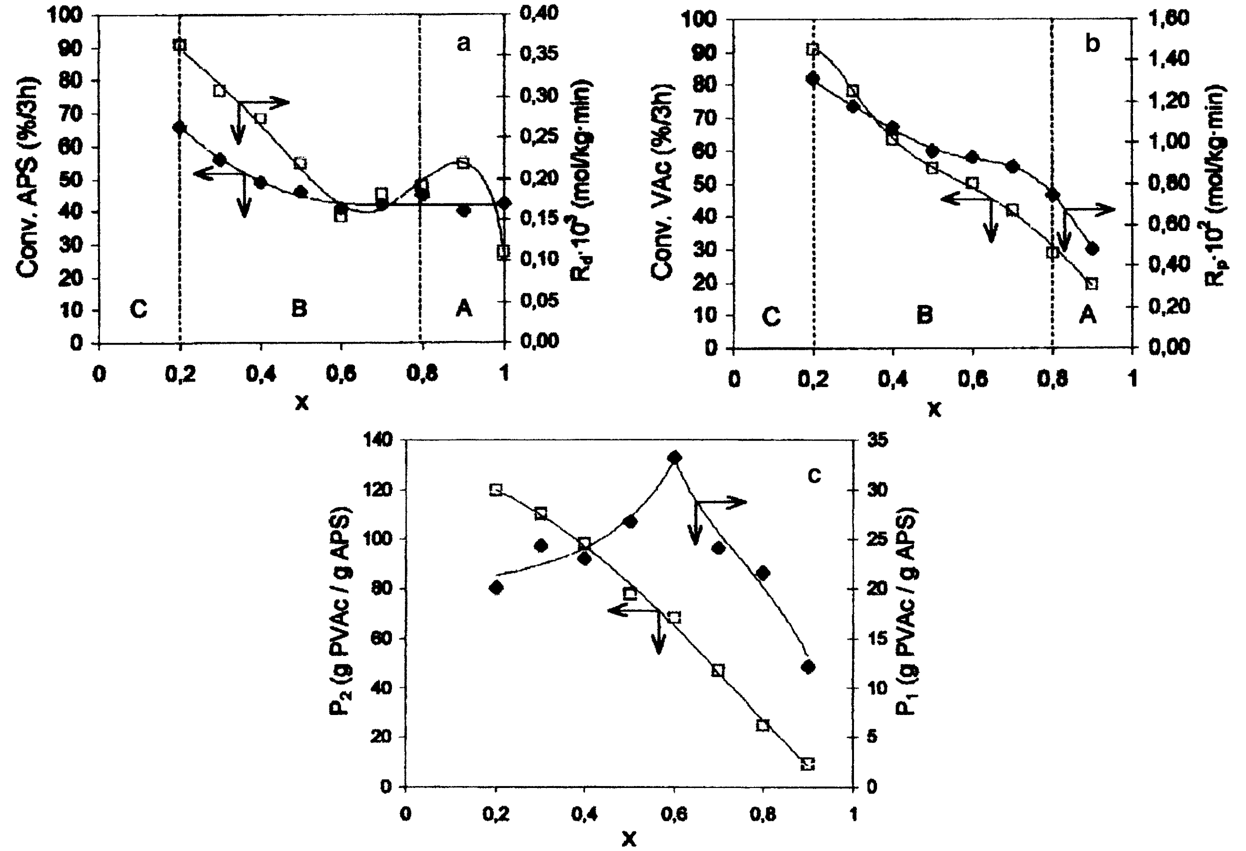


Fig. 7 Initiator conversion after 3 h and initial decomposition rate for the initiator (**a**), conversion of VAc and initial polymerisation rate (**b**) and initiator productivity at the start of the process (P1) and after 3 h (P2) (**c**) as a function of microemulsion composition, listed as $x = w/(w + o)$; VAc/MeOH = 30/70; [I] = 1 g APS/400 g microemulsion; polymerisation in a stirred reactor

rate and the conversion increase significantly when the concentration of the organic phase (or the monomer concentration) increases.

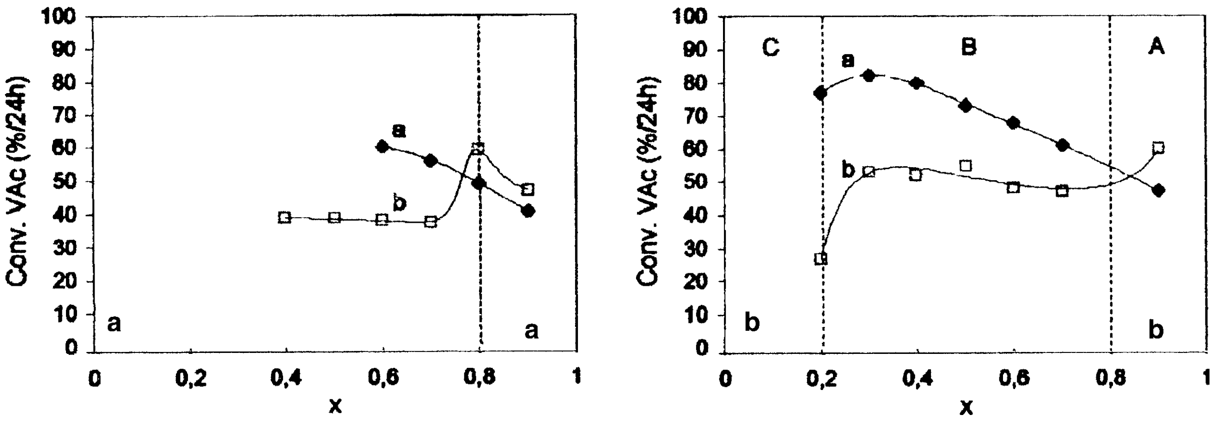
In order to correlate initiator decomposition with VAc polymerisation, we propose a value called the "APS productivity" (P) as the amount of polymer (in grams) formed after the decomposition of 1 g APS. Consequently, knowing the initial rate for initiator decomposition as well as the initial polymerisation rate for VAc, one may calculate the initial productivity (P1); in a similar manner, we calculated the productivity after 3 h of reaction (P2). The results are presented in Fig. 7c.

The initial productivity (P1) shows a maximum in the composition range where the initial decomposition rate of APS is minimal ($x = 0.6$), while P2 increases but in a nonlinear manner with monomer concentration. It may be said that the initial microstructure of the microemulsions is responsible for the changes in the reactivity of the reactants. Moreover, a supplementary proof for the existence of different structures in cases A and B is given by the fact that the decomposition rate for APS exhibits a minimum for a composition close to the critical concentration of MeOH ($x_{\mathrm{water}} = 0.74$). This result is in good agreement with previously published data [2] for microemulsions containing EtOH.

The influence of the carbon chain length of SCC on monomer conversion (after 24 h) was compared for systems containing MeOH and EtOH. Using the ratios VAc/SCC = 30/70 and 10/90, the investigations were only restricted to homogeneous systems; the results are presented in Fig. 8a (microemulsions containing EtOH) and Fig. 8b (microemulsions containing MeOH).

Conversion of VAc (24 h) increases in a nonlinear manner as a function of microemulsion composition for the systems characterised by VAc/SCC = 30/70; for the systems where VAc/SCC = 10/90, we noticed a reduction in conversion when x decreases, a fact that has been mentioned in other work [1, 2] as well, this being attributed to a degradative transfer of macroradicals with the SCC. For the same composition, monomer conversion is higher in the presence of MeOH than for EtOH, probably due to a more pronounced dissociation of APS [18].

Fig. 8 Conversions of VAc (24 h – polymerisation in sealed-off vials) for microemulsions containing **a** EtOH and **b** MeOH; $[I] = 1$ g APS for 400 g microemulsion. *a* VAc/ROH = 30/70; *b* VAc/ROH = 10/90



The solubility of APS is strictly restricted to o/w and bicontinuous microemulsions; accordingly, to investigate the behaviour of VAc throughout the whole domain of compositions, we used Bz_2O_2 as well. At the same time, attempts were made to study the influences introduced by the use of a reactive surfactant (MEMNPEO25); IR investigations [1] have shown that MEMNPEO25 displays a significant conversion in the domain of w/o microemulsions. Of course, this constitutes an additional reason to use an initiator soluble over the whole range of compositions.

The monomer conversion for systems containing MeOH, for all aqueous phase compositions (x) is given in Fig. 9.

Under all circumstances, the final conversion of VAc shows a nonlinear variation with initial monomer concentration. For the ratio VAc/MeOH = 30/70 we noticed a sharp decline in the total conversion when switching from the w/o structure (C) to the bicontinuous one (B). This phenomenon, known also for other systems [1, 2, 19], might be ascribed to a degradative chain transfer with the SCC that is more pronounced for the bicontinuous microstructures (due to an increase in the surface between the organic and aqueous phases); even when doubling the initiator concentration, the conversion still remains low. Additional evidence is given by the very low conversions obtained when VAc/MeOH = 10/90 (Fig. 9).

For the mixture VAc/MeOH = 30/70 with $x = 0.2$, where the molar concentration of Bz_2O_2 is twice the corresponding concentration of APS, the monomer conversion (after 24 h) is only 50% (in the case of Bz_2O_2) compared with 75% for APS (Fig. 9). Such

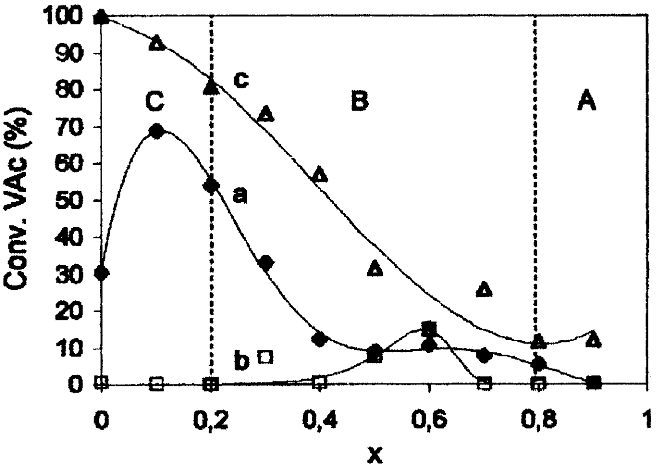


Fig. 9 Conversions (VAc) for microemulsions containing MeOH; first polymerisation method – 24 h: *a* VAc/MeOH = 30/70, 2 g benzoyl peroxide (Bz_2O_2) for 100 g VAc, 24 h; *b* VAc/MeOH = 10/90; 2 g Bz_2O_2 for 100 g VAc, 24 h; *c* VAc/MeOH = 30/70, 4 g Bz_2O_2 for 100 g VAc, 48 h

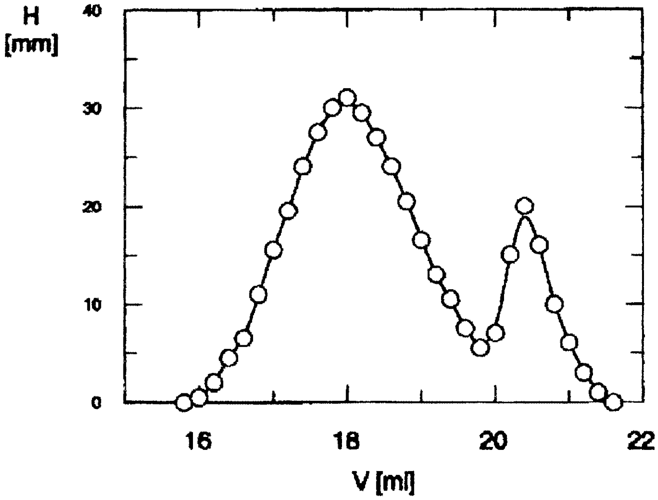


Fig. 10 Chromatogram of a sample obtained as follows: VAc/MeOH = 30/70; $x = 0.1$; $[Bz_2O_2]$ = 2 g for 100 g VAc; reaction time = 24 h

Table 1 GPC results regarding the reactivity of MEMNPEO25 (VAc/MeOH = 30/70)

Conc. of aqueous phase	Initiator concentration	Reaction time	M_n	M_w	Composition of copolymer [% MEMNPEO25]
[% MEMNPEO25]					
0.1	2 g/100 g VAc	24 h	14500	24500	9.1
0.2	2 g/100 g VAc	24 h	14700	24100	17.2
0.3	2 g/100 g VAc	24 h	12100	20500	0
0.2	4 g/100 g VAc	48 h	13100	20200	18.3
0.3	4 g/100 g VAc	48 h	10000	18000	2.29

results are in good agreement with data obtained by other authors on very different systems [20].

As far as we know, the present work is the first that reports the polymerisation of VAc in microemulsions containing MeOH. On the other hand, MeOH is the solvent currently used for VAc polymerisation when the final desired product is poly(vinyl alcohol) [21]; of course, the presence of water would alter the polymerisation rate as well as the properties of the poly(vinyl alcohol) [21] finally obtained. All these changes may be explained through the formation of microemulsions.

By removing all volatile products at the end of the polymerisation we obtained mixtures containing the copolymer poly(VAc–MEMNPEO25) and unreacted MEMNPEO25; the amount of the latter may be obtained by gel permeation chromatography (GPC). A typical chromatogram is given in Fig. 10. The peak corresponding to small elution volumes (high molecular masses) coincides with the polymer. Average molecular weights were calculated from:

$$M_w = \sum (w_i \, M_i) \tag{1}$$

$$1/M_n = \sum (w_i / M_i) \tag{2}$$

where w_i is the mass fraction of molecules with molecular mass M_i; w_i is provided by evaluating the normalised GPC chromatogram data with a computer program and M_i is given by a calibration curve.

The peak recorded for an elution volume of 20.5 ml corresponds to unreacted MEMNPEO25. Taking into account the proportionality between the area under the peak and the MEMNPEO25 concentration, one may calculate the amount of unreacted surfactant. Also, based on the material balance for the reactive surfactant, we calculated the amount of MEMNPEO25 present in the copolymer. The results are presented in Table 1.

We should mention that for $x = 0.3$ the percentage of MEMNPEO25 present in the copolymer is far lower than that corresponding to $x < 0.2$. This represents a proof for the fact that the change in initial microstructure leads to an alteration in surfactant reactivity; this takes place as polar groups are more soluble in water for $x > 0.2$.

For those samples starting from mixtures containing higher amounts of initiator, we obtained lower average molecular weights; therefore, in many situations we obtained in the same GPC chromatogram both the peak corresponding to polymer and that attributed to MEMNPEO25. To solve the problem of separating the effects, each chromatogram was decomposed by using a computer program.

After separating the peak corresponding to the (co)polymer, the molecular-weight distribution was obtained based on the calibration curve (polystyrene standards). To illustrate the dependence of molecular masses against initiator concentration, in Fig. 11 we present the molecular-weight distributions of the copolymers obtained in the following conditions: (I) VAc/MeOH = 30/70, $x = 0.1$, $[Bz_2O_2] = 2$ g for 100 g VAc and (II) VAc/MeOH = 30/70, $x = 0.1$, $[Bz_2O_2] = 4$ g for 100 g VAc.

Also for mixtures containing higher amounts of initiator, the concentration of MEMNPEO25 in the copolymer is lower for $x = 0.3$ than for $x = 0.2$; in all situations, the reactive surfactant does not react entirely with VAc.

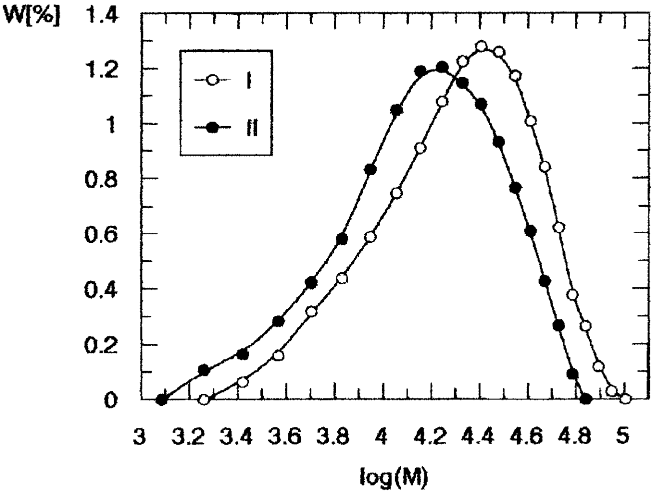


Fig. 11 Typical distributions for samples obtained under the following conditions. *I* VAc/MeOH = 30/70; $x = 0.1$; $[Bz_2O_2] = 2$ g/100 g VAc; reaction time = 24 h; $M_n = 14500$; $M_w = 24500$. *II* VAc/MeOH = 30/70; $x = 0.3$; $[Bz_2O_2] = 4$ g/100 g VAc; reaction time = 48 h; $M_n = 10000$; $M_w = 18000$

Conclusions

Microemulsions of VAc of the type w/o, bicontinuous or o/w (as a function of initial composition) may be achieved in the presence of both EtOH or MeOH as SCCs; the different conceivable structures may be explained by taking into account the behaviour of mixtures of MeOH/water and EtOH/water, respectively.

After introducing the initiator, the homogeneous microemulsions maintain their structure, that in turn is responsible for the degree of ionisation of the initiator. This changes the decomposition rate of the initiator, influencing the total polymerisation rate.

Even when another initiator, soluble in the "organic" phase, is present in the mixture, the monomer conversion is still influenced by the structure of the microemulsions; this microemulsion structure affects the intensity of chain-transfer reactions.

The highest reactivity of the unsaturated surfactant was noticed at a fraction of the aqueous phase of $x = 0.2$; this conclusion was reached by measuring the concentration of unreacted surfactant by GPC. It is important to note that 0.2 represents the threshold between w/o and bicontinuous microemulsions.

All these facts underline the conclusion that the reactivities of initiator, monomer and surfactant are a function of microemulsion structure.

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