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## **COPOLYMERIZATION OF VINYL ACETATE WITH REACTIVE SURFACTANTS IN HOMOGENEOUS MEDIA**

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### **ABSTRACT**

The possibility of extending the homogeneity domains obtained after microemulsion polymerization of vinyl acetate in the presence of polymerizable surfactants was studied. Utilization of the monomaleate of nonyl phenol ethoxylated with 25 moles of ethylene oxide as the reactive surfactant increased the number of homogeneous phases from 18 to 32 for 45 systems studied which contained vinyl acetate, ethanol, water, or 33% weight surfactant solution. After the polymerization of vinyl acetate, the number of homogeneous systems was from 15 to 27. The molar excess volume was minimum over a critical range for an alcohol/water (1 mole/5 moles) mixture. The monomer conversion is also minimum over this concentration range. These phenomena were also evidenced in copolymerization of vinyl acetate with di-2-ethyl hexyl maleate, using *n*-propanol as cosurfactant.

### **INTRODUCTION**

The polymerization of vinyl acetate (VAc) in microemulsions with short chain alcohols (C<sub>2</sub>–C<sub>4</sub>) as cosurfactants was studied in earlier contributions [1–5]. The physicochemical properties of homogeneous systems obtained with various organic phases (O) over aqueous phase (W) ratios are not additive; this phenomenon illustrates the intricacy of structures which are far from ideal. This behavior was ex-

plained by the modification of alcohol-water system structures depending on the ratio of components [6-8].

The microemulsion polymerization of methyl methacrylate with acrylic acid as cosurfactant showed that one can obtain bicontinuous O/W and W/O microemulsion-type structures in the presence and absence of the surfactant at various O/W ratios [9]. The same phenomenon of microemulsion formation was noted in case of the systems containing an isopropanol + water mixture [10].

The similar behavior allows one to assume that these water-soluble compounds which possess a short hydrophobic chain may associate to form distinctively structured systems (depending on concentration) as surfactants [11, 12] yet of smaller size [8].

The systems previously used retain their homogeneity after polymerization only in the case where the alcohol-water mixture solubilizes the polymer [1-5]. Utilization of a polymerizable surfactant widens the homogeneity range after polymerization [3].

In this contribution the microemulsion polymerization of vinyl acetate is extended: C<sub>2</sub> and C<sub>3</sub> alcohols are used as cosurfactants to make use of a polymerizable surfactant. The surfactant employed was maleic monoester of nonyl phenol ethoxylated with 25 moles of ethylene oxide (MEMNPEO<sub>25</sub>).

## EXPERIMENTAL

### Materials

The vinyl acetate, di-2-ethyl hexyl maleate (EHM), methyl methacrylate (MMA), and acrylic acid (AcrA), were commercial products purified by rectification at atmospheric pressure or in a vacuum. Ethanol (EtOH), propanol (PrOH), and maleic anhydride (Reactivul) were used without further purification. Benzoyl peroxide, a CHIMOPAR product, was used as such. Nonyl phenol ethoxylated with 25 moles of ethylene oxide and sodium dodecylsulfate (SDS), a commercial product, were used without purification. The monomaleate of nonyl phenol ethoxylated with 25 moles of ethylene oxide was synthesized by means of the reaction between maleic anhydride and nonyl phenol ethoxylated with 25 moles of ethylene oxide at 60°C for 3 hours.

### Polymerization

Polymerization was effected at 65°C for 20 hours for homogeneous systems. They contained 3% initiator (benzoyl peroxide) against the monomer. They were kept in glass ampules sealed by flame. The VAc/EHM (80/20) copolymers were synthesized in a glass flask under stirring for 5 hours. In all variants, 400 g were employed in the reaction. After 5 hours a similar amount of initiator was added and the mixtures were sealed in glass ampules as above. The reaction continued for 20 hours.

### Determining the Homogeneous Compositions

In order to establish the homogeneity ranges, five monomer/alcohol ratios were prepared: 10/90, 30/70, 50/50, 70/30, 90/10 (weight ratios). Each solution so

prepared represents the organic part (O) which is mixed with the aqueous phase (W) (9 weight ratios). The aqueous phase was a 33% (W) solution of MEMNPEO<sub>25</sub> in water. In this way 45 mixtures were obtained and their evaluation was carried out visually. Their number is indicated in the ternary diagrams. For Fig. 2(c) the conditions were as in Ref. 9: O = MMA/AcrA = 10/90, W = 20 wt% solution of SDS in water.

**Determination of the Properties of Homogeneous Systems**

The refractive index was measured by means of an Abbé refractometer at 25°C. The density was measured at 25° C with a pycnometer. The excess molar volume ( $V^E$ ) was calculated in terms of densities according to Ref. 14-17:

$$\Delta V^E = V_m - V_1x_1 - V_2x_2 \tag{1}$$

where  $V_m$  = the molar volume of the mixture

$V_1, V_2$  = the molar volumes of the two components

$x_1, x_2$  = the mole fractions for the corresponding components

The IR spectra were recorded with a SPECORD 70 apparatus. Samples were deposited as films on KBr from solutions of methyl acetate.

**RESULTS AND DISCUSSION**

**Homogeneity Ranges**

The number of homogeneous systems and their composition ranges for VAc/EtOH are shown in Fig. 1.

A comparison of the number (32) of homogeneity ranges obtained in the presence of MEMNPEO<sub>25</sub> (Fig. 1) with those (18) obtained in the presence of water [5] suggests that the surfactant increases the probability of homogeneous phase formation. Its important contribution lies in the aqueous phase-rich region.

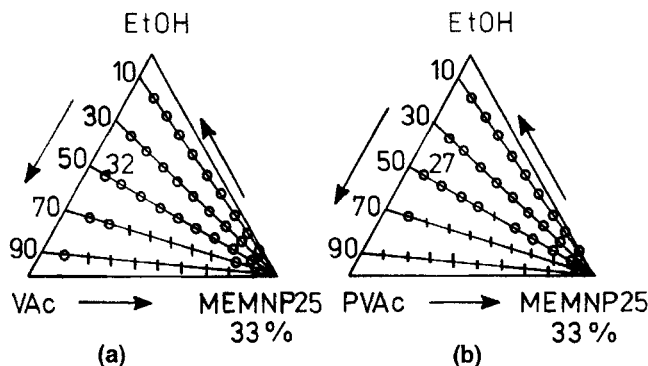


FIG. 1. Homogeneity ranges [O = VAc + EtOH (a), PVAc + EtOH (b), W = MEMNPEO<sub>25</sub> 33%].

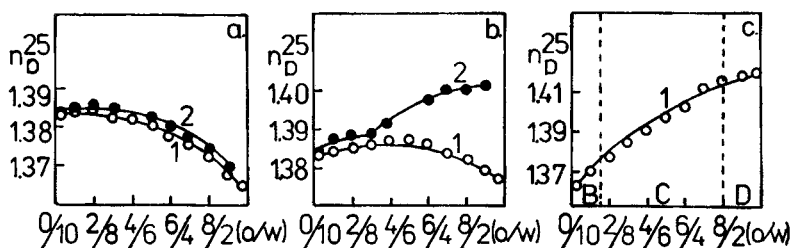


FIG. 2. Modification of refractive indexes as function of O/W ratio [ $\circ$  = VAc/EtOH = 10/90 (a), 50/50 (b), W = MEMNPEO<sub>25</sub> 33%;  $\bullet$  = MMA/AcrA = 10/90, W = SDS 20% (c); Curve 1, initially; Curve 2, after polymerization].

Mixtures consisting of O = VAc/EtOH = 50/50, 30/70, 10/90, and W = 33% MEMNPEO<sub>25</sub> are homogeneous at any O/W ratio.

In this case the refractive indexes of homogeneous phases exhibit deviations from linearity depending on O/W (Fig. 2).

For well-know microemulsions [9] the behavior is the same (Fig. 2c): B = W/O, C = bicontinuous, D = O/W microemulsions.

In the case when the mixture VAc/EHM (80/20) is used for monomers and *n*-propanol as the cosurfactant, one obtains homogeneous phases for any O/W ratio where O is a mixture of monomers/PrOH = 30/70 and W = 33% MEMNPEO<sub>25</sub>.

The refractive indexes of these mixtures also depend nonlinearly on O/W (Fig. 3). This behavior should be assigned to the alcohol-water mixture these systems contain. A negative variation of the excess volume on mixing (volume contraction) and a nonlinear dependence of the refractive index on composition were noted in the propanol-water mixture used in this study (Fig. 4 and 5).

The phenomena presented above arise from to the strong interactions between alcohol and water. The molar volume of propanol is much higher than that of water. On adding larger amounts of alcohol to water ( $X_{\text{H}_2\text{O}} < 0.83$ ), the cluster structure of water coexists with the alcohol-water mixture. At  $X_{\text{H}_2\text{O}} = 0.83$  a molecule of alcohol replaces one of water in the initially formed cluster structures con-

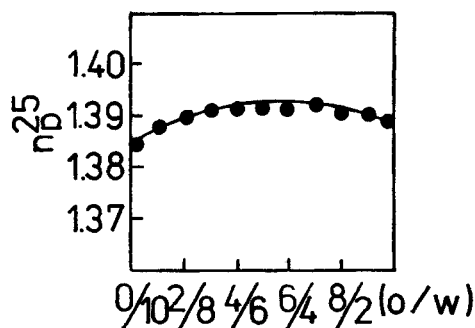


FIG. 3. The dependence of refractive indexes of homogeneous mixtures on O/W [ $\bullet$  = (VAc/EHM = 80/20)/PrOH = 30/70, W = MEMNPEO<sub>25</sub> 33%].

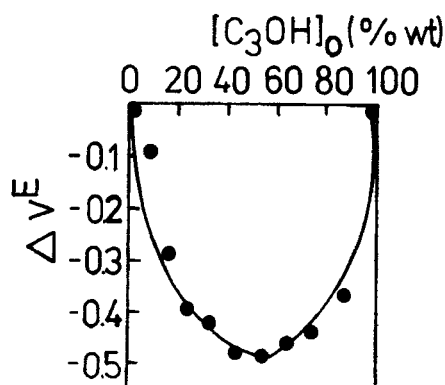


FIG. 4. The dependence of excess molar volume on *n*-propanol concentration for *n*-propanol–aqueous solutions (wt%).

sisting of 6 water molecules [6, 7]. Mixed clusters were evidenced in mixtures with such a composition; they are associated with the overall composition of 8 propanol molecules and 40 water molecules with a diameter in the hydrocarbon phase of 12.4 Å [8]. The formation of these associations may account for the minimum excess molar volume obtained in this concentration range (~40 wt% *n*-propanol) (Fig. 4).

At higher alcohol concentrations the characteristic “chain structure” maintains the water molecules in the OH region. One can imagine bicontinuous hydrocarbon–water structures as in the case of surfactants and microemulsions [11, 12]. This assumption is supported by the following finding: In homogeneous systems with a nonionic surfactant, the introduction of organic acids with a short chain affects the conductance to an extent which depends on the length of the hydrocarbon chain [18]. E.g., acrylic acid, which is more hydrophobic, intercalates in hydrocarbon zones and does not affect the conductivity when its concentration is increased.

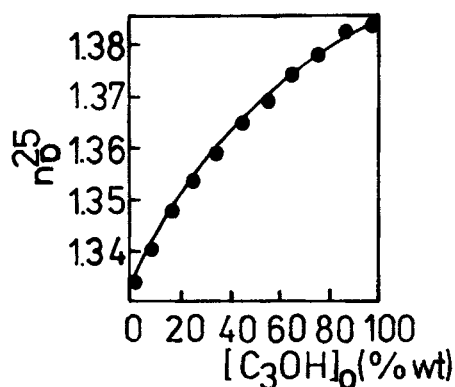


FIG. 5. The dependence of refractive index on *n*-propanol concentration in ProH/ $H_2O$  mixtures (wt%).

Maleic acid, which is more hydrophilic and water-soluble, increases the conductivity because it lies in the aqueous zone and dissociates.

Because acrylic acid used as a cosurfactant may generate various O/W, bicontinuous, and W/O type structures (Fig. 2c), homogeneous systems which contain methyl methacrylate and water systems can be regarded as microemulsions [9]. Isopropyl alcohol exhibits the same behavior and can form microemulsions even in the absence of a surfactant [10].

The nanostructure of the liquids was studied in a recent paper [22]. The possible existence of hydrophobic demixing was evidenced in the case of organic compounds whose chains are too short to form micelles when mixed in water.

The fluorescence probe method was successfully used to show the structural modifications of alcohol–water mixtures [18]. The intensity ratio of pyrene fluorescence bands varies nonlinearly with the composition of the systems. In the case of *n*-propanol, a sudden decrease of the ratio is similar to that of micellar solutions so that a critical concentration of the association can be determined.

The refractive indexes and the excess molar volumes of acrylic acid and isopropanol–water solutions depend nonlinearly as well as on the cosurfactant/water [18] ratio. These compounds are well accepted as efficient cosurfactants for microemulsions [9, 10].

All these experimental results demonstrate that all the short-chain cosurfactants mentioned in the literature [9, 10] and in this paper exhibit the same behavior in the presence of water.

The monomers methyl methacrylate [9] and vinyl acetate [1–5] may penetrate the nanostructures of cosurfactant–water binary systems to yield homogeneous systems.

For microemulsions containing VAc–ethanol [3, 18], the H-NMR spectra, conductivities, and refractive indexes evidence a nonlinear change with O/W as in the case of cosurfactants–water systems.

The classical microemulsions differ from those studied in this contribution: the former result from surfactant association while the latter result from cosurfactant association.

### Polymerization in Homogeneous Systems

Three VAc/EtOH ratios were selected for the polymerization of vinyl acetate in homogeneous mixtures of the compositions shown in Fig. 1: 10/90, 30/70, and 50/50. These ratios ensure the homogeneity for any O/W ratio. In these three series only the mixture with  $O = \text{VAc/EtOH}$  (50/50) and  $O/W = 5/5$  loses homogeneity after polymerization. From the 32 initially homogeneous systems (Fig. 1a), only 27 remain homogeneous after polymerization (Fig. 1b). As for the systems without surfactant, from 18 only 15 remain finally homogeneous. This behavior is the first proof for the formation of very finely dispersed or medium-compatible copolymers. Polymer formation is evidenced by modification of the refractive index after polymerization (Fig. 2) and by an increase of the nonvolatile component content in the mixtures. A plot of final conversions versus O/W ratio yields the results shown in Fig. 6. In the EtOH/H<sub>2</sub>O system the critical concentration of 1/5 moles corresponds to a concentration of 33.8% EtOH. This concentration is indicated by arrows in the

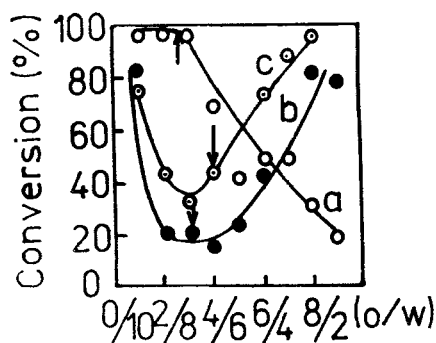


FIG. 6. The final conversion of VAc/EtOH = 10/90 (a), 30/70 (b), and 50/50 (c) versus O/W (65°C, 20 hours).

figure for every mixture. Note that conversion is minimum in this critical concentration range.

The same results were obtained for the system whose comonomer is the VAc/EHM mixture and whose cosurfactant is propanol (Fig. 7). The conversion exhibits a minimum in the concentration range of 1/5 propanol/water (40% weight PrOH), and it is the only system which is not homogeneous after polymerization lies at O/W = 5/5. In the case of systems with VAc/EHM copolymers, the variation of the initial rate as a function of O/W was determined; the deviation from a straight line passing through the origin of this plot lies below the critical concentration range, PrOH/H<sub>2</sub>O = 1/5 (Fig. 8).

Comparison of the results in Figs. 4, 6, and 7 supplies an explanation for the kinetic results. The excess molar volume is minimum over the region of critical alcohol concentration. The formation of clusters containing 1 mole of alcohol and 5 moles of water [6, 7] associated in formations with 8 moles of alcohol and 40 of water [8] determines the maximum contraction of the system. In these concentration

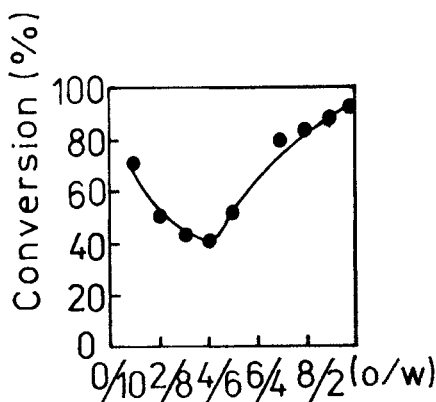


FIG. 7. Modification of final conversions as a function of O/W for ● = (VAc/EHM = 80/20)/PrOH = 30/70, W = MEMNPEO<sub>23</sub>, 33% (65°C, 25 hours).



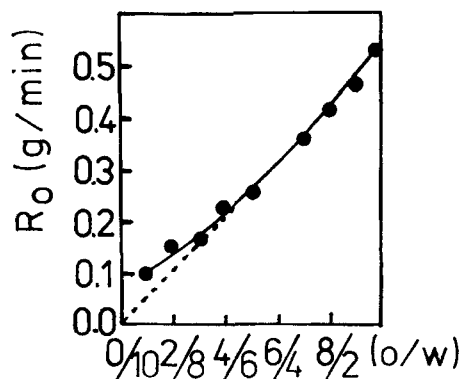


FIG. 8. The variation of initial formation rate of VAc/EHM copolymers (reaction mixture 400 g, 5 hours, 65°C).

domains it is very likely that the reactant diffusion is minimum. One can note that the rate is minimum for ammonium persulfate (water-soluble initiator [4]) as well, and the kinetics of the polymerization is affected by this modification [18].

It is very interesting that a sudden decrease of the polymerization rate at the critical concentration is also noted in styrene polymerized in an acetone-water mixture [19]. Acetone, which behaves like alcohols [7], associates by structuring in water. These results represent an additional proof which supports the hypothesis that alcohol/water behaves like surfactant/water systems [11, 12].

Ternary surfactant-water-alcohol systems exhibit tensioactive properties which no longer depend on the surfactant above a certain concentration of alcohol [20]. Above this propanol concentration, the surfactant is no longer micellized [21].

Some systems obtained after polymerization that contain small amounts of polymer retain the same type of variation of the refractive index with the O/W ratio (Fig. 2a). In those systems with a higher polymer content, the variation of the refractive index is considerably different (Fig. 2b). The presence of macromolecules represents a new contraction of the system and implies new types of interactions.

### Copolymerization of Reactive Surfactants

The fact that homogeneous systems are obtained over a high concentration range of the aqueous phase proves that the surfactant is bonded to the polymer chain. The homogeneity ranges increase after polymerization in the presence of the reactive surfactant, in good agreement with the results published by Chew and Gan [13].

Analysis of VAc/EHM/MEMNPEO<sub>25</sub> copolymers was carried out by IR spectroscopy. In systems with a high reactive surfactant concentration, the surfactant is not completely consumed during polymerization. Double bonds could be detected in all systems that contain a W at higher than O/W = 7/3 ratio. The maximum content of MEMNPEO<sub>25</sub> at which no double bonds are detected is 36.9 wt%. In physical copolymer mixtures (VAc/EHM) with MEMNPEO<sub>25</sub>, the band that characterizes the double bond at 1620 cm<sup>-1</sup> is present in all spectra if the content of

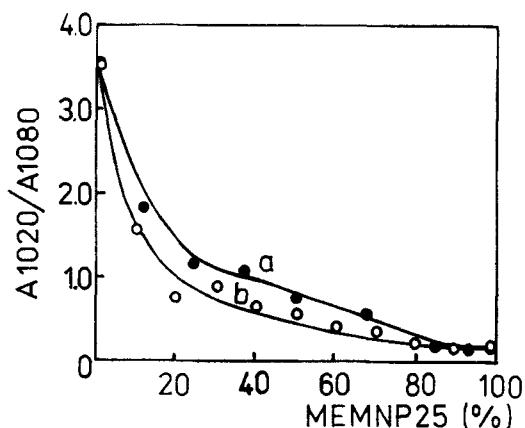


FIG. 9. The variation of  $A_{1020}/A_{1080}$  ratio in IR spectrum of the copolymers with MEMNPEO<sub>25</sub> (a) and of VAc/EHM copolymer mixture (80/20) with MEMNPEO<sub>25</sub> (b).

reactive surfactant lies between 10 and 100 wt%. This proves, beyond doubt, that the reactive surfactant copolymerizes.

The differences between the copolymers obtained in the presence of MEMNPEO<sub>25</sub> and the physical mixtures of VAc/EHM copolymers with a reactive surfactant appear in other zones of the IR spectrum. The strongest band for MEMNPEO<sub>25</sub> lies at 1080 cm<sup>-1</sup>, characteristic of the deformation vibration of the C—O bond. At 1020 cm<sup>-1</sup> a very small maximum appears. There is a very strong band at 1020 cm<sup>-1</sup> and a very weak one within the 1080–1100 cm<sup>-1</sup> range in VAc/EHM copolymers, just the opposite of the case of a reactive surfactant. The changes of the  $A_{1020}/A_{1080}$  ratio in copolymers obtained in the presence of MEMNPEO<sub>25</sub> and VAc/EHM + MEMNPEO<sub>25</sub> physical copolymer mixtures are shown in Fig. 9.

The  $A_{1020}/A_{1080}$  ratio of the copolymers obtained in the presence of MEMNPEO<sub>25</sub> decreases from 3.53 (copolymer without reactive surfactant) to 0.18 for the sample with 89.5% MEMNPEO<sub>25</sub> and then remains constant. In physical mixtures this ratio takes small values at concentrations between 10 and 70%. The two curves superimpose in the case of samples with a MEMNPEO<sub>25</sub> concentration higher than 70%. The difference between the IR spectra of the two types of film proves that the reactive surfactant is not physically dispersed. The disappearance of double bond absorption proves that it is copolymerized.

## CONCLUSIONS

Homogeneous systems containing monomers, C<sub>2</sub> and C<sub>3</sub> alcohols, water, and a surfactant adopt a modified structure which depends on the alcohol/water ratio. Minimal conversions of the monomers were obtained in the range of concentration over which the alcohol–water mixture exhibits a minimum of excess molar volume. The reactive surfactant increases the concentration range within which homogeneous systems are obtained owing to its copolymerization.

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