Emulsion copolymerization of acrylonitrile and butyl acrylate
9. The micellar and polymerization studies in the mixed emulsifier system

I. CAPEK, M. MLYNÁROVÁ, and J. BARTOŇ

Polymer Institute, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava

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The free-radical emulsion copolymerization of acrylonitrile and butyl acrylate initiated by potassium peroxodisulfate at 60 °C in the presence of the blend of anionic and nonionic emulsifier has been investigated. The effect of the emulsifier blend composition on the surface tension of anionic—nonionic emulsifier systems at 30 °C has been described.

Two kinds of micelles (one rich in anionic emulsifier and the other rich in nonionic one) coexisting in the present mixed emulsifier solutions were formed.

The rate of polymerization was found to increase and the latex particle size to decrease with increasing concentration of the anionic emulsifier in the reaction system. An abrupt increase in the polymerization rate within the mole fraction range of the anionic emulsifier from 0 to 0.1 and from 0.9 to 1.0 has been observed.

Over the interval 2 the rate of polymerization is proportional to the 0.55 power of the final polymer particle number, to the 0.36 power of the anionic emulsifier concentration and to the 1.09 power of the total emulsifier concentration.

Исследована свободно-радикальная эмульсионная сополимеризация акрилонитрила и бутилакрилата, инициированная пероксодисульфатом калия при 60 °C в присутствии смеси анионного и неионного эмульгаторов. Описано влияние состава смеси эмульгаторов на поверхностное напряжение анионно-неионных систем эмульгаторов при 30 °C.

Обнаружено образование двух типов мицелл (одного с высоким содержанием анионного эмульгатора, а второго с преобладанием неионного), одновременно находящихся в данной смешанной системе эмульгаторов.

Обнаружено, что скорость полимеризации возрастает, а размер частиц латекса уменьшается при повышении концентрации анионного эмульгатора в реакционной системе. Наблюдался резкий рост скорости полимеризации в границах одномолярной концентрации анионного эмульгатора при переходе от 0 к 0,1 и от 0,9 к 1,0 M концентрации.

В интервале 2 скорость полимеризации пропорциональна конечной концентрации полимерных частиц в степени 0,55, концентрации анионного эмульгатора в степени 0,36 и общей концентрации эмульгаторов в степени 1,09.

The micellar and homogeneous nucleation theories [1, 2] have gained wide acceptance for describing the emulsion polymerization and copolymerization of a wide range of monomers [3—9]. These include primary particle formation by entry of a free radical into a micelle or by homogeneous nucleation of oligomeric free radicals in the aqueous phase. After their formation, primary particles may simply grow by conversion of a monomer to polymer within these particles. There is experimental evidence for nucleation being a coagulative process and the appropriate "coagulative nucleation model" describing especially emulsion polymerizations containing monomers partly soluble in water has been derived [10].

A major problem in deciding which mechanism(s) is (are) applicable to a given monomer under a particular set of conditions is that experimental data are often consistent with more than one mechanism.

In our early papers [11—13] we investigated the effect of anionic, nonionic, and cationic emulsifier and monomer feed composition under low or high initiation rate on the polymerization behaviour. The rate of polymerization was proportional to $[\text{emulsifier}]^{0.6}$ for the system containing monomers insoluble in water or comonomer pairs containing butyl acrylate with low amount of acrylonitrile. Experimental data showed that the exponent on emulsifier concentration decreases with increasing acrylonitrile concentration in the monomer feed. In addition, the value of the order with respect to the emulsifier concentration is lower at high emulsifier concentration.

The aim of the present work is to establish the limits of the validity of emulsion polymerization mechanism(s) if a monomer with appreciable water solubility and the blend of anionic and nonionic emulsifiers are applied.

Experimental

Purification of acrylonitrile (AN), butyl acrylate (BA) and other materials has been described earlier [11].

Reagent grade emulsifiers Dowfax 2A1 (DW) (anionic emulsifier, sodium dodecylphenoxybenzenedisulfonate provided by DOW Chemicals Co., $M_r = 569$) and Slovasol 2430 (SLO) (nonionic emulsifier, alkyl polyoxyethylene ether type — $C_{24}H_{49}O(CH_2CH_2O)_{29}CH_2CH_3$, $M_r = 1660.3$) were used as supplied.

Anal. grade potassium peroxodisulfate (Lachema, Brno) was used as supplied.

The surface tension was determined by the stalagmometric method [11, 14]. Constant temperature (30 °C) was maintained by connecting the jacketed stalagmometer to an adjustable temperature water-bath pump [11].

Emulsion copolymerizations of acrylonitrile and butyl acrylate were carried out at 60 °C. In all runs a recipe containing 180 g of water, 29 g of acrylonitrile, 91 g of butyl acrylate, 2.4 g of emulsifier blend, and 0.18 g of potassium peroxodisulfate was used. Emulsifier ratio (DW/SLO) varied as shown later. Emulsifier concentrations were referred to the aqueous phase. The polymerization technique used has been described in detail elsewhere [3].

The particle sizes of latexes were determined by the light scattering method [15] (here also doubled by electron microscopy).

Conversion of monomers was determined from the data obtained by gravimetry and gas chromatography [16]. The polymerization rate was determined as the mean rate within the region of 40—60 % conversion and equals the maximum rate.

The number of the particles N was estimated from the experimental value of the root-mean-cube average particle radius according to the method described elsewhere [17]. The number of polymer particles per 1 cm^3 of the aqueous phase is illustrated in the present paper.

Results and discussion

Micelle studies

Fig. 1 shows that in the case of the mixed emulsifier (DW—SLO) system, the surface tension *vs.* emulsifier concentration curve breaks at two intervals. Here are illustrated three systems with a different emulsifier blend composition. With

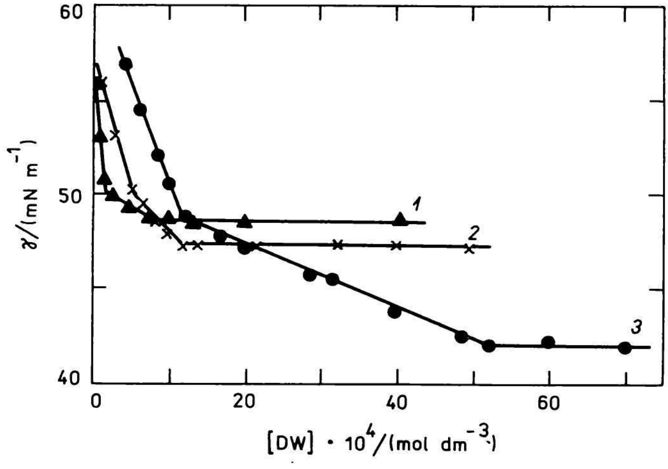

Fig. 1. Variation of the surface tension γ with increasing emulsifier concentration [DW] in mixed emulsifier solutions of the DW—SLO system at different emulsifier blend compositions. $\theta = 30\,°\text{C}$. *1.* $x_{\text{DW}} = 0.2$; *2.* $x_{\text{DW}} = 0.6$; *3.* $x_{\text{DW}} = 0.9$ (given in mole fraction of DW in mixed emulsifier aqueous solutions).

increasing concentration of DW in the emulsifier blend the sharp decrease of the surface tension was observed. Note also that this sharp decrease was the most pronounced in the system with the lowest concentration of anionic emulsifier. In all cases the surface tension decreases temperately after the first CMC point with increasing emulsifier concentration but remains constant above the second critical micelle concentration. Thus the obtained values of CMC_I (rich in anionic emulsifier, curve *2*), CMC_2 (rich in nonionic emulsifier, curve *3*) together with the proposed CMC values (curve *1*) are illustrated in Fig. 2.

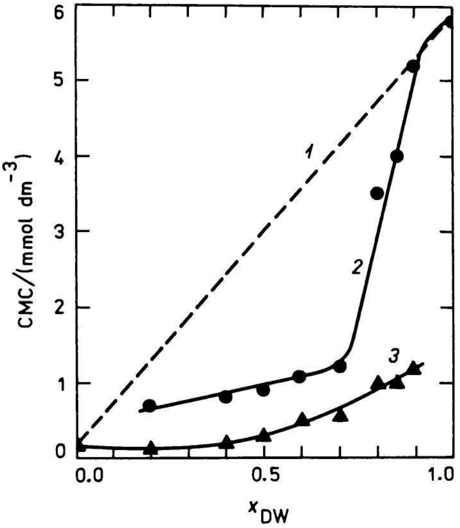

Fig. 2. Variation of the critical micelle concentration with x_{DW} (the mole fraction of DW in mixed emulsifier solutions of the DW—SLO system). $\theta = 30\,°C$.
1. CMC value of the mixed micelle proposed; *2.*, *3.* CMC_I and CMC_2 values observed in mixed emulsifier solutions. Other conditions are given in the legend to Fig. 1 and in Table 1.

Results in Fig. 2 show that both micelles coexisting (one rich in anionic and the other rich in nonionic emulsifier) exhibit negative deviation from ideality. The deviation from ideality (dashed line) is large. It indicates the presence of the strong interaction between both emulsifiers attending the formation of micelle.

These two kinds of micelles are found to be formed in the mixed emulsifier systems with the nonionic emulsifier which has longer polyoxyethylene chain (above 10 or 20 oxyethylene units) [18]. The nonionic emulsifier used (SLO) fulfils this assumption.

Initially the CMC for the emulsifier blend rich in nonionic emulsifier decreases with increasing mole fraction of DW and on the contrary after reaching a minimum at $x_{DW} = 0.5$, increases almost linearly. The depression of CMC may be taken as evidence for micellar stabilization [19]. We come to the conclusion that the anionic emulsifier affects micellization of SLO in a similar way as aliphatic alcohols, *i.e.* it stabilizes at low cosolvent concentrations and de-

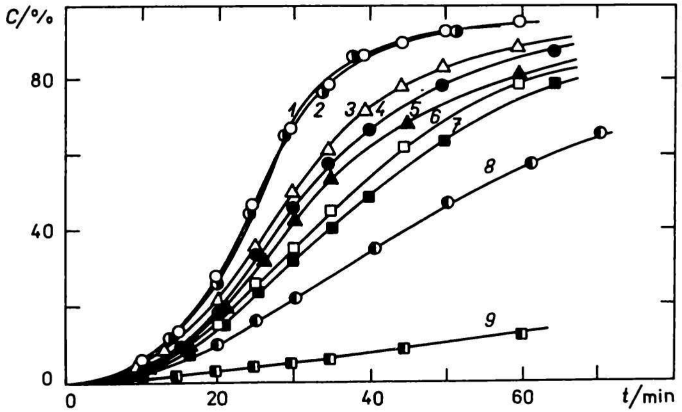

Fig. 3. Variation of the monomer conversion C in the emulsion copolymerization of butyl acrylate (BA) and acrylonitrile (AN) with the reaction time and with the mole fraction of DW in the mixed emulsifier solution (mixtures of DW and SLO). $\theta = 60\,°\mathrm{C}$.
Recipe: 180 g of water, 29 g of AN, 91 g of BA, 0.18 g of $K_2S_2O_8$, 2.4 g of emulsifier blend (DW and SLO).
x_{DW} = *1.* 1.0 (◑); *2.* 0.985 (○); *3.* 0.898 (△); *4.* 0.746 (●); *5.* 0.595 (▲); *6.* 0.4 (□); *7.* 0.255 (■); *8.* 0.11 (◐); *9.* 0 (◧).

stabilizes them at higher concentrations [20]. However, in the case of alcohols the maximum depression of CMC is larger than when DW is used as additive.

The CMC for the mixed emulsifier system rich in anionic emulsifier abruptly decreases with increasing mole fraction of SLO from 0 to 0.3 and then decreases only slightly. Here the depression of CMC indicates the formation of micelles with higher stability.

Thus at low SLO concentrations the additive enters the micellar palisade region and stabilizes the aggregates presumably by hydrophobic interaction with the hydrocarbon chain near the micellar surface (*i.e.* the interaction between the hydrophobic group in anionic emulsifier and that in nonionic one) [19].

Such placement of SLO molecules, however, is expected to increase the free (Helmholtz) energy of micellization by reducing the dielectric constant in the medium between ionic heads. The decrease of the hydrophobic free energy or possibly entropic effects due to the entry of SLO in DW micelles result in an overall stabilization of the micelles as evidenced by the decrease of CMC.

Polymerization studies

The conversion—time data of the emulsion copolymerization of acrylonitrile and butyl acrylate initiated by a water-soluble initiator are shown in Fig. 3. The curves illustrate the effect of the emulsifier blend composition on the polymerization process. The emulsifier blend is composed of the anionic and nonionic emulsifiers. With the exception of the curve *9* (a system containing only a nonionic emulsifier), the curves show two-rate regions: a nonconstant region up to 15 or 20 % conversion and after 70 or 80 % conversion and a constant-rate region within 20—60 % conversion (the so-called interval 2).

The rates of polymerization obtained in the interval 2 (maximum rate) are expressed as a function of the mole fraction of DW x_{DW} in Fig. 4 (curve *1*). As expected, the polymerization proceeds at a high rate in systems rich in the anionic emulsifier ($x_{DW} \rightarrow 1.0$) and at low rate with a nonionic emulsifier ($x_{DW} \rightarrow 0$). One can also observe that the addition of a small amount of anionic emulsifier ($x_{DW} \leq 0.1$) causes an abrupt increase of the polymerization rate. On the contrary, the addition of a small amount of nonionic emulsifier ($x_{DW} \geq 0.9$) causes an abrupt decrease of the polymerization rate. Over the middle amount of DW ($0.1 \leq x_{DW} \leq 0.9$) only slight increase of the polymerization rate with increasing x_{DW} has been observed.

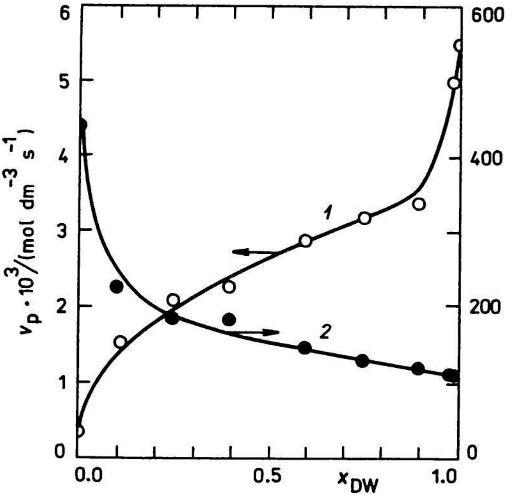

Fig. 4. Variation of the rate of copolymerization v_p and of the mean particle diameter $\bar{d}$ with the mole fraction of DW x_{DW}. Other conditions are given in the legend to Fig. 3 and in Table 1.

According to the simple micellar and homogeneous theories [1, 2] the rate of polymerization is approximately inversely proportional to the polymer particle size. The rate of polymerization is a function of the effective area of polymer particles [21]. The curve *2* (Fig. 4) follows the expected trend, excluding the region with the value of x_{DW} close to 1.0. Here a small decrease of the polymer particle size was parallelled with the abrupt increase in the values of the polymerization rate.

It was shown [22] that the size of mixed micelles decreases with the increasing mole fraction of the anionic emulsifier. Consequently, the radical capture efficiency increases with the increasing effective surface area of micelles, *i.e.* it increases with increasing concentration of the anionic emulsifier in the solution.

The entry of charge radicals (primary and oligomer radicals) into micelles and into polymer particles is somewhat hindered due to electrostatic repulsion [23, 24]. Consequently, micelles and polymer particles rich in nonionic emulsifier absorb negatively charged radicals easier than those rich in anionic emulsifier. The rate of polymerization is related to the rate of the entry of radicals into micelles and polymer particles.

The surface charge density is most probably influenced by the degree of ionization. It was shown that the degree of micellar ionization in the mixed emulsifier system decreases with increasing concentration of nonionic emulsifier over the high concentration range of anionic emulsifier. It is supposed that the abrupt decrease of the polymerization rate observed on the addition of a small amount of nonionic emulsifier ($x_{\mathrm{DW}} \rightarrow 0.9$) is most probably due to the increase of the surface charge density which inversely influences the radical capture efficiency.

It is interesting to note that the efficiency of the nonionic emulsifier is strongly suppressed by the anionic emulsifier present even at low concentration (below its CMC). The addition of a small amount of the anionic emulsifier leads to a decrease of the particle size and simultaneously an increase of the rate of polymerization is observed.

The nonionic emulsifier sterically stabilizes the polymer particle at high surface coverages, *i.e.* polymer colloids are only stable at high emulsifier concentrations. Under these conditions, however, mostly large latex particles are formed.

The theory of steric stabilization predicts that the steric repulsive energy governing particle size is dependent upon the concentration of emulsifier in the adsorbed layer. This concentration is determined by the bulk polymer concentration and the affinity of the emulsifier adsorption to the particle surface. The stability of a sterically stabilized colloid is mainly determined by the magnitude of the Gibbs energy change of the steric interaction produced by the close approach of the emulsifier-coated particles.

It appears that the anionic emulsifier influences strongly the thickness of the adsorbed layer of nonionic emulsifier to the particle surface and favours the change of the steric to the electrostatic interaction accompanied with the high degree of ionization. Besides the interaction between SLO and DW and emulsifier and polymer influences the effective emulsifier surface area.

To specify the effect of the mixed emulsifier solutions and each type of emulsifier the rate of polymerization (maximum rate) was followed as a function of total and simple emulsifier concentrations. The rates of polymerization (taken from Fig. 3) together with the final particle number on a log—log scale are shown in Figs. 5 and 6. The slopes of the straight lines in Fig. 5 give the following reaction orders (obtained by the least-squares method) $v_p \sim [DW]^{0.36}$, $N \sim [DW]^{0.62}$, and $v_p \sim N^{0.55}$. First two equations (considering only DW) give the expression $v_p \sim N^{0.58}$ which is in good agreement with that for the whole system (considering the mixed emulsifier compositions shown in Fig. 3 and Table 1).

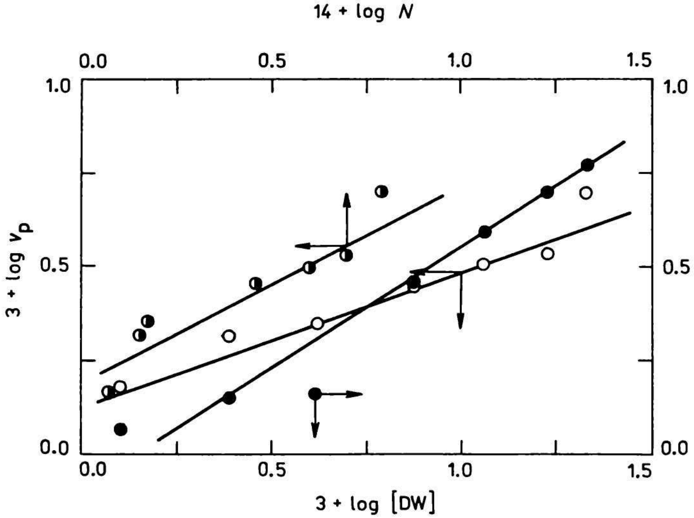

Fig. 5. Variation of the rate of copolymerization (maximum rate) of acrylonitrile and butyl acrylate with the final particle number N and the concentration of DW and of the number of final particles N with the concentration of DW in the mixed emulsifier solutions in log—log scale. Other conditions are given in the legend to Fig. 3 and in Table 1.

We have already reported [13] that the rate of copolymerization of acrylonitrile and butyl acrylate in the presence of DW was proportional to the 0.41 power of the emulsifier concentration. This value is close to 0.36 obtained here in the mixed emulsifier system. This also indicates that the whole mechanism of the emulsion copolymerization in the presence of the emulsifier blend is governed by the anionic emulsifier. Similarly, the slopes of the straight lines in Fig. 6 give reaction orders $v_p \sim ([DW] + [SLO])^{1.09}$ and $N \sim ([DW] + [SLO])^{1.8}$ which somewhat differ from those above. In these calculations dependences v_p and N

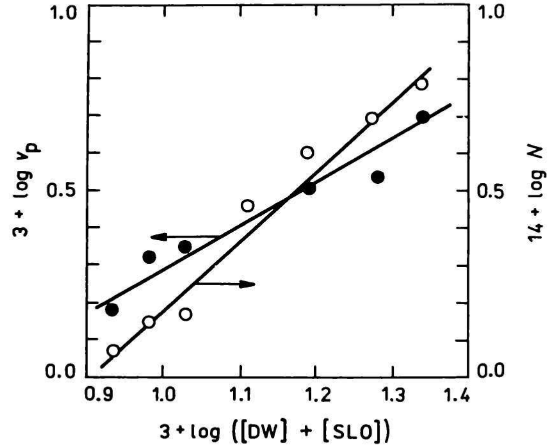

Fig. 6. Variation of the rate of copolymerization (maximum rate) and of the number of final particles with the total emulsifier concentration ([DW] + [SLO]). Other conditions are given in the legend to Fig. 3 and in Table 1.

Table 1

Concentrations of emulsifiers in mixed emulsifier solution of the DW—SLO system used in both micelle and polymerization studies

x_{DW}[a]	$[\mathrm{DW}]\cdot 10^2$	$[\mathrm{SLO}]\cdot 10^2$ [c]	γ [b]
	$\mathrm{mol\,dm^{-3}}$		$\mathrm{mN\,m^{-1}}$
0.0[d]	0.0	0.803	—
0.11[d]	0.092	0.797	—
0.2	0.19	0.73	48.6
0.255[d]	0.24	0.704	—
0.4[d]	0.42	0.646	48.2
0.5	0.587	0.587	48.0
0.6[d]	0.77	0.523	47.6
0.7	1.01	0.437	47.3
0.75[d]	1.15	0.39	—
0.8	1.34	0.32	45.0
0.85	1.52	0.26	43.6
0.9[d]	1.7	0.192	42.0
1.0[d]	2.34	—	—

a) The mole fraction of DW in the mixed solution of the DW—SLO system; *b*) the constant surface tension value (above the second critical micelle concentration); *c*) referred to the aqueous phase; *d*) emulsifier blend compositions used in polymerization runs (see Figs. 3—6).

on ([DW] + [SLO]) give the expression $v_p \sim N^{0.55}$ which is also close to that obtained from the dependence v_p on N. As expected, the rate of polymerization increases with increasing total emulsifier concentration.

On the other hand, the dependences v_p and N *vs.* the concentration of nonionic emulsifier give negative reaction orders. This may be taken as indication that the nonionic emulsifier does not play an important role in the polymerization mechanism (nucleation and growth of polymer particles, *etc.*) but rather stabilizes polymer particles.

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