

# Conductivity of the mixtures of emulsifier with acrylate or methacrylate as a measure of emulsion stability

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The emulsification of vinyl monomers, such as acrylonitrile, methyl methacrylate, butyl acrylate, ethyl acrylate and two different comonomer mixtures of ethyl acrylate and methyl methacrylate was studied by the conductometric titration method.

The dependence of the conductivity on the monomer concentration for a given emulsifier amount of substance ratio nonionic : anionic is described by a curve with minimum and maximum.

Fluctuations in the conductivity are expected to result from the solubilization of monomer in emulsifier micelles, from the releasing or tying up the most conductive species from the aqueous phase, from the changes of the surface particle layer and of the molecular volumes for monomers and from the phase inversion and emulsifier transfer between phases.

The most stable monomer emulsion was formed in the system containing the most water-soluble monomer.

It was found that a pre-emulsification process is time-dependent and is one of the important characteristics of the emulsion polymerization.

С помощью метода кондуктометрического титрования изучена эмульгация винильных мономеров, таких, как акрилонитрил, метилметакрилат, бутилакрилат, этилакрилат и двух разных сополимерных смесей этилакрилата и метилметакрилата.

Зависимость электропроводности от концентрации мономера для данного мольного отношения количеств неионного и анионного эмульгаторов выражается кривой с минимумом и максимумом.

Предполагается, что колебания электропроводности вызваны солюбилизацией мономера в мицеллах эмульгатора, освобождением или связыванием наиболее электропроводящих веществ из водной фазы, изменением слоя поверхностных частиц и молекулярных объемов мономеров, а также инверсией фаз и межфазным переносом эмульгатора.

Наиболее устойчивые эмульсии мономера образовывались в системе, содержащей мономер с наилучшей растворимостью в воде.

Обнаружено, что процесс предэмульгации зависит от времени и является одной из наиболее важных характеристик эмульсионной полимеризации.

The concept of mixed emulsifier systems is applied for the preparation of oil-in-water emulsions. The type of emulsion formed (microemulsion, miniemulsion, and macroemulsion) is controlled by such factors as the stirring rate, the mixing time, the composition of the emulsifier system, the type of emulsifier, and the nature of monomer (oil).

Microemulsions are nearly transparent, relatively viscous emulsions with average droplet size from 10 to 100 nm; miniemulsions are fluid, milky, and opaque with average droplet size of about 200 nm and emulsions with average droplet size of 1000 nm and larger are called macroemulsions.

The microemulsions can be prepared using mixtures of ionic emulsifiers with a fatty alcohol in total mass fractions of 15–30 % based on the oil phase [1]. The oil is dispersed in an aqueous emulsifier solution with stirring to form a miniemulsion, to which is then added an aqueous solution of fatty alcohol. At a critical concentration of fatty alcohol, the opaque crude emulsion becomes translucent or nearly transparent and its viscosity increases.

The mixed emulsifier system containing ionic emulsifiers with mass fraction 0.2–2 % of fatty alcohol can produce stable oil-in-water emulsions, the so-called “miniemulsions” [2].

One point of difference between miniemulsions and microemulsions is in the type and chain length of the coemulsifier used. A miniemulsion can be prepared applying fatty alcohols or normal hydrocarbons with the chain length of eight carbon atoms or longer. A microemulsion can be prepared only with fatty alcohols as a coemulsifier with the chain length longer than eight carbon atoms [3, 4].

The emulsification process is of both theoretical and practical interest. The size of emulsified monomer droplets is a function of the method of emulsification as already mentioned.

Conventional emulsion polymerization comprises emulsification of a water-insoluble monomer in the aqueous emulsifier solution and the polymerization using a water-soluble initiator gives a colloidal dispersion of polymer particles in water. The average particle size of conventional latexes is usually 100–300 nm in contrast to the original emulsion droplet size of 1000–10 000 nm. In these cases, however, the initiation in monomer droplets forms only a minor contribution to the overall particle initiation process; the main locus of initiation are the monomer swollen emulsifier micelles [5] or the aqueous phase [6]. If the monomer droplet size were decreased, initiation in this locus would be more likely.

It was reported that the free radical capture efficiency varies with the particle size [7]. Besides, a stable monomer emulsion formed during the pre-emulsification stage positively influences the kinetics of the emulsion polymerization especially at the nucleation stage.

Conductivity measurements have been used to study the solubilization of water-insoluble oils in emulsifier micelles, but these systems contained ionic emulsifier [8] or the mixed emulsifier solution containing ionic emulsifiers with fatty alcohols [9].

The object of the present work is to extend the conductometric titration technique in studying the effects of the water solubility of monomers and the emulsifier blend containing anionic and nonionic emulsifiers on the emulsification process. Besides that it deals with the effect of the pre-emulsification process on the kinetics of the emulsion copolymerization of methyl methacrylate and ethyl acrylate.

### Experimental

Acrylonitrile (AN), butyl acrylate (BA), methyl methacrylate (MMA), and ethyl acrylate (EA) were, subsequently washed with 5% aqueous sodium hydroxide solution to remove the inhibitor, and with water to remove the base, and finally dried over anhydrous calcium dichloride. Then each monomer was twice distilled in vacuum under nitrogen atmosphere and the middle fraction collected was stored in a refrigerator until used.

Anal. grade ammonium persulfate (AP) (Lachema, Brno) was used as supplied.

Emulsifiers Tween 40 (Tw) (nonionic polyoxyethylene sorbitan monopalmitate (with 20 oxyethylene units) provided by Serva) and Spolapon AOS (Sp) (anionic sodium  $\alpha$ -alkenylsulfonate,  $\text{CH}_2\text{CH}(\text{CH}_2)_{16}\text{SO}_3\text{Na}$ , provided by Spolchemie, Czechoslovakia) were further purified by conventional methods [10, 11] as follows.

Supplied emulsifiers were first purified by filtration through the membrane filter, then by precipitation from organic solutions by freezing and at last by dialysis. Their purity was checked by applying LC, thin-layer chromatography, and the conductivity method. Twice distilled water was used to prepare solutions.

The conductivity of monomer emulsions was measured by a Conductimeter OK 102/1 and electrode OK 902 (Radelkis, Budapest), according to the method described in [12] in a 50 cm<sup>3</sup> jacketed glass beaker covered with a metal and thermostated to 20 °C. Monomer emulsions were prepared by addition of monomer to the aqueous emulsifier solution at intense stirring. All conductivities were measured in nitrogen atmosphere.

The stability of monomer emulsions was determined by the measurements of the oil phase volume after the cessation of agitation. The movement of the meniscus (between the oil and the emulsion (rich in water) phases) in the glass ampoule was followed by means of a cathetometer.

Emulsion copolymerizations of methyl methacrylate and ethyl acrylate were carried out at 60 °C. The polymerization technique used has been described in detail elsewhere [13]. The conversion of monomers was determined from the data obtained by gas chromatography [14]. The polymerization rate was determined as the mean rate within the region of 40–60% conversion and equals the maximum rate.

The particle sizes of latexes were determined by light scattering method [15] and also doubled by electron microscopy.

## Results and discussion

The conductometric titration curve describing changes after the addition of monomers to the aqueous solution of anionic and nonionic emulsifiers presented in Fig. 1 shows the unexpected fluctuations in the conductivity. This curve divides into three parts. All emulsions show a decrease in the initial conductivity with increasing concentration of monomer in the system. In aqueous solutions of mixed emulsifiers with acrylonitrile or methyl methacrylate (partly also with butyl acrylate) a sharp increase in conductivity was observed after the first break point. However, only a slight increase in the conductivity with increasing concentration of ethyl acrylate or ethyl acrylate/methyl methacrylate monomer mixture was observed.

Beyond the second break point the small decrease in the conductivity in systems except of butyl acrylate was observed. The present emulsions are fluid, milky, and opaque even at the total mass fraction of emulsifiers of 50 % or higher based on the monomer phase. This suggests that the coemulsifier (here nonionic emulsifier) does not contribute to the formation of emulsions with average droplet size below 200 nm (diameter).

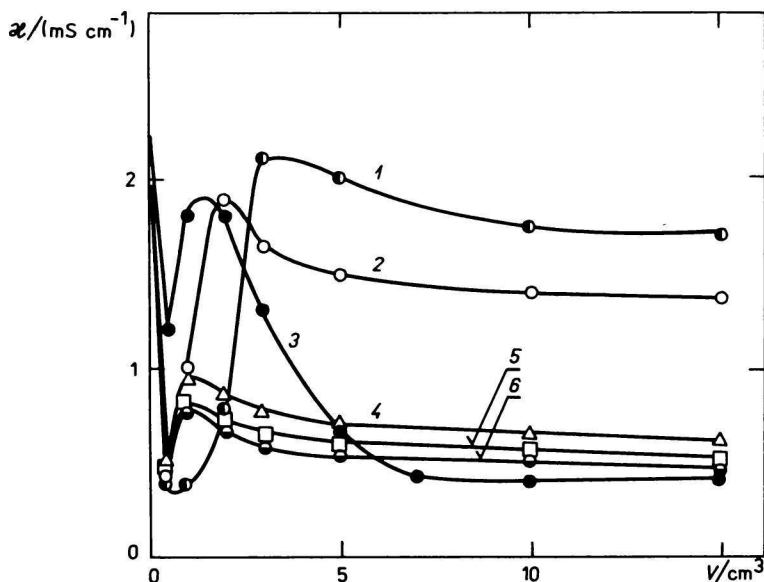


Fig. 1. Conductometric titration curves for the addition of monomer into an aqueous solution ( $V = 30 \text{ cm}^3$ ,  $m(\text{Sp}) = 2.82 \times 10^{-2} \text{ mol kg}^{-1}$ ,  $m(\text{Tw}) = 1.98 \times 10^{-2} \text{ mol kg}^{-1}$ ), agitation time 15 min, temperature  $20^\circ\text{C}$ .

1. Acrylonitrile; 2. methyl methacrylate; 3. butyl acrylate; 4. ethyl acrylate—methyl methacrylate (mass ratio = 50 : 50); 5. ethyl acrylate—methyl methacrylate (mass ratio = 80 : 20); 6. ethyl acrylate.

The trend of the conductivity with increasing concentration of monomer added indicates that the degree and order of association between monomer and emulsifier molecules change due to formation of monomer swollen emulsifier micelles and emulsified monomer droplets with different surface layer characteristics.

This type of association results in "tying up" the anionic emulsifier, thus removing the most conductive species from the aqueous phase. The extent of the decrease in the conductivity should be related to the degree of association that takes place between monomer and emulsifier, and nonionic and anionic molecules. An increase in the conductivity may result from the absorption of the monomer in the surface layer of micelles, causing the release of the counterions [9, 11].

The formation of associated species with different emulsifier composition at different monomer concentrations was presented in [16].

Emulsions containing both the blend of anionic and nonionic emulsifiers and acrylonitrile showed the initial sharp conductivity decrease followed by an abrupt increase and a levelling-off that had been found [17] to be characteristic of stable emulsion formation. The difference in shape between the curves, however, indicates that emulsions with different stability are formed.

Again, based on the shape of the conductivity curve, the most stable emulsion in this series appears to be formed with acrylonitrile. Note also that the less stable emulsion should be formed with methyl methacrylate or butyl acrylate and an unstable emulsion with ethyl acrylate or ethyl acrylate/methyl methacrylate monomer mixtures.

Indeed, a correlation was found between the shape of the conductivity curve

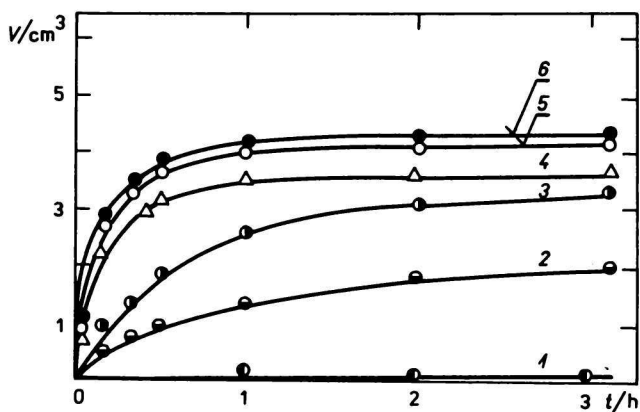


Fig. 2. Time dependence of the phase separation (the oil phase) after the cessation of agitation. Volume ratio water : monomer = 15 : 5. Other conditions as given in the legend to Fig. 1.

and the stability of the resulting emulsion measured by phase separation after the cessation of the agitation (Figs. 1 and 2). As seen in Fig. 2, the stability of emulsion according to the type of monomer decreases in the following order:  $s(\text{acrylonitrile}) (\approx 7) > s(\text{methyl methacrylate}) (\approx 1.5) > s(\text{butyl acrylate}) (\approx 0.2) > s(\text{ethyl acrylate—methyl methacrylate, mass ratio} = 50:50) (\approx 1.5) > s(\text{ethyl acrylate—methyl methacrylate, mass ratio} = 80:20) (\approx 1.5) > s(\text{ethyl acrylate}) (\approx 1.5)$ , where the water solubility  $m(\text{monomer})/100 \text{ g}$  [18] is denoted in the bracket. The trend of emulsion stability here obtained shows that the water solubility of monomer is an important factor of the monomer emulsification process. These experimental data show that a rough correlation exists between the water solubility of monomer and the solubilization efficiency.

Some differences in shape of curves between methyl methacrylate and ethyl acrylate (monomers with the same water solubility) indicate that the emulsification is not regulated by the water solubility of monomer only but also by other factors.

The important characteristics of solubilization is also the ratio of the maximum number of solubilize molecules to the number of emulsifier molecules in a micelle. This ratio, designated as the molar solubilization ratio, has been measured for a variety of solubilizes in a number of emulsifier solutions [8]. The experimental data in [19] showed that, within a chemical family of solubilizes, a rough correlation exists between their molecular volumes and the measured molar solubilization ratios. A reasonable correlation is obtained, with the molar solubilization ratio decreasing as the molecular volume of the solubilize increases.

The molecular volumes for methyl methacrylate and ethyl acrylate have been estimated (from their molecular masses and liquid density data [20]) to be 106 and 108, respectively. Thus this difference is partly responsible for the differences in their emulsification behaviour.

At low monomer concentration range, where the emulsifier forms micelles in the aqueous phase, oil-in-water emulsions are formed and exhibit high conductivity. At high monomer concentrations, however, the emulsifier may reside also in the monomer phase and water-in-oil emulsions are formed. Here the continuous phase is monomer and the conductivity is correspondingly low [21]. Phase inversion and emulsifier transfer between phases associated with the effective geometry of the emulsifier molecules [22] are partly responsible for fluctuations in conductivity.

The partitioning of monomer between the core and shell of emulsifier micelles and emulsified monomer droplets depends on the nature of solubilize and the type of interaction within dispersion particles [23]. Besides, a favourable interac-

Table 1

Variation of conductivity in the pre-emulsification stage (a) with time and of kinetic data of the emulsion copolymerization (b) of methyl methacrylate and ethyl acrylate with the duration of pre-emulsification process

Time <sup>a</sup> min	$\kappa$ <sup>a</sup> mS cm <sup>-1</sup>	Pre-emul.	$R_p \times 10^{-2}$ <sup>b,c</sup> % conv./h	$\bar{D}$ <sup>b,d</sup> nm	Coag. <sup>b,e</sup> mass %
		process min			
10	2.5	15	4.5	180	2.5
15	2.0				
20	1.6	30	5.0	170	1.2
30	1.2				
45	1.1				
60	1.1				

Recipe: 150 g of water<sup>a,b</sup>, 20 g of methyl methacrylate<sup>a,b</sup>, 80 g of ethyl acrylate<sup>a,b</sup>, 60 °C<sup>a,b</sup>,  $m(\text{Sp}) = 2.82 \times 10^{-2} \text{ mol kg}^{-1}$ <sup>a,b</sup>,  $m(\text{Tw}) = 1.98 \times 10^{-2} \text{ mol kg}^{-1}$ <sup>a,b</sup>,  $m(\text{AP}) = 7.7 \times 10^{-3} \text{ mol kg}^{-1}$ <sup>b</sup>.

c) Maximum rate of polymerization in interval 2 (see Ref. [13]).

d) Mean particle diameter of a final latex.

e) Amount of coagulum at the end of polymerization/100 g of monomer.

tion of monomer with water leads to an unexpectedly large percentage of the oil being formed at interfacial sites. The interaction between molecules within micelle seems to be influenced by the type and length of the alkyl of ester group in the monomer.

The degree of ionic dissociation of a mixed micelle increases with increasing number of carbon atoms of the alkyl group in the nonionic emulsifier. Interactions of monomer, oligomer radicals (carrying sulfo end groups) and polymer with emulsifier influence the release of both emulsifiers into the aqueous phase and binding of the counterions with emulsifier by a complex way [24, 25].

The solubilization of monomer takes some time to reach an equilibrium. Results summarized in Table 1 show that a pre-emulsification process is time-dependent. With increasing agitation time the conductivity initially abruptly decreases until the plateau is reached (after ~ 30 min). One can suppose that at this point the solubilization of monomer is nearly complete. We can see that the emulsification process influences the polymerization kinetic data. In the system with longer pre-emulsification time (30 min) one observes a higher rate of polymerization, a more stable latex, smaller polymer particles in comparison with those found in the system with a shorter pre-emulsification period (15 min). Thus, the water-soluble initiator should be feeded in the reaction medium after the complete solubilization of monomer phase.

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