MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Emulsion Polymerization of Styrene in the Presence of a Mixture of Potassium Stearate and Oleate

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Abstract—The features of emulsion polymerization of styrene in the presence of a mixture of potassium stearate and oleate was studied. The effect of these salts on the polymerization rate and the yield and molecular weight of polystyrene was examined.

Making the existing processes for latex production more feasible and efficient remains a topical problem. This goal can be accomplished, in particular, by choosing effective emulsifiers that could provide a high conversion of the monomers and aggregative stability of the latexes.

It is known that effective emulsifying systems for synthesis of diene–styrene and styrene–acrylate dispersions contain mixtures of different types of surfactants [1]. At the same time, impurities of potassium myristate, palmitate, stearate, or linoleate in the commercially used emulsifier, potassium oleate, decrease the polymerization rate and mechanical stability of butadiene–styrene latex [2].

We found previously that a 40 : 60 (by weight) mixture of stearic and oleic acids exhibits synergism in its effect on some properties of rubber stocks and vulcanizates [3–5]. This fact suggests that these surfactants may affect nonadditively the preparation and properties of other polymers.

As a model for examining the effect of a mixture of stearic and oleic acids in the form of potassium salts on the emulsion polymerization, we chose polymerization of styrene.

EXPERIMENTAL

The emulsion polymerization was performed at 80°C for 90 min. The composition (wt parts) of the reaction mixture was as follows: styrene 100, fatty acid 1.2, KOH 0.18, $K_2S_2O_8$ 0.5, and water 160. The reaction progress was monitored gravimetrically. Samples were taken at definite intervals and analyzed to determine the polymer yield (%) by the formula [6]

$$N = P_p \times 100/P_m,$$

where P_p is the polymer weight in the sample (g), and P_m is the monomer weight in the sample (g), calculated from the initial monomer concentration.

The viscosity-average molecular weight of the isolated polystyrene was determined by the procedure described previously [7].

The surface tension of aqueous solutions of potassium soaps of fatty acids was determined by the Du Nouy method [8]. The limiting adsorption Γ_∞ was determined graphically from the adsorption isotherms of the surfactants [9, 10]. The negative logarithm of the surfactant concentration at which σ decreases by 20 mN m^{-1} (pC_{20}) was determined by a procedure described in [11], and the critical micellization concentration (CMC), according to [12, 13].

Figures 1a–1c show that the polymerization kinetics depends on the emulsifier composition, namely, on the ratio of stearic (St) and oleic (Ol) acids in the potassium salts [K(St : Ol)]. The styrene conversion as a function of the emulsifier composition passes through a maximum at the K(St : Ol) ratio ranging from 40 : 60 to 60 : 40 wt %, with the polystyrene yield (Fig. 2, curve *1*) equal to 99.9%.

The viscosity-average molecular weight ($\overline{M}_\eta$) of polystyrene as a function of the K(St : Ol) ratio also passes through a maximum, 460 000, observed at K(St : Ol) = 40 : 60 wt % (Fig. 2, curve *2*).

The dependences of the mean reaction rate (W_m) on the styrene conversion (Fig. 3) are, on the whole, similar at different emulsifier compositions, with the highest W_m attained at 60% conversion. However,
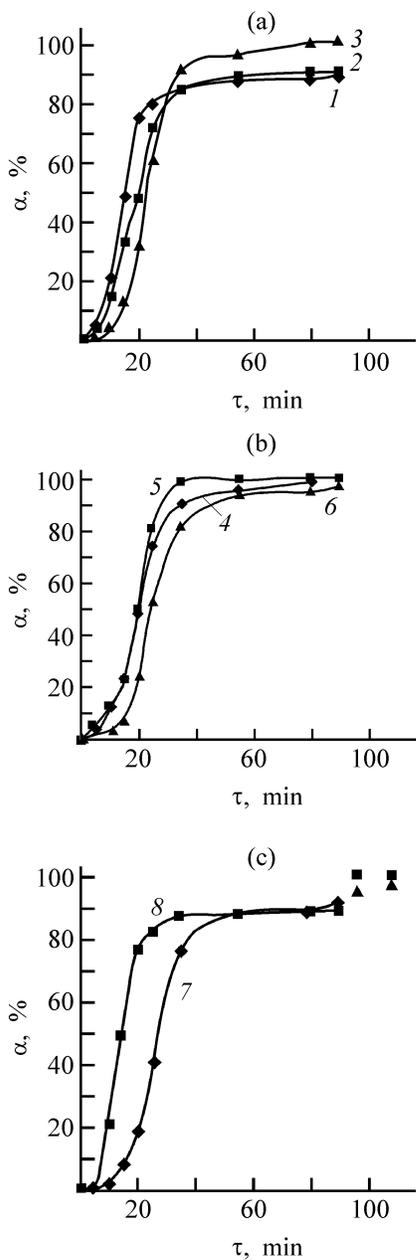
Fig. 1. Styrene conversion α vs. time τ at various ratios of stearic and oleic acids in the emulsifier. St : Ol, wt %: (*1*) 100 : 0, (*2*) 0 : 100, (*3*) 40 : 60, (*4*) 70 : 30, (*5*) 60 : 40, (*6*) 30 : 70, (*7*) 10 : 90, and (*8*) 90 : 10.

Fig. 2. (*1*) Yield *N* and (*2*) viscosity-average molecular weight $\overline{M}_\eta$ of polystyrene vs. the ratio of stearic and oleic acids in the emulsifier.

Fig. 3. Variation of the mean rate of styrene polymerization W_m with the conversion α. Emulsifier: (*1*) potassium stearate, (*2*) potassium oleate, and (*3*) potassium salts of a mixture of stearic (40 wt %) and oleic (60 wt %) acids; the same for Figs. 4 and 5.

Fig. 4. Mean rate of styrene polymerization W_m vs. polymerization time τ.

the curve shape depends on the emulsifier composition. This effect is especially pronounced at high monomer conversions when the mean polymerization rate in the presence of the mixed emulsifier (Fig. 3, curve *3*) is higher than that observed with the individual surfactants. With the mixed emulsifier, virtually 100% conversion of styrene is attained in 1.5 h.
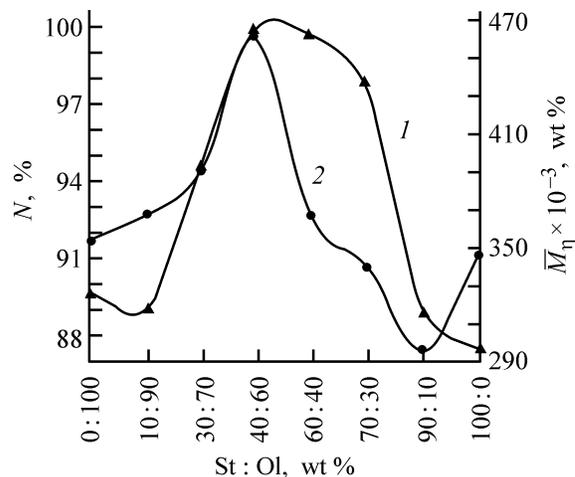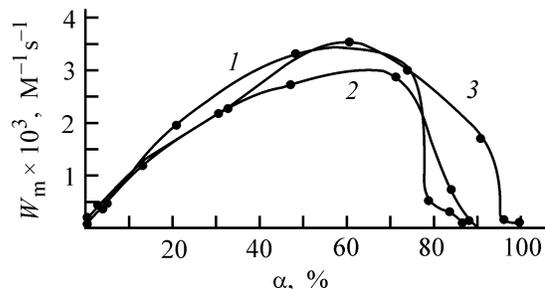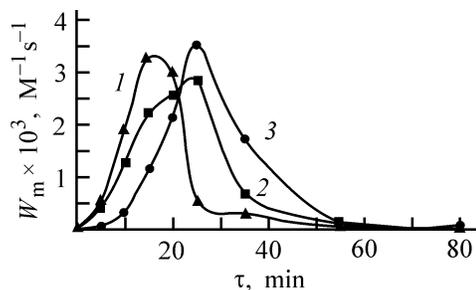
The plots of W_m vs. polymerization time (Fig. 4) show that the K(St : Ol) = 40 : 60 wt % mixture has a nonadditive effect on the reaction kinetics.

It should be noted that, although the mean polymerization rates observed in the presence of the individual emulsifiers are different, the monomer conversions and viscosity-average molecular weights of

Colloid-chemical properties of aqueous solutions of potassium salts of fatty acids

Surfactant	σ, mN m^{-1}	C_{20}, g dm^{-3}	$\Gamma_\infty \times 10^6$, mol m^{-2}	CMC, g dm^{-3}
Potassium stearate	43.0	0.041	3.3	0.48
Potassium oleate	33.5	0.007	4.6	0.75
Mixture of potassium salts of St(40 wt %) and Ol(60 wt %)	33.0	0.003	5.0	0.50

the polymer samples prepared in the presence of both emulsifiers are virtually equal.

The nonadditive effect is most probably associated with the colloid-chemical characteristics of the surfactants used. Stearic and oleic acids do not differ in the length of the hydrocarbon substituent, but differ in its nature: In oleic acid, the hydrocarbon substituent contains a double bond.

It has been found previously that the surface tension of a mixture of stearic and oleic acids is lower than the additive value and has a minimum in the composition range St : Ol (33–40) : (67–60) wt % at temperatures of 60 to 80°C [14]. Similar effects would be expected with aqueous solutions of the potassium salts of St and Ol and of their mixture (40 : 60 wt %). In this connection, we constructred the isotherms of surface tension at the aqueous solution|air phase boundary (Fig. 5).

The lowest σ (11.5% lower than the additive value) was observed with the K(St : Ol) = 40 : 60 wt % mixture (see table). With pure potassium stearate, the surface tension was the highest.

The C_{20} value for potassium stearate is higher by factors of 6 and 11 than that for potassium oleate and K(St : Ol) = 40 : 60 wt % mixture, respectively (see table). Hence, this mixture exhibits synergism with respect not only to an absolute quantity (surface tension) but also to a relative parameter (concentration providing a given decrease in σ).

The dispersing and stabilizing effect of a surfactant is due to its adsorption at the phase boundary. The limiting adsorption can be considered a criterion of the surfactant performance. As can be seen from the table, potassium stearate shows the lowest adsorption, and the K(St : Ol) = 40 : 60 wt % mixture, the highest, and hence it is a more effective dispersant and stabilizer for emulsions, compared to the individual potassium carboxylates.

The critical micelle concentration (CMC) is one of the most important physicochemical characteristics of surfactants. Among the surfactants studied, potassium

oleate has the highest CMC, and potassium stearate, the lowest (see table). The CMC of the K(St : Ol) = 40 : 60 wt % mixture is lower than the additive value and approximately equal to that of potassium stearate. The lower CMC of potassium stearate, compared to oleate, is most probably due to lower degree of dissociation of this soap.

Since the emulsion polymerization of styrene was studied in the range of emulsifier concentrations exceeding CMC of all the emulsifiers examined, the observed effects should be attributed to differences in the amount and size of the micelles, as it is known [15] that the rate of emulsion polymerization depends, under equal other conditions, on the solubilizing power of aqueous solutions of emulsifiers.

CONCLUSIONS

(1) The yield of polystyrene in emulsion polymerization reaches a maximum (99.9%) when a mixture of potassium stearate and oleate (ratio from 40 : 60 to 60 : 40 wt %) is used as emulsifier.

(2) In emulsion polymerization of styrene in the presence of potassium stearate and oleate taken in a ratio of 40 : 60 wt %, the high mean polymerization rate is preserved at high conversions of the monomer, in contrast to the process performed in the presence of each of these salts taken separately.

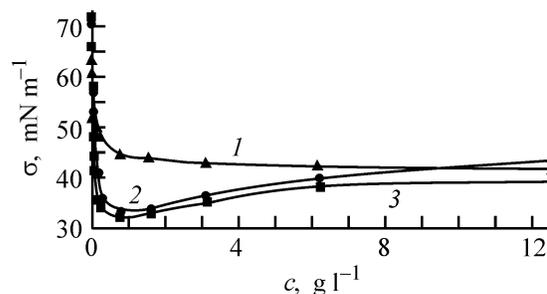(3) Polystyrene prepared using a mixture of potassium stearate and oleate in a ratio of 40 : 60 wt % has

Fig. 5. Surface tension isotherms. (σ) Surface tension and (c) emlusifier concentration.

the highest viscosity-average molecular weight ($\overline{M}_\eta =$ 460 000), whereas $\overline{M}_\eta$ of polystyrene prepared in the presence of potassium stearate or oleate taken separately is about 350 000.

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