

Aqueous polymerization of vinyl monomers in the presence of surfactants

IV. Effect of the chain length of the surfactant on the acrylamide polymerization

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

The kinetics of acrylamide polymerization in water initiated by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was studied in presence of the surfactants $\text{C}_8\text{H}_{17}\text{SO}_3\text{Na}$, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, and $\text{C}_{16}\text{H}_{33}\text{SO}_4\text{Na}$. In the presence of the surfactants an increase in the acrylamide polymerization rate and decrease in the degree of polymerization was observed. At concentrations above critical micellar concentration the surfactant $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ causes a gentle decrease of the overall activation energy of acrylamide polymerization. The length of the n-alkyl chain in the surfactant molecule does not influence the acrylamide polymerization rate.

Изучена кинетика полимеризации акриламида в воде, инициируемая $(\text{NH}_4)_2\text{S}_2\text{O}_8$, в присутствии поверхностно-активных веществ $\text{C}_8\text{H}_{17}\text{SO}_3\text{Na}$, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ и $\text{C}_{16}\text{H}_{33}\text{SO}_4\text{Na}$. В присутствии поверхностно-активных веществ наблюдалось увеличение скорости полимеризации акриламида при одновременном понижении степени полимеризации. При концентрациях высших, чем критическая мицеллярная концентрация, ПАВ $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ вызывает некоторое снижение полной энергии активации полимеризации акриламида. Длина n-алкильной цепи в молекуле ПАВ не влияет на скорость полимеризации акриламида.

In the studies on the kinetics and mechanism of acrylamide polymerization the authors [1] reported that in the presence of an anionic emulsifier in the concentration range above its critical micellar concentration (c.m.c.) an increase in the acrylamide polymerization rate was observed. At the same time, the nonionic emulsifier isooctylphenoxy polyethoxy ethanol did not affect the acrylamide polymerization rate at all. A cationic emulsifier cetyltrimethylammonium bromide caused even a decrease in the acrylamide polymerization rate. Similar results were mentioned by *Kim et al.* [2] in the kinetics study of the acrylamide polymerization.

In our earlier papers [3, 4] we reported on the effect of the emulsifier and/or poly(butyl acrylate) latex on the homogeneous acrylamide polymerization initiated

by water-soluble initiators. It was found that the commercial emulsifier Dowfax 2A1 (sodium dodecylphenoxybenzenedisulfonate) did not affect the acrylamide polymerization rate. It worked only as an effective chain transfer agent [3]. In the presence of poly(butyl acrylate) latex, however, an increase of the acrylamide polymerization rate was observed. That was believed to be a consequence of the simultaneous grafting to the poly(butyl acrylate) latex with acrylamide [4].

The aim of the present study is to find out the influence of the chain length of the alkyl substituent of the anionic surfactants on the aqueous acrylamide polymerization initiated by water-soluble initiator ammonium peroxodisulfate.

Experimental

Materials

Anal. grade ammonium peroxodisulfate (Merck—Schuchard), acrylamide (Merck—Schuchard), and the surfactants (Merck—Schuchard) were used as supplied. The surfactants used were: sodium octanesulfonate, sodium dodecyl sulfate, and sodium hexadecyl sulfate, all chemicals for tenside research. Sodium hydrogen sulfate monohydrate was an anal. grade chemical. The polymerization medium water was distilled and then deaerated by boiling and bubbling with argon before use.

Procedure

Polymerization was carried out under a stream of argon at given polymerization temperature. Monomer acrylamide, surfactant, and water were charged into the reaction vessel. The reaction mixture was then thermostated under an argon stream to the temperature of polymerization. The aqueous solution of initiator was then injected into the polymerization system. Gravimetric determination of conversion and the isolation of polymer from the reaction product have already been described in detail elsewhere [3, 4].

The limiting viscosity numbers of the polymer $[\eta]$ were established in water at 30 °C. According to the procedure [3], the viscosity average relative molecular mass, $(M_r)_\eta$, of polyacrylamide was calculated according to the relation

$$[\eta]/(\text{m}^3 \text{ kg}^{-1}) = 6.31 \times 10^{-4} (M_r)_\eta^{0.8} \quad (1)$$

$(M_r)_\eta$ was converted to number average relative molecular mass $(M_r)_N$ according to the relation (2) valid when termination occurs via disproportionation

$$\frac{(M_r)_\eta}{(M_r)_N} = \Gamma(\alpha + 2) \quad (2)$$

where Γ is the gamma function and α is the exponent in relation (1) equal to 0.8.

Absorption spectra of the initiator and surfactant solutions were measured on the Beckmann UV spectrophotometer at 25 °C.

Results and discussion

The effect of the type and of the concentration of the emulsifier on the acrylamide polymerization rate is summarized in Table 1. As shown the surfactants $C_8H_{17}SO_3Na$, $C_{12}H_{25}SO_4Na$, and $C_{16}H_{33}SO_4Na$ increase the rate of acrylamide polymerization. It is reasonable to assume that the SO_3^- as well as SO_4^{2-} groups are not responsible for the increase of the polymerization rate, which follows from the results obtained for the acrylamide polymerization rate in the presence of $NaHSO_3$ and $NaHSO_4$ in a concentration range from 10^{-3} to 10^{-1} mol dm^{-3} . Under these conditions the acrylamide polymerization rate remains practically unaffected. For the surfactant $C_{12}H_{25}SO_4Na$ a c.m.c. value of 9×10^{-3} mol dm^{-3} was established at 20 °C. As seen from Fig. 1 the increase of the acrylamide polymerization rate is evident at surfactant concentrations under as well as above c.m.c. In Fig. 2 is illustrated the dependence of the logarithms of the acrylamide polymerization rate on the logarithms of the surfactant concentrations for all three surfactants studied.

Table 1

Initial acrylamide polymerization rates R_{po} and degrees of polymerization P_N in argon atmosphere at the temperature of 50 °C in the presence of the surfactants E, initiated by ammonium peroxodisulfate ($c = 5 \times 10^{-4}$ mol dm^{-3})
 $[AAM]_0 = 0.5$ mol dm^{-3}

Surfactant (E)	$\frac{[E]_0 \cdot 10^4}{\text{mol } dm^{-3}}$	$\frac{R_{po} \cdot 10^4}{\text{mol } dm^{-3} \text{ s}^{-1}}$	$P_N \cdot 10^{-4}^*$
none	0	0.80	2.52
$C_8H_{17}SO_3Na$	5	1.17	—
	10	1.21	1.91
	50	1.46	1.70
	100	1.63	1.96
	500	2.08	1.68
	$C_{12}H_{25}SO_4Na$	5	0.96
10		1.10	2.17
50		1.40	—
100		1.60	1.80
500		1.83	1.68
$C_{16}H_{33}SO_4Na$		5	1.30
	10	1.33	—
	50	1.60	—
	100	1.67	2.16
	500	1.90	1.80

* Estimated for samples with the mass conversion under 20 %.

From the results obtained it can be deduced that the increase in the acrylamide polymerization rate is influenced only by the surfactant concentration but not by the length of the surfactant *n*-alkyl substituent chain. From the plot in Fig. 2 obtained formal reaction order to the surfactant for all three surfactants studied is 0.13.

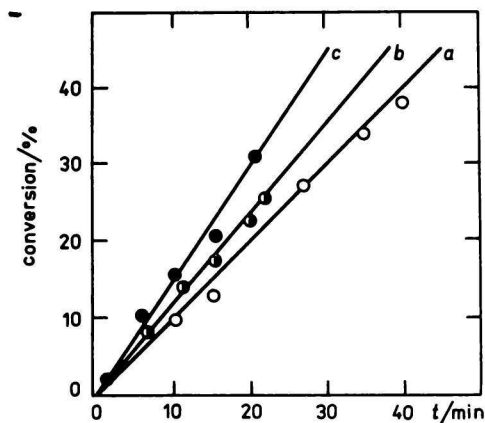


Fig. 1. Dependence of the acrylamide conversion on the surfactant $C_{12}H_{25}SO_4Na$ ($[E]_0$) concentration. Reaction temperature $50^\circ C$, $[AAM]_0 = 0.5 \text{ mol dm}^{-3}$, $[(NH_4)_2S_2O_8]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$.
a) Without surfactant; b) $[E]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$; c) $[E]_0 = 5 \times 10^{-2} \text{ mol dm}^{-3}$.

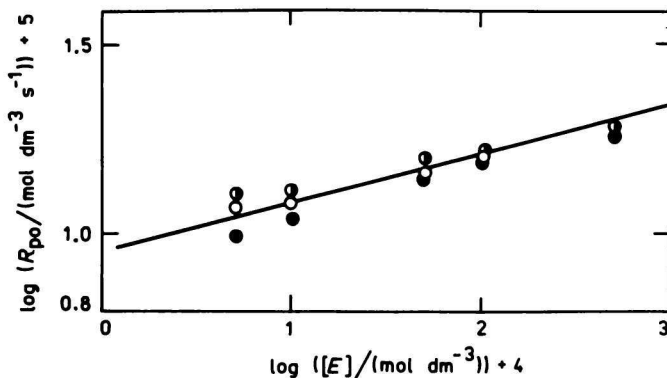


Fig. 2. Dependence of the logarithms of the initial acrylamide polymerization rate R_{po} on the logarithms of the initial surfactants concentration. Reaction temperature $50^\circ C$, $[(NH_4)_2S_2O_8]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[AAM]_0 = 0.5 \text{ mol dm}^{-3}$.
 \circ $C_8H_{17}SO_3Na$; \bullet $C_{12}H_{25}SO_4Na$; \ominus $C_{16}H_{33}SO_4Na$.

For explanation of the influence of the surfactants on the course of the acrylamide polymerization in water the interaction in the system initiator—surfactant was studied. For this purpose the absorption spectra of the initiator and surfactant $C_{12}H_{25}SO_4Na$ solution in UV region were analyzed (Fig. 3). After mixing both components together no new absorption band is formed, but the intensity of the surfactant absorption band with a maximum at 200 nm decreases proportionally to the concentration of the initiator added. The maxima of the absorption band are simultaneously shifted towards the higher wavelengths (e.g. 220 nm for the system with initiator concentration of $5 \times 10^{-3} \text{ mol dm}^{-3}$). The initiator absorbance was eliminated in such manner that in reference cell the initiator solutions in water were used. The initiator concentrations in the reference cells were the same as in the measured samples in the mixture with the surfactant.

Table 2

Dependence of the initial acrylamide polymerization rates R_{po} in water initiated by ammonium peroxodisulfate on the reaction temperature at various concentrations of the surfactant $C_{12}H_{25}SO_4Na$ ($[E]_0$)
 $[AAM]_0 = 0.5 \text{ mol dm}^{-3}$, $[(NH_4)_2S_2O_8]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$

θ °C	$[E]_0 = 10^{-2} \text{ mol dm}^{-3}$	$[E]_0 = 10^{-3} \text{ mol dm}^{-3}$	$[E]_0 = 0$
	$\frac{R_{po} \cdot 10^4}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$\frac{R_{po} \cdot 10^4}{\text{mol dm}^{-3} \text{ s}^{-1}}$	$\frac{R_{po} \cdot 10^4}{\text{mol dm}^{-3} \text{ s}^{-1}}$
50	1.42	1.11	0.79
55	1.82	1.43	—
60	2.40	1.65	1.25
70	5.00	3.50	3.33
77	8.12	7.70	—
Activation energy kJ mol ⁻¹	61 ± 0.53	66 ± 1.39	66 ± 1.33
Regression coefficient	0.996	0.977	0.975

From the results obtained it is evident that an interaction between the surfactant $C_{12}H_{25}SO_4Na$ and the initiator ammonium peroxodisulfate takes place. An exact explanation of that interaction will be the object of further study. This fact could be responsible also for the little decrease in the overall activation energy of the acrylamide polymerization in the presence of the surfactant $C_{12}H_{25}SO_4Na$. Activa-

tion energy of acrylamide polymerization known from the literature [5] has a value of 70 kJ mol^{-1} . Experimentally determined overall activation energy of the acrylamide polymerization in water initiated by ammonium peroxodisulfate has a value of 66 kJ mol^{-1} which is in good agreement with the literature value [5]. In a polymerization system containing the surfactant $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ in a concentration of $10^{-3} \text{ mol dm}^{-3}$ the activation energy value remains the same but in a system containing that surfactant in a concentration of $10^{-2} \text{ mol dm}^{-3}$ (above c.m.c.) within the temperature interval $50\text{--}77^\circ\text{C}$ it decreases to a value 61 kJ mol^{-1} (Table 2).

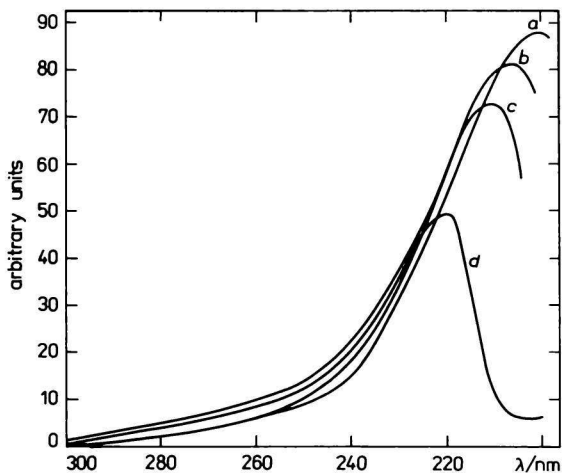


Fig. 3. Absorption spectra of the aqueous solutions of the surfactant $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ (E) and of the initiator $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (I) in UV region.

Solution in reference cell	Solution in sample cell
a) Water	$[\text{E}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$
b) $[\text{I}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$	$[\text{E}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$
	$[\text{I}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$
c) $[\text{I}] = 10^{-3} \text{ mol dm}^{-3}$	$[\text{E}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$
	$[\text{I}] = 10^{-3} \text{ mol dm}^{-3}$
d) $[\text{I}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$	$[\text{E}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$
	$[\text{I}] = 5 \times 10^{-3} \text{ mol dm}^{-3}$

As could be assumed all surfactants studied in the present work act as chain transfer agents in acrylamide polymerization. In comparison with the emulsifier Dowfax 2A1 their chain transfer effect is markedly smaller.

In Table 3 are listed dependences of the degree of polymerization P_N on the ratio

between the surfactant and monomer concentrations. As can be seen from the results the change in P_N with the surfactant concentration is essentially more expressive in the acrylamide polymerization at 60 °C in the presence of Dowfax 2A1 than in the presence of the surfactant $C_{12}H_{25}SO_4Na$. From Table 3 it is also evident that the surfactant alkyl chain length does not substantially influence P_N of the polyacrylamide produced and therefore neither the chain transfer efficiency of the surfactants studied.

Table 3

Alternation of the degree of polymerization P_N in acrylamide polymerization in water as a function of the ratio of the surfactant and monomer concentrations $[E]_0/[AAM]_0$ for various surfactants $[(NH_4)_2S_2O_8]_0 = 5 \times 10^{-4} \text{ mol dm}^{-3}$

$\frac{\theta}{^\circ C}$	Surfactant	$[E]_0/[AAM]_0 \cdot 10^3$	$P_{N-1} \cdot 10^5$
60	— ^a	0	5.30
60	Dowfax 2A1 ^a	2	5.80
		20	10.00
60	$C_{12}H_{25}SO_4Na$	2	7.40
		20	8.00
50	$C_8H_{17}SO_3Na$	20	5.10
		100	5.95
50	$C_{12}H_{25}SO_4Na$	20	5.60
		100	5.95
50	$C_{16}H_{33}SO_4Na$	20	4.60
		100	5.60

a) Taken from Ref. [3].

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