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L.R. Harutyunyan [a], R.S. Harutyunyan [b]

ON THE EFFECT OF LOWER ALIPHATIC ALCOHOLS ON THE MECHANISM OF CHLOROPRENE AND STYRENE EMULSION POLYMERIZATION

[a] Department of Bioscience and General Chemistry, Armenian National Agrarian University, Yerevan, Armenia
[b] Chemistry Research Center, Yerevan State University, Yerevan, Armenia

The mechanism of the participation of lower alcohols of the series methanol–decanol in the process of chloroprene and styrene polymerization in the emulsion has been studied. The dependence of the emulsion polymerization rate, the average diameter of polymer-monomer particles and the average molecular mass of polymers on the concentration and alkyl chain length of alcohols has been obtained. It is established that with increasing concentration of alcohols in the system, the rate of emulsion polymerization passes through a maximum and decreases with increasing alkyl chain length of alcohols. For the evaluation of the effect of alcohols on the kinetics of the emulsion polymerization, the participation of the alcohols in elementary steps of the emulsion polymerization process and their effect on colloidal-chemical properties of the emulsion polymerization system have been studied. It is established that neither alcohol concentration nor alkyl chain length of the alcohols affects the initiation step. However, alcohols significantly affect the interfacial tension of the polymerization system, solubilization of monomers, precipitation of polymers, and formation of mixed adsorption layers on drops of monomers, which, in turn, affects the kinetics of emulsion polymerization of chloroprene and styrene.

Keywords: emulsion polymerization, chloroprene, styrene, polymerization mechanism, kinetics of polymerization.

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Introduction

Researchers have always paid great attention to developing various approaches to the synthesis of polymers with specified molecular characteristics and structure of macromolecules by radical polymerization process [1–3], and also to the kinetics and mechanism of that process [2,3].

For evaluating different problems of emulsion polymerization (EP) very often the effect of the aliphatic alcohols on the polymerization process has been studied [4,5]. At the beginnings, the lower alcohols have been used for providing polymerization at the relatively low temperatures [1]. However, further, researchers drew attention to the effect of alcohols on the properties of micellar systems and on the properties of the initial emulsion, which, in the result, affects the EP kinetics. The obtained behaviors have been explained by the micellar theory of EP [1–3] which, in our opinion, requires more detailed consideration and some justifications. Two monomers- chloroprene and styrene, have been chosen for studies. The choice of monomers is conditioned by the wide use of their polymers- polychloroprene and polystyrene, and thus, the study of the polymerization of chloroprene and

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styrene continues to remain a topical problem.

Based on the above, the effect of aliphatic alcohols with the general formula $C_nH_{2n+1}OH$ (where n=1÷10) on the kinetics of chloroprene and styrene EP, on the average diameter of polymer-monomer particles (PMPs) and on the average molecular mass (AMM) of the produced polymer has been studied.

Depending on the length of the alkyl chain the distribution of alcohols in aqueous and micellar, and, therefore, in monomeric phases is changed (Table 1). These lead to a change in the properties of aqueous and micellar phases, which affect the kinetics of EP.

The degree of alcohols' distribution in aqueous solutions of anionic surfactant alpha olefin sulfonate (C_{14}–C_{16}AOS) determines the nature of the interaction between molecules of alcohols and their medium. Thus, the lower homologues (methanol, ethanol) interact with molecules and micelles of C_{14}–C_{16}AOS forming a solvate shell. Starting with propanol, alcohols solubilize into micelles, while starting with hexanol- they have the ability to form mixed micelles with molecules of C_{14}–C_{16}AOS. It is precisely this circumstance that determines the diverse influence of alcohols on physicochemical properties of aqueous solutions of surfactants and, as a result, on the changes of properties of aqueous and micellar phases. From the above mentioned, it is suggested that all mentioned factors must have an influence on EP kinetics. And it is also logical to expect certain correlations between colloidal-chemical properties of the studied system and EP kinetics in the presence of alcohols.

Experimental

Materials

Emulsifier anionic surfactant alpha olefin sulfonate C_{14}–C_{16} (C_{14}–C_{16}AOS, $C_nH_{2n+1}SO_3Na$, n-14–16, Parchem, US), monomers chloroprene ($CH_3CCl=CH_2$, Sigma-Aldrich, 98%) and styrene ($C_6H_5CH=CH_2$, analytical standard, Supelco), initiators potassium persulfate (PP, $K_2S_2O_8$, ACS reagent, ≥99.0%, Sigma-Aldrich) and 2,2'-azobisisobutyronitrile (AIBN, $(CH_3)_2C(CN)N=NC(CH_3)_2CN$, pure, ≥98.0% (GC), Sigma-Aldrich), alcohols methanol (CH_3OH, anhydrous, ≥99.8%, Sigma-Aldrich, CAS no. 67-56-1), ethanol (C_2H_5OH, absolute EMPLURA, Supelco), n-propanol (C_3H_7OH, anhydrous, 99.7%, Sigma-Aldrich), n-butanol (C_4H_9OH, ACS reagent, ≥99.4%, Sigma-Aldrich), 2-butanol (ReagentPlus, ≥99.0%, Sigma-Aldrich), n-pentanol ($C_5H_{11}OH$, ACS reagent, i99.0%, Sigma-Aldrich), n-hexanol ($C_6H_{13}OH$, anhydrous, ≥99.0%, Sigma-Aldrich), n-heptanol ($C_7H_{15}OH$, ≥99.5% (GC), Sigma-Aldrich), n-octanol ($C_8H_{17}OH$, ACS reagent, ≥99.0%), n-nonanol ($C_9H_{19}OH$, ≥98.0% Sigma-Aldrich) and n-decanol ($C_{10}H_{21}OH$, ≥98.0%, Sigma-Aldrich), water-soluble inhibitor stable iminoxyl radical 2,2,6,6-tetramethyl-4-piperidone-1-oxyd ($RNO–C_9H_{17}NO$, Sigma-Aldrich, 95%), regulator of AMM *tert*-dodecylmercaptan ($C_{12}H_{25}SH$, mixture of isomers, 98.5%, Sigma-Aldrich), stabilizator 2,2-methylene-bis (4 methyl-6-tert-butylphenol) ($C_{23}H_{32}O$, Sigma-Aldrich), benzene (C_6H_6, ACS reagent, ≥99.0%, Sigma-Aldrich) have been used without purification.

Methods

EP of chloroprene was carried out in air conditions at 313.15 K according to recipe: chloroprene 100 g, water 150 ml, C_{14}–C_{16}AOS 2 g, PP 0.4 g, and *tert*-dodecylmercaptan 0.9 g. The conversion was monitored by measuring the density of the system. Polychloroprene stood out from the formed latex. The polychloroprene was dried at 323.15 K. The ratio between phases was water:organic solvent=3:2.

The rate of polymerization of styrene was determined by the dilatometric method, V_{water}:$V_{benzene}$=1:2. The dilatometer was filled up under vacuum after degassing (~10^{-4} MPa). Under the stream of high-purity helium, the dilatometer was separated from installation and placed in the thermostat. The volume of the dilatometer was 5.6 ml; the height change in the dilatometer capillary tube was measured with accuracy of ±0.5 mm. The temperature was controlled with an accuracy of ±0.5 K. The emulsion

Table 1

Solubility of alcohols in aqueous solution of alpha olefin sulfonate C_{14}–C_{16} (C_{14}–C_{16} AOS=6.4·10^{-2} mol/l), their distribution constant* (K_P^*) in the aqueous and micellar phases and the change of free energy of distribution process (−ΔG), T=313.15 K

Alcohols	Solubility, mol/l	$K_P^* \cdot 10^{-3}$	–ΔG, kJ/mol
n- butanol	1.588	0.016	7.2
n- pentanol	0.568	0.072	11.1
n-hexanol	0.298	0.223	14.1
n-octanol	0.152	4.980	22.2
n-decanol	0.023	30.000	26.8

Note: * – is the ratio of the equilibrium concentrations of alcohols in the micelles and water.

was prepared by magnetic shaker stirring with a constant rate. The estimated error in W_P is no more than ±2%.

The initiation rate was obtained by the inhibition method and calculated according to the following equation:

$$W_i = \frac{f[Inh]}{\tau}, \quad (1)$$

where [*Inh*] is the initial concentration of inhibitor; τ is the induction period. For iminoxyl stable radicals, f=1.

For determination of average molecular mass (AMM) of polymers, the viscosity method was carried out. Determination of the characteristic viscosity of polymers was carried out in benzene. The flow times of the solutions and the solvent were measured using an Ubbelhode-type viscometer placed in a thermostated water bath at a temperature of 303.15 K. The AMM of polymers was calculated by the following equations:

$$[\eta] = 1.6 \cdot 10^{-4} M^{0.7}, \quad \text{(for polychloroprene)}, \quad (2)$$

$$[\eta] = 1.23 \cdot 10^{-4} M^{0.74}, \quad \text{(for polystyrene)}. \quad (3)$$

The average diameter of latex particles has been determined by the light scattering method by carrying out the Particle size analyzer Litesizer 500 (Anton Paar).

The surface tension of samples (γ) was determined and carried out with a SITA science line t60 tensiometer. Dynamic surface tension of each sample was determined by the maximum bubble pressure method. The lifetime of the bubble was controlled in an optimal diapason of 50–55 s. with a resolution of 1 ms. Temperature was controlled automatically with resolution of 0.1 K. The estimated error in γ is no more than ±2%. The critical micelle concentration (cmc) of C_{14}–C_{16}AOS both in the absence and presence of alcohols in aqueous solutions at 313.15 K was obtained as the break point on the isotherms surface tension-logarithm of C_{14}–C_{16}AOS concentration. The value of surface tension at the cmc (γ_{cmc}) of aqueous solutions of C_{14}–C_{16}AOS at 303.15 K (31.14 mN·m^{-1} in the absence of additive) is in good agreement with literature data [6].

Results and discussion

The experimental data show that alcohols significantly affect chloroprene and styrene EP kinetics. With increasing the concentration of alcohols the rate of emulsion polymerization (W_P) of both chloroprene and styrene increases at first and then decreases passing through the maximum (Tables 2 and 3; Fig. 1). The alcohols' concentration at which the maximum value of W_P is detected decreases as the alkyl chain length of the alcohols increases. In the presence of ethanol the maximum value of W_P of chloroprene is obtained at 0.1 mol/l, while in the case of hexanol, it is at 0.05 mol/l. At the same time at the same concentration of alcohols, the W_P of chloroprene decreases with the increase of alkyl chain length of alcohols (Table 4). From the data of Tables 2–4, it also follows that the AMM of polychloroprene decreases with the increase in the alcohols concentration

Table 2

Values of AMM of polychloroprene, average diameter (D) of polychloroprene latex particles and rate of chloroprene EP (W_P) at the different concentrations of ethanol. Degree of conversion 98%. T=313.15 K

C, mol/l	AMM·10^{-3}	D, Å	W_P, %/min
0.00	800	820	0.70
0.05	740	800	0.84
0.10	700	770	1.00
0.15	680	810	0.75
1.00	350	840	0.58

Table 3

Values of AMM of polychloroprene and rate of chloroprene EP (W_P) at the different concentrations of hexanol. Degree of conversion 98%. T=313.15 K

C, mol/l	AMM·10^{-3}	W_P, %/min
0.00	800	0.70
0.03	570	0.82
0.05	402	0.90
0.15	330	0.62
0.32	214	0.55

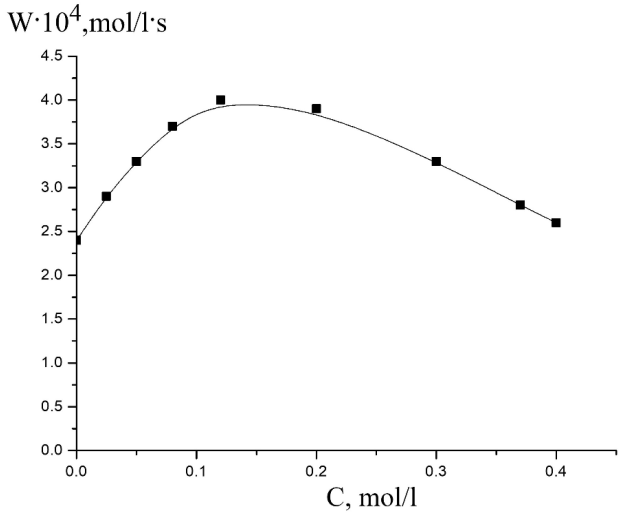


Fig. 1. Dependence of styrene EP rate on concentration of methanol. [PP]=4·10^{-3} mol/l, [C_{14}–C_{16}AOS]=3.19·10^{-2} mol/l, ratio of phases monomer:water=1:2, T=313.15 K

and the alkyl chain length of its molecules (at the same concentration). In the case of EP of styrene, W_P of the process reached maximum with the increase in the alkyl chain length of alcohols (Fig. 2 and 3). Similar dependence is also observed in the case of EP of chloroprene, but very slightly (Table 4).

The effect of alcohols on the kinetics of chloroprene and styrene EP can be the result of two factors. The first is their participation in elementary steps of the EP process and the second is by the effect of alcohols on properties of phases and, particularly, on colloidal-chemical properties of the system. Only after a detailed consideration of both factors, it is possible to estimate the share of each of them in the total contribution of the influence of alcohols on the chloroprene and styrene EP kinetics.

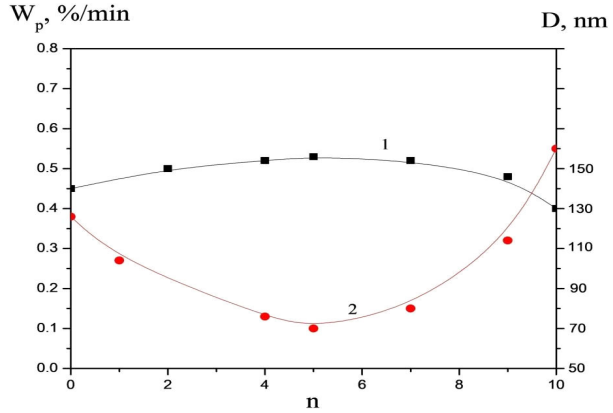


Fig. 2. Dependence of styrene EP rate (1) and PMP size (2) from alkyl chain length of alcohols. [PP]=$8\cdot10^{-3}$ mol/l, [C_{14}–C_{16}AOS]=$6.4\cdot10^{-2}$ mol/l, T=313.15 K

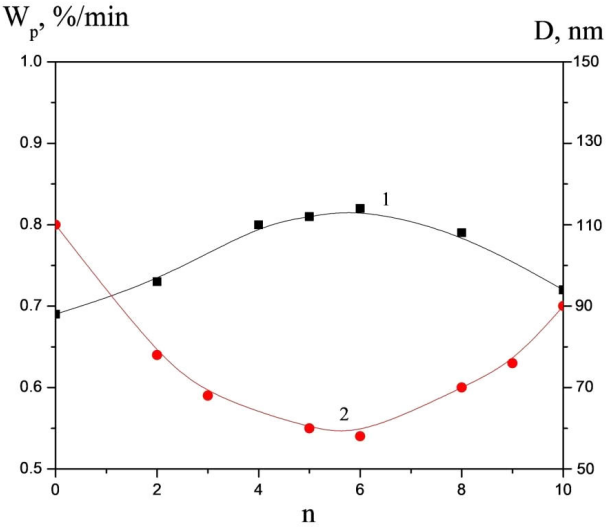


Fig. 3. Dependence of styrene EP rate (1) and PMP size (2) from alkyl chain length of alcohols. [AIBN]=$2.5\cdot10^{-2}$ mol/l, [C_{14}–C_{16}AOS]=$6.4\cdot10^{-2}$ mol/l, T=333.15 K

At the first stage of the experiments, the effect of alcohols on the initiation step of EP of monomers has been studied. The decomposition of PP in the presence of alcohols in aqueous medium is well studied [7,8]. According to refs. [7,8], reaction PP+alcohol is initiated by two parallel occurring processes: spontaneous homolytic decomposition of PP and bimolecular reaction of PP with alcohol molecule:

$$S_2O_8^{-2} \rightarrow 2\dot{SO}_4^- , \quad (4)$$

$$S_2O_8^{-2} + CH_3OH \rightarrow \dot{SO}_4^- + HSO_4^- + \dot{C}H_2OH . \quad (5)$$

However, for the same process, ref. [9] reported that reaction (5) does not occur at the PP homolysis step and the decomposition of PP is occurring only by reaction (4). It was suggested [9] that the radical chain mechanism of PP decomposition in the presence of alcohols can be presented as follows:

1. Decomposition of PP:

$$S_2O_8^{-2} \rightarrow 2\dot{SO}_4^- .$$

2. Propagation:

$$\dot{SO}_4^- + RCH_2OH \rightarrow HSO_4^- + R\dot{C}HOH , \quad (6a)$$

$$\dot{SO}_4^- + R\dot{C}HOH \rightarrow HSO_4^- + RCHO , \quad (6b)$$

3. Termination:

$$\dot{SO}_4^- + R\dot{C}HOH \rightarrow HSO_4^- + RCHO , \quad (7a)$$

Table 4

Values of AMM of polychloroprene, average diameter (D) of polychloroprene latex particles and rate of chloroprene EP (W_P) in the presence of different alcohols. [alcohol]=0.15 mol/l. Degree of conversion 98%. T=313.15 K

Alcohols	AMM·10^{-3}	D, Å	W_P, %/min
in the absence	800	820	0.70
methanol	700	820	0.72
ethanol	680	810	0.75
propanol	660	810	0.75
n-butanol	560	820	0.73
2-butanol	380	830	0.72
n-pentanol	360	850	0.68
n-hexanol	330	900	0.62
n-heptanol	325	890	0.57
n-octanol	340	920	0.51
n-nonanol	320	930	0.45
n-decanol	320	960	0.40

$$R\dot{C}HOH + R\dot{C}HOH \rightarrow RCH_2OH + RCHO \cdot \quad (7b)$$

According to refs. [7,8] the alcohols must influence the EP initiation step, while if referring to the work [9], the EP initiation process must not be dependent on the presence of alcohols in polymerization systems.

The studies have shown that the rate of initiation does not depend on the nature and concentration of alcohols. From this fact, it can be concluded that alcohols do not act on the PP decomposition rate. From this can it be concluded that not only alcohols but also C_{14}–C_{16}AOS and monomers practically do not affect the PP decomposition rate.

The alcohol radicals are very active [9] and directly interact with the monomer, initiating the chain:

$$R\dot{C}HOH + M \rightarrow RCHOH\dot{M} \cdot \quad (8)$$

It has also been stated that alcohols do not directly participate in initiation step when as initiator has been used AIBN. However, it must be noted that the possibility of interaction of the AIBN radical with the alcohol molecule is not ruled out:

$$R^{\bullet} + R_1CH_2OH \rightarrow RH + R_1\dot{C}HOH \cdot \quad (9)$$

Step (9) can also compete with the following step:

$$R^{\bullet} + M \rightarrow RM \cdot \quad (10)$$

As the concentration of monomer is many times higher than the concentration of alcohol the probability of participation of radicals in step (9) is little compared to the step (10), and, therefore, contribution of step (9) in the polymerization process can be neglected.

Based on abovementioned, the process of studied monomers' polymerization in the presence of alcohols in an anaerobic medium can be presented by the following sequence:

1. Formation of initial radicals:

$$S_2O_8^{-2} \rightarrow 2\dot{SO}_4^-,$$

$$\dot{SO}_4^- + RCH_2OH \rightarrow HSO_4^- + R\dot{C}HOH \cdot \quad (11)$$

2. Initiation:

$$\dot{SO}_4^- + M_1 \rightarrow SO_4^-\dot{M}_1, \quad (12)$$

$$R\dot{C}HOH + M_1 \rightarrow RCHOH - \dot{M}_1 \cdot$$

3. Propagation:

$$\dot{M}_{n-1} + M \rightarrow \dot{M}_n \cdot \quad (13)$$

4. Chain transfer: the alcohols are known as the chain transfer agents and the following step is possible to occur:

$$\dot{M}_n + RCH_2OH \rightarrow M_nH + R\dot{C}HOH \cdot \quad (14)$$

5. Termination:

$$\dot{M}_n + \dot{SO}_4^- \rightarrow M_nSO_4^-, \quad (15a)$$

$$\dot{M}_n + R\dot{C}HOH \rightarrow RCHOHM_n, \quad (15b)$$

$$\dot{M}_n + \dot{M}_m \rightarrow M_n - M_m \cdot \quad (15c)$$

Due to the steps (6b) and (7), the molecules of aldehyde can form in the polymerization process. As it is known [9], aldehydes react with ion-radicals and also are polymer chain transfer agents [10]:

$$\dot{SO}_4^- + RCHO \rightarrow HSO_4^- + R\dot{C}O, \quad (16)$$

$$\dot{M}_n + RCHO \rightarrow M_nH + R\dot{C}O \cdot \quad (17)$$

As a result of the (16) and (17) steps, more passive aldehyde radicals are formed [18] which can lead to the decrease of the rate of process. However, depending on the distribution of alcohols in the phases their participation in the step (11) will differ, and, therefore, the amount of formed aldehyde will depend on the nature of the alcohol. In the case of the application of lower alcohols due to their high solubility in water, their participation in the step (11) and the formation of aldehydes in the steps (6) and (7) are more probable. The higher alcohols are practically insoluble in the water and their participation in the step (11) and, therefore, the formation of aldehydes is less probable. However, it must be noted that in rigorous discussion of this issue the effect of aldehydes cannot be neglected.

Another process occurs when the EP has been carried out in the air conditions because in this case the participation of oxygen in the step (11) must be taken into consideration. Oxygen reacts with alcohol radicals by the following:

$$R\dot{C}HOH + O_2 \rightarrow RCHOH - O - O \cdot \quad (18)$$

The formed radicals inhibit the radical

decomposition of PP [9]; thus, the step (6b) can be excluded and the initiation of the chain by alcohol radicals becomes less probable.

In the presence of anionic emulsifier C_{14}–C_{16}AOS, the alcohol radicals, formed in the step (6a), are more hydrophobic than radicals of persulfate which makes it easier for them to get in through the negative charge surface of particles (polymer-monomeric particles (PPM), monomer drops, micelles) in which the polymerization process is starting or continuous. With the increase of alkyl chain length of alcohols, the participation of alcohols in the step (11) becomes less probable as their solubility in the water decreases, and due to this they mainly act as chain transfer agents. At the first glance, one might assume that the obtained dependence of EP rate on alkyl chain length of alcohol molecules (Fig. 2) must be related to the formation of alcohol radicals in the step (11) and with their participation in the step of polymer chain initiation (12). However, the analogous behavior also has been obtained when oil-soluble AIBN was used as the initiator (Fig. 3). Due to the oil-soluble nature of AIBN, the concentration of AIBN in water is negligible, and the probability of initiation in water, in analogy to step (9), is very little. With the increase of alkyl chain length in molecules of alcohols, their participation in step (9), which in the case of AIBN occurs in the aqueous phase, becomes possible. However, this should not lead to the increasing of process rate because, at first, the total number of radicals in the system does not change, and, second, the hydrophobicity of radicals in this case cannot be decisive.

The alcohol or aldehyde radicals, which have been formed in various steps of the EP general process, can participate in the termination step. The radicals, forming in the steps of chain transfer, are located in the immediate zone of polymerization, making their participation in the step (15b) more probable. It is led to a decrease in of both the AMM of polymer and the rate of the process. With increasing the alcohols concentration, their influence on AMM and EP rate is significant as follows from experimental data (Tables 2 and 3, Fig. 1).

For detailed evaluation of the mechanism of alcohols' effect on the EP kinetics, it is also necessary to study the effect of alcohols on colloidal-chemical properties of system.

The additives of the polymerization system can affect interphase tension, viscosity and density of phases, on which the kinetics of EP depend. It has been observed that with increasing alkyl chain length of alcohols surface tension (γ) of C_{14}–C_{16}AOS–water system decreases (Fig. 4). As a result, the dispersibility of the monomer becomes easy due to the formation of smaller drops. The arising of dispersity of the monomeric phase led to decreasing the size and increasing the number of PPM in the polymerization system (Fig. 2 and 3, Tables 2 and 4). However, at the same time, it is known [11] that an increase in the alkyl chain length in molecules of alcohols can result in their incorporation into micelles forming mixed chains, and, therefore, to mixed adsorption layers on the monomer drops and PPM. It leads to a decrease in the density of surface charge of adsorption layers. As a result, the stability of particles decreases and, therefore, decreases their number in the system.

Although with increasing the alkyl chain length of alcohols the critical micelle concentration (cmc), and, therefore, the concentration of C_{14}–C_{16}AOS, which is necessary for stabilization of disperse particles in the polymerization system, decrease (Fig. 4), the behavior of PMPs size has an extremum. It must be noted that the smallest size and therefore the largest number of PMPs are obtained for the middle members of homologues series of alcohols (Fig. 2 and 3).

The idea of Smith and Ewart considering the number of PMPs as the basic kinetic factor [12] was successfully applied for the description of the behaviors of EP rate changes in the various conditions. The EP rate is proportional to the number of PMPs or inversely proportional to the size of PMPs. The similar pattern also has been established during our studies (Fig. 2 and 3, Table 2). This is to once again state that in order to explain the effect of various factors on EP rate, it is necessary, first of all, to consider their influence on the size or number of PMP.

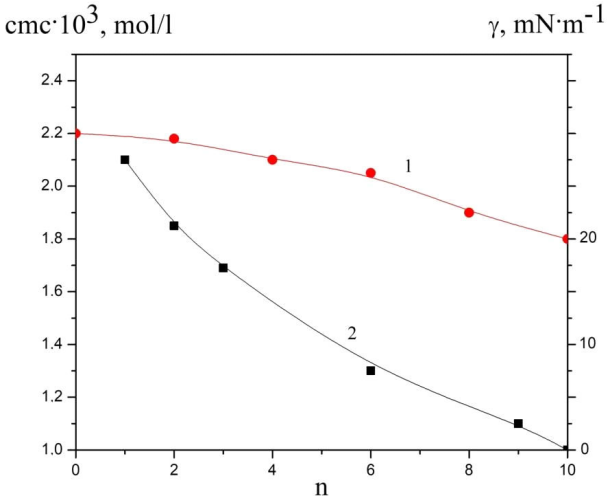


Fig. 4. Dependence of surface tension (1) ([C_{14}–C_{16}AOS]=3.2·10^{-2} mol/l) and cmc (2) of C_{14}–C_{16}AOS aqueous solutions on the alkyl chain length of alcohols. [alcohol]=0.3 mol/l, T=313.15 K

Alcohols increase the real solubility of chloroprene and styrene [13], which leads to the increasing of the rate of the step (12) and the rate of EP, in general. However, the solubility of monomers in the micelles should not influence the EP rate practically. Depending on the solubility of the monomer in the aqueous phase, the amount of polymer formed in the aqueous phase due to real soluble and solubilized monomer can change. However, its share in the total amount of formed polymer will be very small and will not have a significant effect on EP behavior and also on the properties of the formed polymer.

The dependences of PMPs size and EP rate have the antibatal character (Fig. 2 and 3, Table 2). It must be noted that lower alcohols decrease the EP rate without penetrating into the adsorption layer because they do not form mixed micelles or adsorption layers. With increasing the alcohols concentration, the degree of adsorption layer hydration and thickness of the electrical double layer decrease [14] due to which the stabilization ability of C_{14}–C_{16}AOS greatly reduced. As a result, the biggest PMPs are formed and the rate of EP decreases. This is also facilitated by partial desorption of C_{14}–C_{16}AOS from the surface of disperse particles due to the rise of its molecular solubility in the aqueous phase. The alcohols are precipitators for polychloroprene and polystyrene. With an increase in the alcohol concentration, their precipitation ability is more pronounced and the PMPs start to grow, while the rate of EP decreases. In the case of higher homologues of alcohols, their ability to implement into the adsorption layer is added to this, which, as it discusses above, also can lead to the growth of PMPs and decrease of EP rate. It follows that increasing the alkyl chain length of the alcohols increases their coagulating ability. Consequently, in the methanol–decanol series, the concentration at which the maximum rate is reached decreases. As it has been mentioned above, in the case of chloroprene polymerization, the concentration of ethanol at which the EP rate reaches maximum value is equal to about 0.1 mol/l, while for hexanol it is about 0.05 mol/l (Tables 2 and 3). In the case of styrene polymerization, the concentration of methanol at which the EP rate reaches maximum value is equal to about 0.12 mol/l (Fig. 1), while for decanol it is about 0.004 mol/l (the emulsifier is sodium oleate).

Conclusions

The effect of alcohols on the mechanism of chloroprene and styrene polymerization in emulsions has a multifactor character. It is established that the influence of alcohols on monomers emulsion polymerization kinetics are conditioned by both their participation in the chain transfer and termination elementary steps and changes of physical-chemical and colloidal properties of the emulsion system in the presence of alcohols. Although, at the same concentration of alcohols, the rate of polymerization of chloroprene and styrene decreases monotonously with the increase of alkyl chain length of alcohols. It is occurring due to the formation of the biggest polymer-monomeric particles with increasing the alkyl chain length of alcohol.

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ВПЛИВ НИЖЧИХ АЛІФАТИЧНИХ СПИРТІВ НА МЕХАНІЗМ ЕМУЛЬСІЙНОЇ ПОЛІМЕРИЗАЦІЇ ХЛОРОПРЕНУ ТА СТИРОЛУ

Л.Р. Арутюнян, Р.С. Арутюнян

Досліджено механізм участі нижчих спиртів ряду метанол–деканол у процесі емульсійної полімеризації хлоропрену та стиролу. Встановлено залежності швидкості емульсійної полімеризації, середнього діаметра полімер-мономерних частинок і середньої молекулярної маси полімерів від концентрації та довжини алкільного ланцюга спиртів. Встановлено, що зі збільшенням концентрації спиртів у системі швидкість емульсійної полімеризації проходить через максимум, а зі збільшенням довжини алкільного ланцюга спиртів зменшується. Для оцінювання впливу спиртів на кінетику емульсійної полімеризації досліджено участь спиртів в елементарних стадіях процесу емульсійної полімеризації та їхній вплив на колоїдно-хімічні властивості системи емульсійної полімеризації. Встановлено, що ні концентрація спиртів, ні довжина їхнього алкільного ланцюга не впливають на стадію ініціювання. Водночас спирти істотно впливають на міжфазний натяг у полімеризаційній системі, солюбілізацію мономерів, осадження полімерів та утворення змішаних адсорбційних шарів на краплях мономерів, що, своєю чергою, впливає на кінетику емульсійної полімеризації хлоропрену та стиролу.

Ключові слова: емульсійна полімеризація; хлоропрен; стирол; механізм полімеризації; кінетика полімеризації.

ON THE EFFECT OF LOWER ALIPHATIC ALCOHOLS ON THE MECHANISM OF CHLOROPRENE AND STYRENE EMULSION POLYMERIZATION

L.R. Harutyunyan [a, *], R.S. Harutyunyan [b]

[a] Department of Bioscience and General Chemistry, Armenian National Agrarian University, Yerevan, Armenia

[b] Chemistry Research Center, Yerevan State University, Yerevan, Armenia

[*] e-mail: l.harutyunyan@anau.am

The mechanism of the participation of lower alcohols of the series methanol–decanol in the process of chloroprene and styrene polymerization in the emulsion has been studied. The dependence of the emulsion polymerization rate, the average diameter of polymer-monomer particles and the average molecular mass of polymers on the concentration and alkyl chain length of alcohols has been obtained. It is established that with increasing concentration of alcohols in the system, the rate of emulsion polymerization passes through a maximum and decreases with increasing alkyl chain length of alcohols. For the evaluation of the effect of alcohols on the kinetics of the emulsion polymerization, the participation of the alcohols in elementary steps of the emulsion polymerization process and their effect on colloidal-chemical properties of the emulsion polymerization system have been studied. It is established that neither alcohol concentration nor alkyl chain length of the alcohols affects the initiation step. However, alcohols significantly affect the interfacial tension of the polymerization system, solubilization of monomers, precipitation of polymers, and formation of mixed adsorption layers on drops of monomers, which, in turn, affects the kinetics of emulsion polymerization of chloroprene and styrene.

Keywords: emulsion polymerization; chloroprene; styrene; polymerization mechanism; kinetics of polymerization.

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