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Effect of Mechanochemical Processing Parameters on Ethoxylation of Benzoic Acid Derivatives

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Abstract

The regularities of ethoxylation of benzoic acid derivatives during interaction with polyethylene glycol through mechanochemical solid-phase synthesis in a vibrating apparatus have been studied. The conditions for carrying out mechanochemical reactions to increase the conversion degree of initial reagents into reaction products are analysed. The products of ethoxylation are characterized by IR spectroscopy, acid-base potentiometric titration, tensiometry, and dilatational rheology. It has been established that the degree of starting reagents conversion into ethoxylation products depends on the nature of the substituent and its position in the benzene ring. The degree of conversion into reaction products is higher for *ortho*-substituted derivatives of benzoic acid. It is shown that the salts of ethoxylated derivatives of benzoic acid exhibit pronounced surfactant properties at the air – solution interface.

Keywords: benzoic acids, polyethylene glycol, mechanochemical processing, IR spectroscopy, acid-base potentiometric titration, tensiometry, dilatational rheology

INTRODUCTION

At present, much attention is paid to the mechanosynthesis of organic compounds. It is known that the synthesis of organic compounds is a multi-stage process, which is carried out in a liquid medium as a rule, using organic solvents at different stages of synthesis and product purification. The traditional production of organic substances is accompanied by large amounts of waste liquids and the necessity to neutralize and utilize them. Mechanochemical processes belong to environmentally friendly technologies and are highly effective, they do not require solvents to conduct chemical reactions. These processes are not connected with the use of catalysts, reactions are carried out at room temperature and substantially decreased reaction time [1–4].

Mechanochemical synthesis of organic compounds is the subject of a comparatively small number of works. Solid-phase esterification, cyclisation, halogenation, halogen substitution, hydrogenolysis, oxidation, acylation, *etc.* have been described [5–8]. Mechanochemical methods were successfully applied to coupling, condensation, asymmetric synthesis, isolation of reaction intermediates, *etc.* [9–12].

Ethoxylation of organic compounds is usually carried out by blowing gaseous ethylene oxide through compounds containing active hydrogen [13, 14]. These reactions involve gaseous ethylene oxide under high pressure, catalysts (acid or alkaline). The reactions are carried out at high temperature (up to 150 °C) for a long time (several hours) [15, 16]. The possibility to carry out ethoxylation by the mechanochemical solid-phase

method will simplify this process substantially in comparison with more complicated and labour-intensive traditional chemical methods.

It is known that halogenated, nitro-, amino-, and oxygenated derivatives of benzoic acid are used as antimicrobial agents in medicine, food and processing industries [17, 18], as fungicides and insecticides in agriculture [19], as corrosion inhibitors in the composition of petroleum products [20], and as additives for preparing pharmaceutical compositions [21].

Ethoxylation of the derivatives of benzoic acid involves the introduction of long ethoxylated "tails" into their molecules, and it is possible to obtain substituted non-ionogenic surfactants exhibiting biologically active and corrosion-inhibiting properties.

The goal of the work was to investigate the interaction of benzoic acid derivatives with polyethylene glycol during mechanochemical synthesis with the variation of reaction conditions, and to study the products of ethoxylation by IR spectroscopy, acid-base potentiometric titration, tensiometry, and dilatational rheology.

EXPERIMENTAL

Materials

The reagents used in the work include: benzoic acid (GOST 10521-78, $T_m = 122\text{ }^{\circ}\text{C}$), *ortho*-nitrobenzoic acid (CAS 552-16-9, $T_m = 147\text{ }^{\circ}\text{C}$), *meta*-nitrobenzoic acid (CAS 121-92-6, $T_m = 141\text{ }^{\circ}\text{C}$), *para*-nitrobenzoic acid (CAS 62-23-7, $T_m = 238\text{ }^{\circ}\text{C}$), 3,5-dinitrobenzoic acid (CAS 99-34-3, $T_m = 106\text{ }^{\circ}\text{C}$), *ortho*-oxybenzoic acid (GOST 624-70, $T_m = 158\text{ }^{\circ}\text{C}$), *ortho*-aminobenzoic acid (CAS 118-92-3, $T_m = 148\text{ }^{\circ}\text{C}$), *ortho*-chlorobenzoic acid (TU 6-09-319-70, $T_m = 142\text{ }^{\circ}\text{C}$), *ortho*-iodobenzoic acid (CAS 88-67-5, $T_m = 162\text{ }^{\circ}\text{C}$), polyethylene glycol PEG-6000 (PEG, TU 2483-008-71150986-2006, $T_m = 55\text{--}60\text{ }^{\circ}\text{C}$).

Investigation procedures

The amount of carboxylic groups in the solutions of carboxylates and in reaction mixtures after their ethoxylation was determined by acid-base potentiometric titration. The solutions of the salts of carboxylic acids (0.05 %) were titrated with a 0.1 M HCl solution. After the addition of each portion of the titrant (0.1 mL), the system was mixed with a magnetic mixer for 2 min. The maxima on the differential titration curves, which were the dependences of $\Delta\text{pH}/\Delta V$ on V_{HCl} (where

ΔpH is the change of pH value after the addition of a portion of titrant (0.2 mL 0.1 M HCl); $\Delta V = 0.2\text{ mL}$ – the volume of each titrant portion added; V_{HCl} – titrant volume), corresponded to equivalence points.

The degree of initial reagents ethoxylation into reaction products (S , %) was determined as the difference between the amount of carboxylic groups in the initial acid ($[\text{COOH}]_A$) and in the reaction product ($[\text{COOH}]_P$) divided by the amount of these groups in the initial acid:

$$S = \frac{[\text{COOH}]_A - [\text{COOH}]_P}{[\text{COOH}]_A} \cdot 100$$

The solutions of the salts of organic acids for the measurement of surfactant characteristics at the liquid – gas interface were prepared in purified water (water purification system Milli-Q, Merck, France) characterised by surface tension $72.0 \pm 0.2\text{ mN/m}$.

Methods of investigation

Mechanochemical ethoxylation of aromatic acids was carried out with polyethylene glycol (PEG-6000) in a 75T-DrM vibration instrument (Teplogorsk Plant of Hydraulic Equipment) at vibration frequency 50 Hz and amplitude 3.0–5.0 mm. The grinding cell of the instrument is composed of a steel beaker with a cap and the working body (B), which is a steel cylinder of regular shape, with the mass (m_B) equal to 1.13 kg. The time of mechanical processing (τ_{MP}) was varied from 5 to 10 min. The mass of reagents loaded into the vibration apparatus was varied, too. The total mass of reaction mixture loaded into the apparatus (m_{RM}) was 2.0 or 1.0 g, with the ratio of component masses equal to 1:1.

A precise pH meter (Metrohm 744 pH Meter, Switzerland) was used to measure the acidity (pH) of the solutions.

Infrared spectra were recorded in KBr tablets (the concentration of the substance in the tablet was 0.5 %) with a Bruker Tensor 37 FTIR Spectrometer (Germany).

The equilibrium surface tension (γ_e , mN/m) of the aqueous solutions of the salts of aromatic acids within a broad surface lifetime range (from 1 to 10^5 s) was measured using the pendent drop shape method with the help of a PAT-2P tensiometer (Sinterface Technologies, Germany). The error of surface tension measurement did not exceed $\pm 0.1\text{ mN/m}$.

Dilatational rheological characteristics of the surface layers of solutions were determined using

the PAT-2P tensiometer with the harmonic oscillations of the drop after reaching the adsorption equilibrium. Results were analysed with the help of Fourier transform. The principle of PAT-2P tensiometer operation was described in [22, 23].

RESULTS AND DISCUSSION

It is known [1] that an essential characteristic of mechanochemical reactions is the degree of initial components transformation into reaction products, which depends first of all on the nature of reacting substances, the value of mechanical energy supplied to the reaction mixture, and reaction time. So, investigation of the regularities of specific solid-phase mechanochemical reactions depending on variations in the parameters of mechanical strain is highly relevant.

The authors of [24–27] demonstrated the possibility of the interaction of humic acids and halogen-substituted benzoic acids with polyethylene glycol under the conditions of solid-phase mechanochemical synthesis. A scheme of the possible ethoxylation of aromatic compounds containing a carboxylic group is shown in Fig. 1.

In the present work, we studied ethoxylation of some nitro-, *ortho*-oxy- and *ortho*-aminobenzoic acids with polyethylene glycol (PEG-6000), carried out mechanochemically in a vibration apparatus.

The IR spectra of components in the reaction of *ortho*-nitrobenzoic acid with PEG-6000 are presented in Fig. 2. The IR spectrum of a mixture of initial reagents without mechanical treatment does not exhibit any changes in comparison with the spectra of initial substances, while the IR spectra of mixtures obtained as a result of mechanical treatment contain absorption bands (a. b.) of initial reagents and the new ones, which may

be assigned to reaction products. Two bands are observed in the region of the stretching vibrations of carbonyl group, their frequencies are presented in Table 1. One of them relates to absorption by the stretching C=O vibration of the carboxylic group of the acid (Ar-C(O)OH), while the other, shifted to higher frequencies by 20–45 cm⁻¹, may be related to the stretching vibration of the carbonyl group in the formed reaction product – ester (Ar-C(O)O-R). The intensity of a. b. of the vibrations of OH groups in the acid within the range 2700–2500 cm⁻¹ decreases. These bands disappear after purification of the reaction mass from unreacted acid. The region of the bending vibrations of OH groups (960–890 cm⁻¹) also exhibits changes. Instead of a broad a. b. of polyethylene glycol with the maximum at 960 cm⁻¹, new bands are recorded at 950–940 cm⁻¹, which may be due either to the presence of the second unreacted OH group in polyethylene glycol or to structural changes resulting from the solid-phase reaction. This allows us to assume that benzoic acids under investigation interact with PEG-6000 during mechanochemical treatment, however, the reactions do not proceed till completeness under the conditions of our experiment: the degree of transformation of initial reagents into reaction products depends on the nature of the substituent and on its position in the benzene ring (see Table 1).

Comparison between the degrees of initial components transformation into ethoxylation products, as determined by means of acid-base potentiometric titration, shows that the transformation degree in the series of nitro-derivatives of benzoic acid is higher for the *ortho*-substituted acid, similar to the case of previously investigated halogenated derivatives [26, 27].

The introduction of the second nitro group into the *meta*-position of the benzene ring (3,5-di-

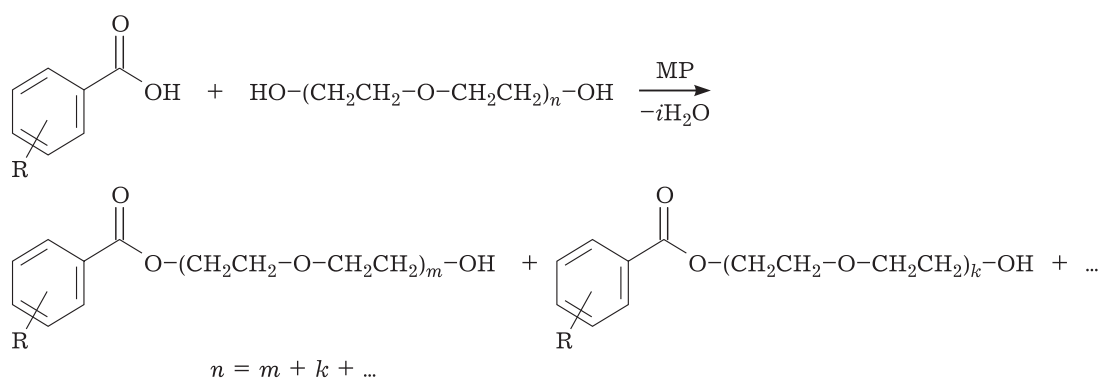


Fig. 1. Scheme of solid-phase ethoxylation of substituted benzoic acids. MP – mechanical processing.

nitrobenzoic acid) is accompanied by a decrease in the yield of reaction products in the mixture in comparison with *meta*-nitrobenzoic acid (see Table 1).

It should be stressed that for *ortho*-substitution, in the case of nitrobenzoic acid (electron-withdrawing substituent), a higher degree of initial components transformation into reaction products is observed, in comparison with the case of electron-donating substituents in *ortho*-position (OH-, NH₂-) (see Table 1).

It follows from the data shown in Fig. 3 that a trend to increased ethoxylation degree with an increase in the constant of acid dissociation (K_a), or with a decrease in acidity index of the acid (pK_a) may be revealed. These parameters characterise the behaviour of an acid in the aqueous solution and are used to calculate the values of Hammett constants σ and to determine the total electron effect of the substituents on the reactivity of aromatic compounds. In addition, K_a and pK_a values characterise the ability of acid proton to be detached, which is important for esterification, in particular in the case of mechanochemical synthesis.

The result for *ortho*-oxybenzoic acid stands out of the common pattern (see Fig. 3). This may be due to specific spatial effects. In the solid state, the molecule of this acid may form a conformation with a stable six-membered cycle with strong intramolecular hydrogen bond between the proton of carboxylic group and oxygen atom of the hydroxyl group of the acid (the energy of this hydrogen bond is 10.5 kcal/mol)[28]:

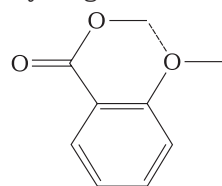


TABLE 1

Characteristics of organic acids and the products of their mechanochemical ethoxylation through the interaction with PEG-6000 ($\tau_{MP} = 5$ min, $m_{RM} = 2.0$ g)

Acid	pK_a	Transformation degree, %	Frequency of C=O vibrations in IR spectra, cm ⁻¹	
			in acid	in reaction product
<i>ortho</i> -Nitrobenzoic	2.17	40	1683	1728
<i>meta</i> -Nitrobenzoic	3.50	32	1694	1726
<i>para</i> -Nitrobenzoic	4.44	19	1697	1727
3,5-Dinitrobenzoic	4.82	25	1705	1729
<i>ortho</i> -Aminobenzoic	4.80	28	1676	1689
<i>ortho</i> -Oxybenzoic	2.98	17	1662	1666

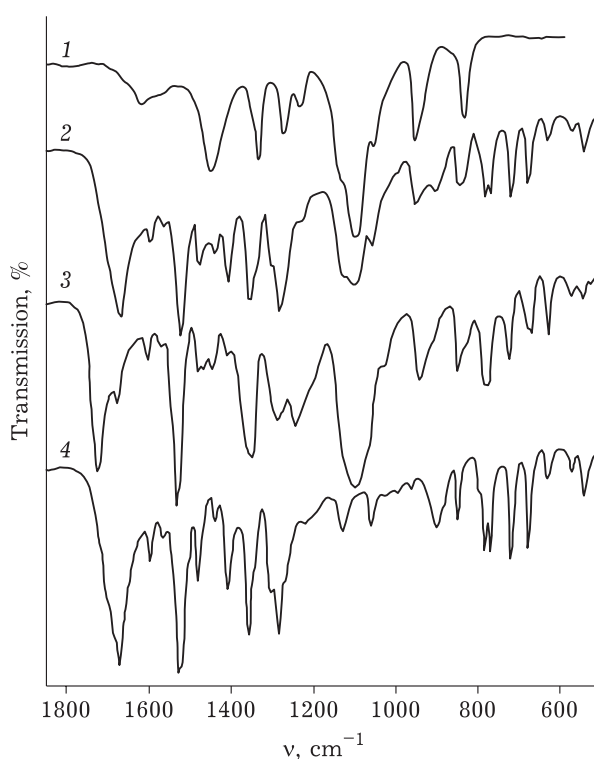


Fig. 2. IR-spectra of *ortho*-nitrobenzoic acid, polyethylene glycol (PEG) and reaction mixture in KBr tablets: 1 – PEG-6000; 2 – mixture (*ortho*-nitrobenzoic acid + PEG-6000) before mechanical processing; 3 – mixture (*ortho*-nitrobenzoic acid + PEG-6000) after mechanical processing ($\tau_{MP} = 5$ min, $m_{PC} = 2.0$ g); 4-*ortho*-nitrobenzoic acid. Designations, here and in Fig. 3–6: τ_{MP} – duration of mechanical processing; m_{RM} – mass of reaction mixture.

Investigation of the effect of mechanochemical processing conditions on solid-phase ethoxylation of organic acids, which included variations of the time of mechanical treatment and the energy consumed per unit mass of the reaction mixture (m_{RM} was equal to 1 and 2 g), was carried out with a number of benzoic acids (benzoic acid, *ortho*-chloro-, *ortho*-iodo-, *ortho*-nitro- and *meta*-nitrobenzoic acids) and PEG-6000. Reaction prod-

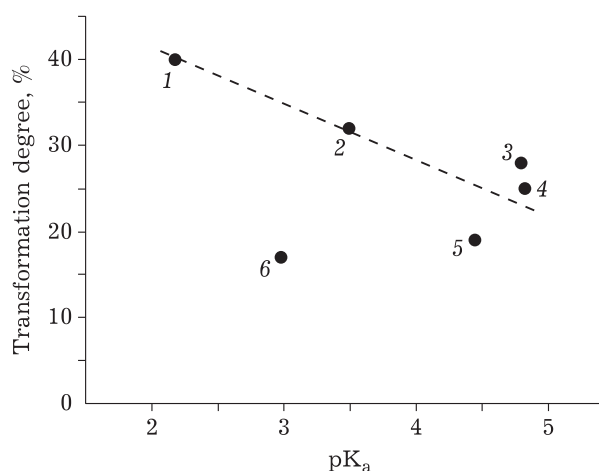


Fig. 3. Dependence of the degree of benzoic acid ethoxylation on their acidity index (pK_a): 1 - *ortho*-nitrobenzoic acid; 2 - *meta*-nitrobenzoic acid; 3 - *ortho*-aminobenzoic acid; 4 - 3,5-dinitrobenzoic acid; 5 - *para*-nitrobenzoic acid; 6 - *ortho*-oxybenzoic acid. $T_{MP} = 5$ min, reagents mass, $m_{RM} = 2.0$ g. For designations, see Fig. 2.

ucts were also investigated by IR spectroscopy and acid-base potentiometric titration.

Absorption bands related to the stretching vibrations of the carbonyl group ($\nu_{C=O}$, cm^{-1}) during mechanochemical ethoxylation of *ortho*-nitrobenzoic acid are shown in Fig. 4. It follows from these data that a gradual increase in the time of mechanochemical treatment from 5 to 10 min causes changes in the ratios of a. b. intensities for the stretching vibrations of C=O groups of initial acids and ethoxylated reaction products. The intensity of absorption bands related to ethoxylated products increases, which is evidence in favour of an increase in the degree of initial components transformation into the products of mechanochemical synthesis.

The absorption bands shown in Fig. 5 relate to the stretching vibrations of carbonyl groups ($\nu_{C=O}$) during solid-phase ethoxylation of *ortho*-chlorobenzoic (a) and *meta*-nitrobenzoic acids (b). For *ortho*-chlorobenzoic acid, an increase in the time of mechanochemical treatment from 5 to 10 min causes changes in the intensity ratios of a. b. related to the stretching vibrations of C=O groups of initial acids and those of ethoxylated reaction products, which is accompanied by an increase in the intensities of a. b. related to ethoxylated products (see Fig. 5, a). According to the data of acid-base potentiometric titration presented in Table 2, the degree of initial components transformation into ethoxylates increases.

A decrease in the mass of reaction mixture leads to an increase in the degree of initial components transformation into ethoxylation prod-

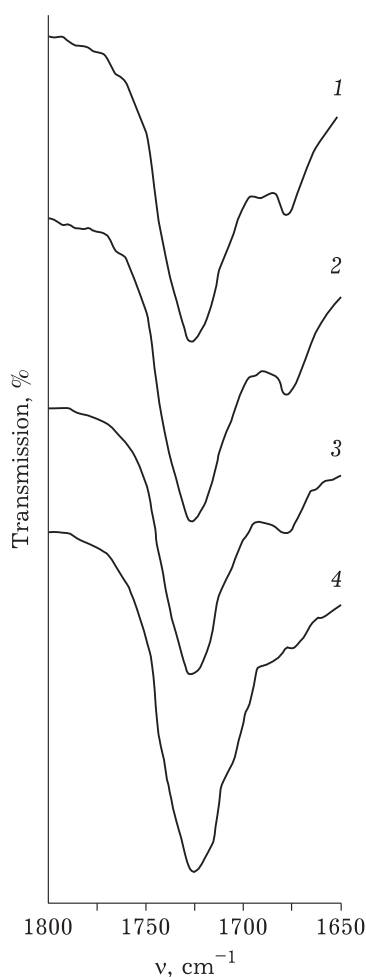


Fig. 4. Changes in the absorption bands of the stretching vibrations of C=O group in the IR spectrum during ethoxylation of *ortho*-nitrobenzoic acid depending on the time of mechanochemical reaction: 5 (1), 6 (2), 7.5 (3), 10 min (4). The total mass of reagents, $m_{RM} = 2.0$ g. For designations, see Fig. 2.

ucts because the energy per unit mass of the reaction mixture increases by a factor of 2. This is clearly exhibited by the data shown in Fig. 5, b and in Table 2. The results obtained after the treatment of 2 g of the mixture for 10 min and 1 g for 5 min the results are almost identical. The transformation degree of 1 g of the mixture after treatment for 10 min is twice as large as that obtained for 2 g of the mixture treated for 5 min, and both conclusions are true for all acids (see Table 2).

An increase in the amount of ethoxylated reaction products in the reaction mixture with further increase in the energy of mechanochemical treatment may turn out to be useful from the viewpoint of the technology for obtaining non-ionogenic surfactants.

The next stage of the work was to study the solutions of the salts of ethoxylated derivatives by

TABLE 2

Degree of initial reagents transformation into the products of ethoxylation of substituted benzoic acids with PEG-6000 depending on the total mass of reaction mixture (m_{RM}) and the time of mechanochemical processing (τ_{MP})

Acid	Transformation degree, %			
	$\tau_{MP} = 5 \text{ min},$ $m_{RM} = 2.0 \text{ g}$	$\tau_{MP} = 10 \text{ min},$ $m_{RM} = 2.0 \text{ g}$	$\tau_{MP} = 5 \text{ min},$ $m_{RM} = 1.0 \text{ g}$	$\tau_{MP} = 10 \text{ min},$ $m_{RM} = 1.0 \text{ g}$
Benzoic	18	24	23	35
<i>ortho</i> -Iodobenzoic	25	50	48	53
<i>ortho</i> -Nitrobenzoic	40	65	68	82

means of tensiometry and dilatational rheology for the mixture “*ortho*-nitrobenzoic acid + PEG-6000” as an example.

It is known that the surface layers of ionogenic surfactants, with clearly pronounced diphlic nature of their molecular structure (the presence of hydrophobic and hydrophilic fragments), differ in their structure from the adsorption layers of non-ionogenic surfactants without a hydrophobic centre. The presence of hydrophobic cen-

tres in the form of aromatic fragments of benzoic acids and long ethoxylated ‘tails’ in the structure of ethoxylated derivatives should cause a difference between their adsorption layers and the surface layers of polyethylene glycol due to the change of their adsorption mechanism at the aqueous solution – air interface.

Dependences of changes in the equilibrium surface tension on concentration for the solutions of ethoxylated salts of benzoic acids and poly-

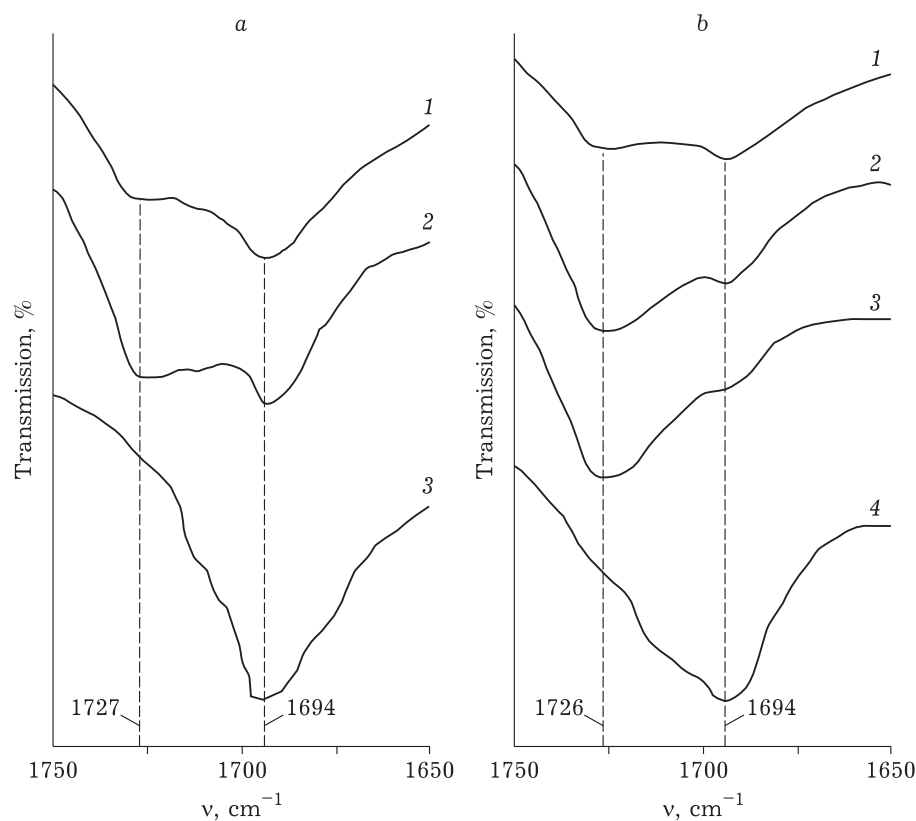


Fig. 5. Changes of the absorption bands of stretching vibrations of C=O group in the IR spectra of mechanically activated reaction mixtures depending on the mode of mechanochemical reaction: time of mechanical processing (τ_{MP}) and total mass of the reaction mixture (m_{RM}): a – mixture (*ortho*-chlorobenzoic acid + PEG-6000) (1, 2); *ortho*-chlorobenzoic acid (3). Conditions of mechanical processing: 1 – $m_{RM} = 2.0 \text{ g}$, $\tau_{MP} = 5 \text{ min}$; 2 – $m_{RM} = 2.0 \text{ g}$, $\tau_{MP} = 10 \text{ min}$; b – mixture (*meta*-nitrobenzoic acid + PEG-6000) (1, 2, 3); *meta*-nitrobenzoic acid (4). Conditions of mechanical processing: 1 – $m_{RM} = 2.0 \text{ g}$, $\tau_{MP} = 5 \text{ min}$; 2 – $m_{RM} = 1.0 \text{ g}$, $\tau_{MP} = 5 \text{ min}$; 3 – $m_{RM} = 1.0 \text{ g}$, $\tau_{MP} = 10 \text{ min}$. For designations, see Fig. 2.

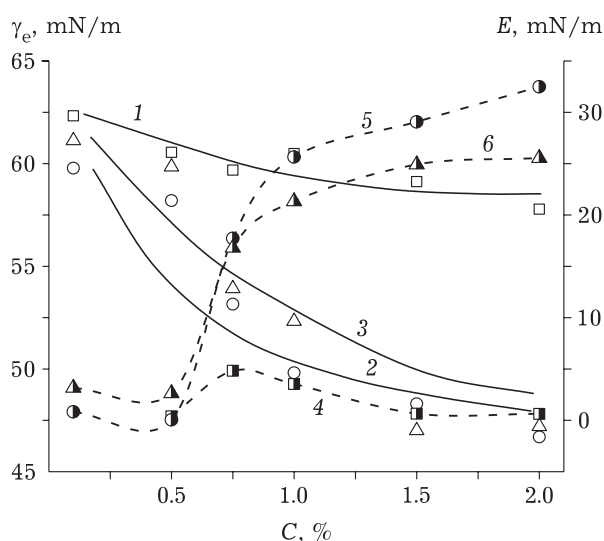


Fig. 6. Changes of the equilibrium surface tension (γ_e) (1, 2, 3) and dilatational viscoelasticity modulus (E) (4, 5, 6) depending on concentration (C). Solutions: 1, 4 – PEG-6000; 2, 5 – mixture (*ortho*-nitrobenzoic acid + PEG-6000); 3, 6 – mixture (benzoic acid + PEG-6000). Conditions of mechanical processing: $\tau_{MP} = 5$ min, $m_{RM} = 2.0$ g. The frequency of drop oscillation $f = 0.1$ Hz. For designations, see Fig. 2.

ethylene glycol differ substantially. It follows from Fig. 6 that ethoxylated derivatives can provide a more substantial decrease in surface tension in comparison with polyethylene glycol solutions. In addition, according to these data, viscoelasticity modulus values for the solutions of mechanically processed mixtures of benzoic acids with polyethylene glycol are substantially higher in comparison with the solutions of pure polyethylene glycol.

Since ethoxylation proceeds not until completeness under our experimental conditions, mechanochemical action on the mixture of benzoic acids with polyethylene glycol leads to a mixture of ethoxylated derivatives of benzoic acids and polyethylene glycol in excess. This is accompanied by a substantial change in the overall surface activity of these mixtures at the liquid – gas interface.

It is known that the studies of mixed surfactant compositions are of substantial theoretical and practical significance. These systems are widely used for developing the formulations of detergents, foaming agents, emulsifiers, cosmetics, pharmaceutical and other preparations.

In this connection, solid-phase ethoxylation of the derivatives of benzoic acid with polyethylene glycol leads to obtaining surfactant mixtures with different mechanisms of adsorption at the interface, which may have practical importance for developing surfactant compositions possessing biologically active and corrosion-proof characteristics.

CONCLUSION

The effect of the time of mechanochemical processing and the mass of reaction mixture on the degree of transformation of substituted benzoic acids in a mixture with polyethylene glycol into ethoxylated products has been studied by means of IR spectroscopy and acid-base potentiometric titration. An increase in the time of mechanochemical processing and a decrease in the mass of reaction mixture cause an increase in the yield of reaction products.

Higher reactivity in ethoxylation is characteristic of *ortho*-nitrobenzoic acid in comparison with *meta*-, *para*-derivatives and 3,5-dinitrobenzoic acid.

The effect of dissociation capacity (pK_a) of substituted benzoic acids on their reactivity in mechanochemical ethylation has been detected.

The solutions of sodium salts of benzoic acid ethoxylates exhibit stronger pronounced surfactant properties at the liquid – gas interface than polyethylene glycol solutions do.

Solid-phase ethoxylation of the derivatives of benzoic acids with polyethylene glycol leads to the formation of a mixture of surfactants with different adsorption mechanisms at the aqueous solution – air interface, which may be of practical significance for formulating surfactant compositions possessing biologically active and corrosion-proof properties.

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