Supramolecular catalytic systems in biomimetic oxidation

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Oxidation of alkylaromatic hydrocarbons and benzene with hydrogen peroxide was studied under homogeneous and heterophase conditions. The catalytic systems contained the transition metal complex and salt along with the phase-transfer catalysts of different nature (micelle-forming surfactants, compounds containing a substrate in the polymer globule, macromolecules capable of forming host—guest complexes) and cosolvents. This substantially enhanced the yield of the oxidation product and selectivity of the process compared to the classical systems of hydrocarbon oxidation with hydrogen peroxide.

Key words: supramolecular catalytic systems, biomimetic oxidation, alkylbenzenes, benzene, ethylbenzene, tetralin, metal complex catalysts, surfactants, polyethylene glycol, β-cyclodextrin, host—guest complexes, hydrogen peroxide.

Introduction

The development of new highly efficient catalysts for hydrocarbon oxidation is a very important direction of modern catalysis. Despite considerable progress in this area, only few examples are known for catalytic systems that could oxidize alkanes and alkylaromatic compounds selectively and with high rate.[1—3] At the same time, in cells of bacteria, algae, and animals and in the human organism these substrates are oxidized by air oxygen in quantitative yield and with high rates due to catalysis by enzymes.[4] Therefore, one of the most promising routes for the development of catalysts for oxidation is the biomimetic approach, *i.e.*, development of chemical analogs of natural enzymes.

Monooxygenases activating molecular oxygen to form oxo- and peroxometal complexes should first be distinguished among the enzymes that can efficiently catalyze hydrocarbon oxidation.[5] When studying models of these enzymes, the most attention was given to the family of cytochrome P450 containing the heme (porphyrin iron complex), because they are highly active in reactions with a wide set of organic substrates.[6—8] Interest in a wide family of non-heme monooxygenases that catalyze the oxidation of C—H bonds in aliphatic and aromatic fragments of organic molecules has recently increased.[5,9—12] These are iron-containing enzymes of the type of ω-hydroxylases that promote selective hydroxylation of the methyl group in *n*-alkyl chains of various compounds[5,13] as well as enzymes containing the binuclear active centers, such as methane monooxygenases or toluene monooxygenases.[5,9—15] It should be mentioned that methane monooxygenases can oxidize even inert methane[13] to methanol, and toluene monooxygenases T2MO, T3MO, and T4MO can catalyze the selective oxidation of toluene to *o*-, *m*-, and *p*-cresols without oxidizing the substituent at the aromatic ring.[9,15]

The simulation of the behavior of metal-containing enzymes capable of transforming hydrocarbons into oxygen-containing compounds assumes, as a rule, the use of ligands of complicated structure that model the structure of the metal center of the natural catalyst.[1,16—29] At the same time, it has been known long ago that the secondary and tertiary structure of an enzyme molecule predetermining the selective binding of the substrate and stabilization of the transition state of the reaction is substantial for the development of highly active catalysts.[20,21] For instance, methane oxygenase and enzymes of the superfamily of cytochrome P450 contain in their structure, in addition to the active metal center, a hydrophobic "package" favoring binding and subsequent selective functionalization of hydrocarbon.[14] That is why the realization of the biomimetic approach needs special attention to be paid to investigations of supramolecular interactions between the ligand and substrate. This modeling is possible, in particular, when the catalytic systems used involve substances that form, under the reaction conditions, unique "nanoreactors": micelle-forming surfactants, water-soluble polymers, and compounds capable of forming host—guest complexes in solutions.

Compounds possessing surface activity in aqueous solutions can be used as components of the catalytic system: various quaternary ammonium and sulfonium salts, such as cetyltrimethylammonium bromide (CTMAB), tetra-

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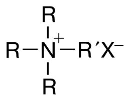
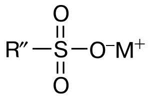
ethylammonium bromide (TEAB), triethylbenzylammonium chloride (TEBAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium chloride (TBAC), sodium dodecyl sulfate, sodium hexadecyl sulfate, potassium hexadecylbenzenesulfonate, and sodium dodecylbenzenesulfonate. For this group of substances, changes in the oxidation rate are achieved, as a rule, due to the solubilization of the metal center and the substrate itself in aggregates or micelles of surfactants at different concentrations of the latter.[22—25]



R_4N^+: $R-\overset{R}{\underset{R}{N^+}}-R'X^-$

	R	R′	X
CTMAB	Me	$C_{16}H_{33}$	Br
TEBAC	Et	Bn	Cl
TBAI	Bu	Bu	I
TEAB	Et	Et	Br
TBAI	Bu	Bu	I
TBAC	Bu	Bu	Cl



$R''-\overset{O}{\underset{O}{S}}-O^-M^+$

	R″	M
Sodium dodecyl sulfate	$C_{12}H_{25}O$	Na
Sodium hexadecyl sulfate	$C_{16}H_{33}O$	Na
Sodium dodecylbenzenesulfonate	$4-C_{12}H_{25}C_6H_4$	Na
Potassium hexadecylbenzenesulfonate	$4-C_{16}H_{33}C_6H_4$	K

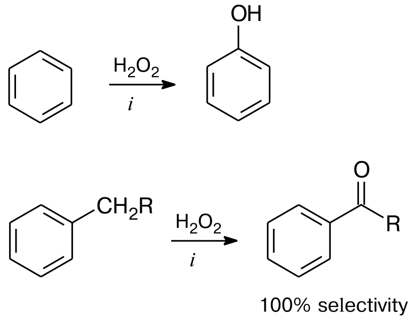
When soluble polymers are used as components of the catalytic system, the oxidation rate can increase if the reaction proceeds in the polymer globule where the substrate is concentrated.[1,26—28] Such polymers are polyethylene glycol (PEG) of different molecular weight and its ethers (REOH), block copolymers of polyethylene oxide and polypropylene oxide (RPEOH and REPOH), and analogous terminally modified polymers.[29,30]

Compounds capable of forming host—guest complexes are of special interest for the construction of enzyme models. The presence of a hydrophobic cavity in these molecules favors the formation of stable complexes with nonpolar substrates. These compounds are exemplified by the macrocyclic receptors cyclodextrins (CD). β-Cyclodextrin is a macrocyclic organic compound consisting of seven D-glucopyranose fragments bound through 1,4-bonds. Seven primary OH groups arranged around one edge of the cone and fourteen secondary OH groups localized around another edge form the polar environment of the molecule. The C—H bonds oriented inside the inner cavity make the latter nonpolar, which allows it to form host—guest inclusion complexes with nonpolar molecules of alkylaromatic compounds.

Note that the use of just these molecules allows one to attain unique selectivity of oxidation. For example, the high selectivity of steroid oxidation using the manganese complexes with specially synthesized porphyrin-containing cyclodextrins was observed.[31—33] The use of the ruthenium complexes with porphyrins modified by the cyclodextrin-containing fragments substantially enhances the selectivity of β-carotene oxidation.[34—36] For this group of catalysts, an increase in the reaction rate and a change in the selectivity can be achieved due to the "pre-orientation" of the substrate in the activated complex that formed.

To develop catalysts for the oxidation of aromatic and alkylaromatic compounds, we used all the three above mentioned approaches. The catalytic systems containing the iron compound and a source of active oxygen (hydrogen peroxide) were chosen as simplest functional models of enzymes. The main attention was given to benzene and ethylbenzene as model substrates. In the first case, we studied a possibility of selective introduction of the hydroxy group into the aromatic fragment of the substrate, and a possibility of selective oxidation of the alkyl chain without oxidizing the aromatic fragment itself was examined in the second case (Scheme 1).

Scheme 1



i. Metal complex catalyst

1. Oxidation of benzene and ethylbenzene with hydrogen peroxide in the biphase system using ionogenic surfactants

We showed that for the oxidation of benzene and ethylbenzene with hydrogen peroxide the use of surfactants, such as various quaternary ammonium and sulfonium salts, made it possible to substantially increase the reaction rate and prevent the subsequent oxidation of the formed reaction products. For instance, for ethylbenzene oxidation catalyzed by the iron salts the addition of a surfactant to the biphase system increases the turnover number of the reaction by 2—3 times, whereas for benzene hydroxylation the increase is 3—10 times.[37—44]

The activity of the catalytic systems depended substantially on the surfactant structure. A considerable efficiency was manifested by the catalysts including the cat-

Table 1. Ethylbenzene oxidation with hydrogen peroxide using various phase-transfer catalysts[33]

Entry	Phase-transfer catalyst	Yield of acetophenone (%)	TOF[a]
1	—	4—5	249
2	CTMAB	20	996
3	CTMAB[b]	38	200
4	TEBAC	15	735
5	TBAI	9.5	474
6	TEAB	9	438
7	Sodium dodecyl sulfate	16	798

Note. Reaction conditions: 65 °C, reaction time 20 min, phase-transfer catalyst concentration 9.16 mmol L^{-1}, $[PhC_2H_5]$ = 0.256 mol L^{-1}, $[H_2O_2]$ = 0.253 mol L^{-1}, $[Fe^{3+}]$ = 15.4 mmol L^{-1}.

[a] TOF is 1 mole of acetophenone/ 1 mole of Fe per 1 h.

[b] $[PhC_2H_5]$ = 0.051 mol L^{-1}.

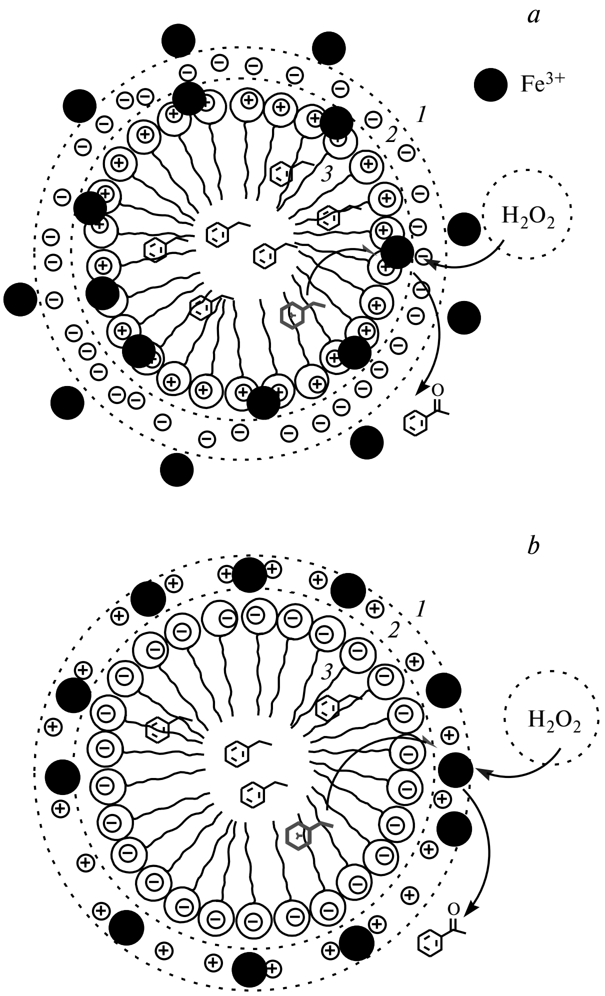


Fig. 1. Scheme of a micelle of the ionogenic surfactant in water: *a*, quaternary ammonium salt; *b*, anionic surfactant; *1,* Stern layer; *2*, Gouy—Chapman layer; *3*, hydrocarbon core of the micelle.

ionic surfactants, and the anionic surfactants have somewhat lower activity. The highest yields of the reaction products were attained when the hydrophobic hydrocarbon chain of a surfactant molecule was rather long. Among micelle-forming surfactants, the systems containing cetyltrimethylammonium bromide were the most efficient (Tables 1 and 2).[40,41,44]

The rate increase can be explained by the fact that the reaction proceeds under the conditions of micellar catalysis. It is known[44,45] that the considered ammonium and sulfonium salts present in solutions in amount above the critical micelle concentration (CMC) can form micelles inside which the nonpolar fragments are localized and the surface contains the charged surfactant groups (Fig. 1). Nonpolar alkylaromatic compounds are solubilized in the micelle core and on the micellar surface, enhancing their local concentration in water. In this case, the reaction occurs in the Gouy—Chapman layer, where near the double electrical layer the micelles absorb the charged iron ions.[45—48] This was confirmed by us using spectrophotometry.[40]

Table 2. Benzene hydroxylation with hydrogen peroxide in the presence of the $Fe(NO_3)_3 \cdot 9H_2O$—surfactant catalyst

Entry	Surfactant	Yield of phenol (wt.%)	TOF
1	—	10	30
2	CTMAB	80	240
3	TBAB	30	90
4	TBAC	35	105
5	TBAI	38	114
6	TEBAC	70	210
7	TEAI	27	81
8	Sodium hexadecyl sulfate	35	105
9	Potassium hexadecylbenzenesulfonate	48	144

Note. Reaction conditions: 50 °C, $[Fe(NO_3)_3 \cdot 9H_2O] = 3.35 \cdot 10^3$ mol L^{-1}, $[H_2O_2]$ = 1.0 mol L^{-1}, $[C_6H_6]$ = 1.0 mol L^{-1}, reaction time 3 h, $H_2O_2 : C_6H_6 : Fe(NO_3)_3 \cdot 9H_2O$: Surf = 300 : 300 : 1 : 2.5 (see Refs 29 and 30).

It is most likely that precisely in this site the metal ions interact with the main part of hydrogen peroxide to form particles active in oxidation. Since the capacity of micelles and their homogeneity increase with an increase in the hydrophobic part of the molecule, just for these surfactants (CTMAB, TEBAC, sodium dodecyl sulfate, sulfanol, sodium hexadecyl sulfate, sodium dodecylbenzenesulfonate) the effect of rate increasing due to the occurrence of the reactions in micelles is very pronounced. Most probably, benzene is concentrated in the surface layer of the micelle where oxidation occurs, and ethylbenzene is localized closer to the micelle core. Thus, the rate of oxidation of the first substrate is substantially higher.[49]

The dependences of the rate and yield of the reaction products of benzene hydroxylation and ethylbenzene oxidation were found to be resembling to a great extent and can easily be explained by the occurrence of the process in micelles.[40,41,43] For benzene hydroxylation and ethylbenzene oxidation, there is an optimum concentration of the metal ions and surfactant, which corresponds to the ratio of the concentrations of the phase-transfer catalyst (PTC) and Fe^{3+} salt in a range of 1.5—2. It is most likely that with an increase in the concentration of the Fe^{3+} salt the yield of the reaction product increases until virtually all iron ions are adsorbed near the double electrical layer. The efficiency of the use of hydrogen peroxide is substantially enhanced. When all vacant sites in the Gouy—Chapman layer are occupied, some metal ions are also arranged in the solvent bulk, which leads to the nonproductive decomposition of hydrogen peroxide and, hence, to a decrease in the product yield and efficiency of the catalytic system.

The dependence of the reaction rate on the substrate concentration is related to a peculiar "saturation" of the micellar phase with the substrate. With an increase in the latter beginning from some value (500 mmol L^{-1}), the initial rate of product formation decreases gradually (Fig. 2).[40,41,43]

For all micelle-forming surfactants used in the reactions of benzene and ethylbenzene oxidation, the dependence of the yields of the oxidation products on the amount of the surfactant introduced into the system has a slightly extreme character (Figs 3 and 4).[38—42,44] The maximum oxidation rate is observed near the CMC of sodium dodecyl sulfate (8.3 mmol L^{-1} according to published data[50]) and then decreases sharply, which is due, most likely, to an increase in the micelle size with an increase in the concentration of this surfactant.[51] For CTMAB the increase in the reaction rates is observed with an increase in the surfactant concentration above CMC (~1 mmol L^{-1}) up to 10 mmol L^{-1}. Under the reaction conditions for CTMAB, no sharp increase in the micelle size is observed in this concentration interval and only their number increases.[50,51] The further increase in the concentration changes the shape of the micelles, which impedes, most likely, the oxidation process.[52]

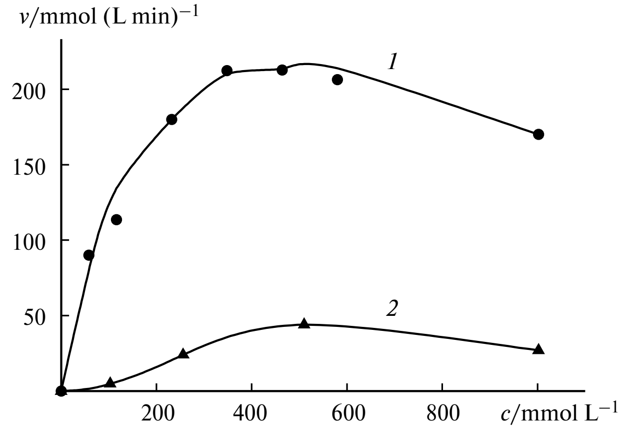


Fig. 2. Dependence of the rate (*v*) of formation of the reaction products (acetophenone and phenol) on the substrate concentration (*c*). Conditions: *1*, ethylbenzene, 60 °C, [CTMAB] = 9.16 mmol L^{-1}, $[H_2O_2]$ = 2.53 mol L^{-1}, $[Fe^{3+}]$ = 15.5 mmol L^{-1}; *2*, benzene, 50 °C, [CTMAB] = 9.16 mmol L^{-1}, $[H_2O_2]$ = 2.6 mol L^{-1}, $[Fe^{3+}]$ = 4.5 mmol L^{-1}.

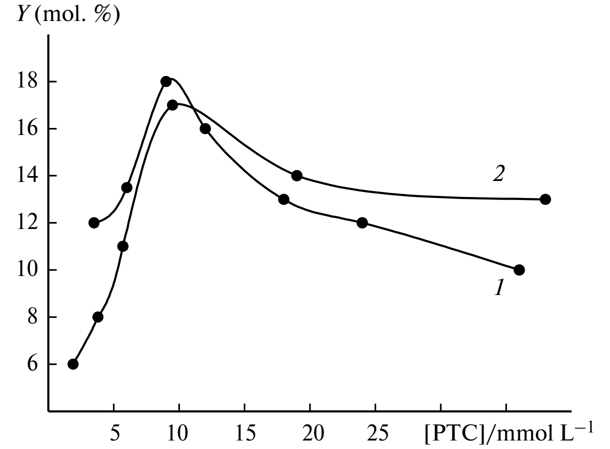


Fig. 3. Ethylbenzene oxidation at various concentrations of sodium dodecyl sulfate (*1*) and CTMAB (*2*). *Y* is the yield of acetophenone. Conditions: reaction time 1 h, 65 °C, $[PhC_2H_5]$ = 0.256 mol L^{-1}, $[H_2O_2]$ = 0.253 mol L^{-1}, $[Fe^{3+}]$ = 15.4 mmol L^{-1}.

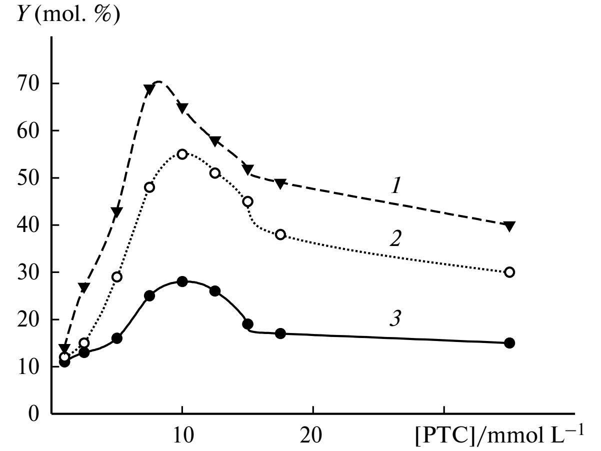
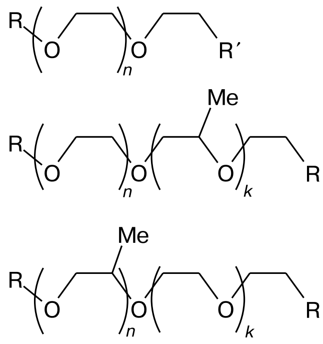


Fig. 4. Plots of the yield of phenol (*Y*) *vs.* surfactant concentration for benzene hydroxylation by hydrogen peroxide in a heterophase system in the presence of Fe^{III}—CTMAB (*1*), Fe^{III}—BTEAC (*2*), Fe^{III}—TBAC (*3*); $H_2O_2 : C_6H_6 = 2 : 1$; $[C_6H_6]$ = 1.0 mol L^{-1}, $[Fe(NO_3)_3 \cdot 9H_2O]$ = 4.5 mmol L^{-1}, 50 °C.

Similar effects were observed for the hydroxylation with hydrogen peroxide of several other substrates: anisole, benzoic acid, and others, which confirms the general character of the regularities found by us.[53,54]

2. Oxidation of benzene and ethylbenzene with hydrogen peroxide using water-soluble polyethers as components of catalytic systems

Water-soluble polymers capable of including a substrate molecule into the polymeric globule can be an alternative to ionogenic surfactants when the reaction occurs in the biphase system.



	R	R′
PEG	H	OH
REOH	Pr^n	OH
RE-acac	Pr^n	acac
REPOH	Pr^n	acac
REP-acac	Pr^n	OH
RPE-acac	Pr^n	acac

Water-soluble polymers can represent "monomolecular" aggregates in the case of high weights of the polymer or aggregates of several polyethylene oxide molecules. In particular, for PEG-400 the onset of this process is observed at concentrations higher than 0.2 mol L^{-1} (see Refs 55 and 56). In this case, a considerable portion of ethylbenzene molecules is localized inside polymeric balls, where the Fe^{3+} ions are "immobilized" due to the interaction with the oxygen atoms. Thus, the particles active in oxidation are formed in the immediate vicinity of the substrate, favoring an increase in the reaction rate.

For ethylbenzene oxidation in the biphase medium for 2.5 h, the addition of catalytic amounts of polyethylene oxide or its ethers leaded to only a slight increase in the acetophenone yield: up to 11% (Table 3). At the same time, in the hydroxylation of benzene, whose polarity is somewhat higher, the phenol yields reached 50% but only when using high-molecular-weight polyethers (PEG-12 000 and PEG-40 000) capable of forming monomolecular polymeric aggregates in solution.[41,42—44]

Table 3. Oxidation of benzene and ethylbenzene with hydrogen peroxide at 65 °C in a water—substrate biphase system in the presence of polyethylene glycol and its ethers

Entry	Water-soluble polymer	Yield of phenol (%)	Yield of acetophenone (%)
1	PEG-400	11	1
2	PEG-1500	16	3
3	PEG-12000	30	6
4	PEG-40000	49	11
5	PEG-succinate	25	10
6	PEG-adipinate	32	9
7	PEG-monolaurylate	36	9

Note. Reaction conditions: reaction time 150 min, polymer concentration 0.09 mmol L^{-1}, [Substrate] = 0.256 mol L^{-1}, $[H_2O_2]$ = 0.253 mol L^{-1}, $[Fe^{3+}]$ = 15.4 mmol L^{-1}.

In ethylbenzene oxidation a similar effect was observed at high concentrations of polyethylene oxide (~0.3 mol L^{-1} based on one ethylene glycol unit),[44] which corresponds to the concentration of aggregate formation even for low-molecular-weight polymers of this nature. The yield increased with an increase in the molecular weight of the polymer and reached 20% already within 10 min. It has been shown that the elongation of the reaction time to 2 h allows one to achieve, in this case, only a slight increase in conversion because of catalyst deactivation. The replacement of the iron salt by the iron complex with 2,2′-dipyridine increases the yield of acetophenone to 84% for 2 h.

It should be mentioned that the ability to solubilization of organic compounds by aggregates of polyethylene oxide molecules can change substantially when using a cosolvent capable of good mixing with water.[57] The addition of 30 mol.% acetonitrile to water was shown to result in a sharp increase in the acetophenone yield. In hydrogen peroxide excess the transformation of ethylbenzene into acetophenone was 75% already for 15 min of the reaction. It is essential that the maximum activity of the system was reached at 50 mol.% cosolvent, and a polymer additive made it possible to enhance the product yield at any acetonitrile to water ratio (Fig. 5). The effect of increasing the product yield was also observed for benzene hydroxylation, although it was much less pronounced.

This result can be explained by specific features of structure formation of water—acetonitrile mixtures. The X-ray diffraction and IR spectroscopic studies showed that this mixture is not truly homogeneous at the microlevel in the whole concentration interval.[58,59] For ex-

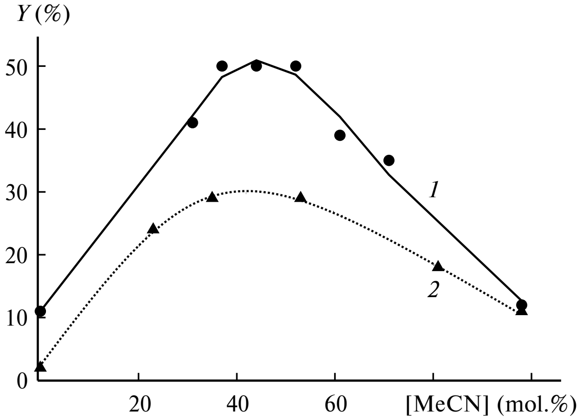


Fig. 5. Plots of the acetophenone yield (*Y*) *vs.* acetonitrile to water ratio for ethylbenzene oxidation in the presence of PEG (*1*) and without PEG (*2*). Conditions: 65 °C, reaction time 1 h, [PhEt] = 0.256 mol L^{-1}, $[H_2O_2]$ = 0.253 mol L^{-1}, $[Fe^{3+}]$ = 15.4 mmol L^{-1}, [PEG] = 0.09 mmol L^{-1} (see Ref. 31).

ample, at the acetonitrile content in the mixture higher than 80 mol.% its molecules form clusters due to dipole-dipole interactions and the water molecules localized near these clusters form hydrogen bonds with acetonitrile. When the acetonitrile content in the mixture ranges from 20 to 80%, its molecules, as well as the water molecules, form small clusters alternating with each other, and only at the water content higher than 80% the acetonitrile molecules are surrounded by the water molecules to form a true solution. A polyethylene oxide molecule capable of coordinating the iron ions acts, most likely, as a unique microreactor and includes first the acetonitrile and substrate molecule, which increases the concentration of the latter near the active center due to the optimization of the polarity of the medium. The solubilization of acetonitrile can substantially increase the size of the polymeric ball itself, which enhances, in turn, accessibility of the substrate for an oxidant. The latter assumption is confirmed by published data,[60] according to which for polyethylene oxide in water—acetonitrile mixtures the size of the monomolecular "balls" is maximum at the molar concentration of acetonitrile ~50%. At higher acetonitrile concentrations, a portion of the substrate exists in solution, which decreases the oxidation rate.

It should be emphasized that the effect of PEG on ethylbenzene oxidation, as in the case of the biphase system without acetonitrile, differed depending on its molecular weight (Table 4).

The rate increase is observed for PEG with the number of monomeric units more than 25. A molecule of PEG-400 containing only nine monomeric units is small and its polymeric ball does not incorporate a substrate molecule, and the substance concentration is insufficient for its aggregation. The use of longer PEG molecules (with a chain length of 30—450 monomeric units) made it possible to increase the acetophenone yield by 1.5 times. The catalytic systems containing PEG with a molecular weight of 35 000 or 40 000 (750—900 monomeric units) exhibited the highest activity.[27,42—44] In the case of benzene, this effect is much less pronounced (the increase is observed only on going to PEG-1500), which is due, most likely, to a substantially higher polarity of the substrate and its higher solubility in water—acetonitrile mixtures.

Table 4. Yields of acetophenone and phenol using PEG of various weight and their ethers in a water—acetonitrile (50 mol.%) mixture on ethylbenzene and benzene oxidation

Entry	Polymer	Average number of PEG units	Yield of acetophenone (%)	Yield of phenol(%)
1	PEG-400	9	30	13
2	PEG-1500	25	44	18
3	PEG-20000	450	43	20
4	PEG-35000	750	50	21
5	PEG-40000	900	50	21

Note. Reaction conditions: 65 °C, reaction time 1 h, $[PhC_2H_5]$ = 0.256 mol L^{-1}, $[H_2O_2]$ = 0.253 mol L^{-1}, $[Fe^{3+}]$ = 15.4 mmol L^{-1}, [PEG-35000] = 0.09 mmol L^{-1}.

Table 5. Yield of the oxidation products of ethylbenzene with hydrogen peroxide

Catalyst	Yield of products (%)	
	Acetophenone	1-Phenylethanol
PEG-1500 ($HOE_{61}OH$)/acacH/Fe^{3+}*	40	2
Fe^{3+}—acac-E_{61}-acac—Fe^{3+}	71	2
$RE_{88}P_{22}OH$/acacH/Fe^{3+}*	17	1
$RE_{88}P_{22}$acac-Fe^{3+}	37	<1

Note. Reaction conditions: 75 °C, [PhEt] = 0.36 mol L^{-1}, $[H_2O_2]$ = 0.93 mol L^{-1}, $[Fe^{III}]$ = 3.6 mmol L^{-1}, MeCN : H_2O = 3.5 : 1 v/v (56 mol.% MeCN).

* Non-modified polymer—iron salt—ligand mixture.

Another route for increasing the activity of the catalysts based on polyethylene oxides can be the immobilization of an active center directly on a macromolecule.[61—63] For instance, the iron(III) complexes based on terminally acetylacetone-functionalized polyethylene oxide and monobutyl ethers of block copolymers of ethylene oxide and propylene oxide showed substantially higher activities than the corresponding mixed systems (Table 5).

Note that the unification of the polymer and metal complex in the same molecule is very efficient for the development of catalysts for benzene and phenol hydroxylation (Table 6).[64,65] The catalysts based on the complexes with modified polyethers are more active than mixtures of the corresponding polymer, pyrocatechol, and iron(III) salt.

Table 6. Yields of the hydroxylation products of benzene with hydrogen peroxide involving the pyrocatechol iron macrocomplexes and their mixture analogs

Catalyst	Yield of products (%)		
	Phenol	Hydroquinone	Pyrocatechol
$RE_{67}OH$+pyrocatechol+Fe^{3+}*	17	2	3
RE_{67}-cat—Fe^{3+}	30	2	5
$RE_{54}P_{10}OH$+pyrocatechol+Fe^{3+}*	8	1	1
$RE_{54}P_{10}$-cat—Fe^{3+}	20	2	4
$RP_{10}E_{54}OH$+pyrocatechol+Fe^{3+}*	9	1	2
$RP_{10}E_{54}$-cat—Fe^{3+}	16	1	3
$RE_{40}P_{20}OH$+pyrocatechol+Fe^{3+}*	5	Traces	Traces
$RE_{40}P_{20}$-cat—Fe^{3+}	14	1	2
$RP_{20}E_{40}OH$+pyrocatechol+Fe^{3+}*	4	Traces	Traces
$RP_{20}E_{40}$-cat—Fe^{3+}	8	1	3

Note. Reaction conditions: 50 °C, reaction time 60 min.

* Non-modified polymer—pyrocatechol—$FeCl_3$ mixture.

This can also be attributed to the fact that the active centers of the macrocomplexes are localized in the polymeric balls where the benzene concentration is higher than in the solution. For mixed systems, some active centers are arranged outside the polymeric associates, due to which the active centers are less accessible for the substrate.

3. Oxidation of ethylbenzene and benzene with hydrogen peroxide using the cyclodextrin-based catalytic systems

The biphase catalytic systems containing, in addition to the transition metal ion, compounds capable of forming host—guest inclusion complexes, such as cyclodextrins, turned out to be efficient in benzene and ethylbenzene oxidation.[2,66,67]

Since the solubility of β-cyclodextrin in water is low, we used polyhydroxyethylated cyclodextrins and hydroxypropylcyclodextrins as components of the catalytic system. In this case, the modification of the receptor molecule makes it possible to increase the solubility in water of the receptor itself and its inclusion complexes. In addition, we used acetylated with the protocatechic acid residue β-cyclodextrin as a ligand (β-CD-Cat).

The use of the catalytic systems based on receptor molecules made it possible to substantially increase the oxidation rate under the biphase conditions in the case of both benzene and ethylbenzene (Table 7).

The high yields of phenols in benzene hydroxylation were observed for the use of the catalytic system containing the iron(III) salt and hydroxyethylated cyclodextrin.

The use of β-cyclodextrin acylated with protocatechic acid residue as a ligand made it possible to obtain pyrocatechol directly from benzene, and the selectivity with respect to the latter exceeded 85% (see Refs 2, 64, and 65).

This difference in the behavior of the modified cyclodextrins can be explained as follows: phenol formed by the hydroxylation in the presence of the β-CD-Cat complex with iron is coordinated on the metal ion and remains in the cyclodextrin cavity. In this case, the stability constant of the complex with phenol is substantially higher than that of the complex with benzene.[2,65] Its further oxidation affords pyrocatechol due to the accessibility of the *ortho*-position of the substrate for the attack from the active particle. This assumption is confirmed by the results on benzene oxidation with hydrogen peroxide. The predominant formation of the *ortho*-hydroxylation product is observed at the high conversion of the substrate.[2]

The use of the catalytic systems containing β-cyclodextrins in ethylbenzene oxidation provides the acetophenone yields close to quantitative (Table 8). For example, upon ethylbenzene oxidation in the presence of ethoxyethylated β-cyclodextrin and the iron(III) salt for 4 h the yield of acetophenone was higher than 90% and acetophenone remained to be the single reaction product. As in the case of using polyethers, the catalytic system containing, along with the receptor, 2,2´-dipyridine as a ligand stabilizing the iron(III) ions in solution manifested the highest activity.

For instance, for ethylbenzene oxidation in the presence of the ethoxylated β-cyclodextrin—2,2´-dipyridine—Fe^{3+} system, the quantitative yield of acetophenone was reached 2 h after the onset of the reaction, whereas in the absence of 2,2´-dipyridine this yield was attained only after 4 h (see Table 8).

It should be noted that, unlike the process in a water—acetonitrile mixture, the problem of the recycling of

Table 7. Hydroxylation of benzene and phenol using the iron(III) complexes with cyclodextrins

Substrate	Catalytic system	Yields (%)		
		Phenol	Pyrocatechol	Hydroquinone
Benzene	Ethoxylated β-cyclodextrin/Fe^{3+}	75	—	1
	β-Cyclodextrin modified by pyrocatechol (CD-cat)/Fe^{3+}	8	18	3
Phenol	Ethoxylated β-cyclodextrin/Fe^{3+}	—	8	43
	β-Cyclodextrin modified by pyrocatechol (CD-cat)/Fe^{3+}	—	80	6

Table 8. Oxidation of ethylbenzene with hydrogen peroxide in a water—substrate system in the presence of ethoxylated β-cyclodextrin

Ligand	τ/min	Yield of acetophenone (mol.%)
Ethoxylated β-cyclodextrin	20	27
	240	98
Ethoxylated β-cyclodextrin/2,2´-dipyridine	20	40 37*
Ethoxylated β-cyclodextrin/2,2´-dipyridine	120	97 93*
2,6-Hydroxypropyl β-cyclodextrin	20	21
2,6-Hydroxypropyl β-cyclodextrin/2,2´-dipyridine	20	30

Note. Reaction conditions: 65 °C, concentration of macromolecules 40 mmol L^{-1}, [PhEt] = 0.273 mol L^{-1}, [H_2O_2] = 0.253 mol L^{-1}, [Fe^{3+}] = 5.4 mmol L^{-1}.

* Repeated use of the catalytic system.

Table 9. Oxidation of alkylaromatic compounds with hydrogen peroxide in various catalytic systems

Substrate	Reaction products	Yield of reaction products (%)			
		Substrate—water system		Water—acetonitrile medium[c]	
		CTMAB[a]	Ethoxylated β-cyclodextrin—2,2′-dipyridine—Fe^{3+} [b]	—	PEG-35000
Toluene	Benzoic acid,	20	50	50	58
	Benzaldehyde	Traces			
n-Propylbenzene	PhC(O)Et	8	55	15	15
Isopropylbenzene	PhC(OH)Me_2	Traces	Traces	3	3
tert-Butylbenzene	—	Traces	Traces	Traces	Traces
n-Amylbenzene	PhC(O)Bu	4—5	55	14	14
p-Diethylbenzene	4-EtC_6H_4C(O)Me	10	50	22	19
	4-MeC(O)C_6H_4C(O)Me	1-2	50	6	10
Tetralin	Tetralone	11	45	14	65
	Diketotetralin		15		

Note. Reaction conditions: substrate concentration 0.25 mmol L^{-1}, [H_2O_2] = 0.253 mmol L^{-1}.

[a] [Fe^{3+}] = 15.4 mmol L^{-1}, [CTMAB] = 9.16 mmol L^{-1}, 75 °C, reaction time 1 h.

[b] Concentration of catalyst macromolecules 40 mmol L^{-1}, substrate concentration 0.25 mmol L^{-1}, [H_2O_2] = 0.253 mmol L^{-1}, [Fe^{3+}] = 5.4 mmol L^{-1}, 65 °C, reaction time 20 min.

[c] Substrate concentration 0.25 mmol L^{-1}, [H_2O_2] = 0.253 mmol L^{-1}, [Fe^{3+}] = 15.4 mmol L^{-1}, MeCN : H_2O = 2 : 1, 65 °C, reaction time 15 min.

the catalyst can be solved when the reaction is carried out in the biphase system and ethoxylated β-cyclodextrin is used. The aqueous phase containing the metal complex can be used mutiply without substantial loss of the catalytic activity.

It should specially be emphasized that the catalytic system containing cyclodextrins demonstrated advantages over other catalytic systems used by us and allowed the oxidation of several alkylaromatic compounds (1,4-diethylbenzene, *n*-propylbenzene, *n*-amylbenzene, isopropylbenzene, *tert*-butylbenzene, tetralin, and toluene) to be carried out in the biphase system (Table 9).[44] In the case of toluene, benzoic acid was formed, and the corresponding phenones were the major products in the case of the higher homologs. It should be noted that in the oxidation of isopropyl- and *sec*-butylbenzenes the yields of the reaction products were very low even for the most active systems, indicating in favor of the nonradical reaction mechanism.

The non-radical character of the reacting particles is also indicated by the fact that when ethylbenzene is oxidized in the absence of the iron salts under UV irradiation, *i.e.*, under conditions of generation of $OH^{\bullet}$ radicals from hydrogen peroxide, the yield of acetophenone did not exceed 1%.

Different mechanisms of transport by catalytic systems of a nonpolar organic substrate to the polar aqueous medium determined different efficiencies of the used catalytic systems. For instance, the catalytic system consisting of ethoxylated β-cyclodextrin and the 2,2′-dipyridine complex of Fe^{3+} turned out to be the most efficient in the oxidation of almost all tested alkylaromatic compounds (except for toluene) due to high stability constants of the corresponding host—guest complexes.[68] In propylbenzene oxidation propiophenone was formed for 20 min in a yield higher than 20%, and for 2 h the yield was 55%; the oxidation of *n*-amylbenzene afforded valerophenone in ~25% yield, whereas for 2 h the yield was 55%; in tetralin oxidation the yield of tetralone for 2 h was more than 50% and the diethylbenzene conversion was close to 100% (see Table 9). The use of the quaternary ammonium salts as phase-transfer catalysts made it possible to increase the yields of the oxidation products in a water—substrate biphase system only for the lower homologs. For example, when CTMAB is used, the yield of acetophenone in ethylbenzene oxidation can be increased to 20%; however, for propylbenzene oxidation the yield of ketone did not exceed 9%, whereas the yield of butyl phenyl ketone in *n*-amylbenzene oxidation remained to be trace.

Probably, alkylaromatic molecules with a sufficiently long nonpolar fragment are arranged in the micelle core rather than near the surface where they can be oxidized.

Note that two products were formed in the case of toluene oxidation and when using the systems based on cyclodextrin: benzoic acid and benzaldehyde, and the selectivity with respect to aldehyde depended on the catalyst used (Table 10).[33]

In the most cases, acid was the major reaction product, because the aldehyde that formed is very rapidly oxidized to the acid. The high selectivity with respect to

Table 10. Oxidation of toluene with hydrogen peroxide using various catalytic systems

Catalytic system	Conversion (%)	Selectivity (%)	
		PhCHO	PhCOOH
Fe^{3+}/dipy	<3	—	—
Fe^{3+}/dipy/CD-(EO)$_n$, n = 3—5	20	1	99
Fe^{3+}/dipy/CD-(EO)$_n$, n = 6—10	42	50	50
V^{5+}/dipy/CD-(EO)$_n$, n = 6—10	75	36	64
V^{5+}/dipy/CD-(EO)$_n$, n = 3—5	42	0	100

Note. Reaction conditions: 50 °C, reaction time 40 min, concentration of metal salt 7 mmol L^{-1}, concentration of 2,2´-dipyridyl 3.2 mmol L^{-1}, [CD-(EO)$_n$] = 5 mmol L^{-1}, [hydrogen peroxide] : [toluene] = 1 : 1.

aldehyde was observed only when the iron complex with 2,2´-dipyridine and cyclodextrin with the high extent of hydroxyethylation (from six to ten ethylene glycol units per one glucoside unit of β-cyclodextrin) were used. A decrease in this value decreased both the reaction rate and selectivity with respect to aldehyde. This selectivity retained when iron was replaced by another metal, for example, vanadium, whose complexes with 2,2´-dipyridine can activate hydrogen peroxide.

Conclusion

In the conclusion, we studied the catalytic systems including the transition metal ion and the compound capable of substrate transferring to the aqueous medium *via* different mechanisms in benzene and alkylaromatics oxygenation by hydrogen peroxide. The proposed catalysts can be considered as simplest models of the redox enzymes combining a metal and a component responsible for concentrating and binding of the substrate. The nature of the second component, which determines the mechanism of substrate transport to the aqueous medium and its orientation relative to the metal center, exerts a substantial effect on the yield of the reaction products and selectivity. The best results were obtained when using β-cyclodextrins capable of forming host—guest inclusion complexes as components of the catalytic system. This makes it possible to model successfully the interaction between the enzyme and substrate. Both the high selectivity of the reaction with respect to the target product and high activity of the catalysts are achieved due to the high stability of the corresponding complexes. Note that this approach can also be used for the modification of metal complex systems that are unknown in nature but very important for the syntheses of products in real chemical processes applied in industry, *e.g.*, hydroformylation, Wacker process, and hydrogenation.[69—73] The catalysts based on metal complexes with modified cyclodextrins allow one to perform reactions with hydrophobic substrates in aqueous media without activity loss. Further development of this series of investigation assumes to use methods of self-assembling based on principles of molecular imprinting for the synthesis of the macroligand.[74,75]

References

1. E. Karakhanov and A. Maximov, *Catalysis by Soluble Macromolecule Metal Complexes*, in *Metal Complexes and Metals in Macromolecules*, Eds D. Wohrle and A. Pomogajlo, Wiley-VCH, 2003, 457.
2. E. A. Karakhanov, L. M. Karapetyan, Yu. S. Kardasheva, A. L. Maksimov, E. A. Runova, V. A. Skorkin, and M. V. Terenina, *Macromol. Symp.*, Ed. R. Barbucci, F. Ciardelli, and G. Ruggeri, 2006, **235**, 39.
3. E. A. Karakhanov, A. L. Maksimov, and E. A. Runova, *Usp. Khim.*, 2005, **74**, 104 [*Russ. Chem. Rev.*, 2005, **74**, 97 (Engl. Transl.)].
4. R. Breslow, *Chem. Record*, 2001, **1**, 3.
5. E. I. Karasevich, V. S. Kulikova, A. E. Shilov, and A. A. Shteinman, *Usp. Khim.*, 1998, **67**, 376 [*Russ. Chem. Rev.*, 1998, **67**, 335 (Engl. Transl.)].
6. B. Meunier, S. P. de Visser, and S. Shaik, *Chem. Rev.*, 2004, **104**, 3947.
7. A. A. Shteim, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, **50**, 1712 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 1795].
8. I. G. Denisov, T. M. Makris, S. G. Sligar, and I. Schlichting, *Chem. Rev.*, 2005, **105**, 2253.
9. M. Costas, K. Chen, and L. Jr. Que, *Coord. Chem. Rev.*, 2000, **200—202**, 517.
10. J. W. Bradley and J. D. Lipscom, *Chem. Rev.*, 1996, **96**, 2625.
11. L. Jr. Que and R. Y. N. Ho, *Chem. Rev.*, 1996, **96**, 2607.
12. M. M. Abu-Omar, A. Loaiza, and N. Hontzeas, *Chem. Rev.*, 2005, **105**, 2227.
13. E. J. McKenna and M. J. Coon, *J. Biol. Chem.*, 1970, **245**, 3882.
14. A. A. Shteim, *Izv. Akad. Nauk*, *Ser. Khim.*, 1995, **44**, 1011 [*Russ. Chem. Bull.*, 1995, **44**, 975 (Engl. Transl.)].
15. M. H. Sazinsky, J. Bard, A. Di Donato, and S. J. Lippard, *J. Biol. Chem.*, 2004, **279**, 30600.
16. J. A. Labinger, *J. Mol. Cat. A: Chem.*, 2004, **220**, 27.
17. G. B. Shul´pin, *J. Mol. Cat. A: Chem.*, 2002, **189**, 39.
18. X. Shan and L. Jr. Que, *J. Inorg. Biochem.*, 2006, **100**, 421.
19. L. Westerheide, M. Pascaly, and B. Krebs, *Current Opinion in Chemical Biology*, 2000, **4**, 235.
20. K. N. Houk, A. G. Leach, S. P. Kim, and X. Zhang, *Angew. Chem.*, *Int. Ed.*, 2003, **42**, 4872.
21. A. Tousignant and J. N. Pelletier, *Chem. Biol.*, 2004, **11**, 1037.
22. U. Tonellato, *Pure Appl. Chem.*, 1998, **70**, 1961.
23. S. M. S. Chauhan, P. P. Mohapatra, Bh. Kalra, T. S. Kohli, and S. Satapathy, *J. Mol. Cat. A: Chem.*, 1996, **113**, 239.
24. J. H. M. Heijnen, V. G. de Bruijn, L. J. P. van den Broeke, and J. T. F. Keurentjes, *Chem. Eng. Processing*, 2003, **42**, 223.
25. A. Rabiona, R. M. Buchananb, J.-L. Serisc, and R. H. Fish, *J. Mol. Cat. A: Chem.*, 1997, **116**, 43.
26. E. A. Karakhanov, A. L. Maximov, T. Yu. Filippova, Y. S. Kardasheva, T. S. Buchneva, M. A. Gayevskiy, and A. Yu. Zhuchkova, *Polym. Adv. Tech.*, 2001, **12**, 161.

27. R. A. W. Johnstone, A. J. Simpson, and P. A. Stocks, *Chem. Commun.*, **199**7, 2277.
28. J. P. Collman, W. Fudickar, and I. Shiryaeva, *Inorg. Chem.*, 2003, **42**, 3384.
29. E. A. Karakhanov, Y. S. Kardasheva, A. V. Kirillov, A. L. Maximov, V. V. Predeina, and E. A. Runova, *Macromol. Symp.*, 2000, **156**, 137.
30. J Chen, S. K. Spear, J. G. Huddleston, and R. D. Rogers, *Green Chem.*, 2005, **7**, 64.
31. R. Breslow, J. Yang, and J. Yan, *Tetrahedron*, 2002, **58**, 653.
32. R. Breslow, J. Yang, and S. Belvedere, *Tetrahedron Lett.*, 2002, **43**, 363.
33. R. Breslow and Zh. Fang, *Tetrahedron Lett.*, 2002, **43**, 5197.
34. D. Woggon, *Chimia*, 2000, **54**, 564.
35. R. R. French, Ph. Holzer, M. Leuenberger, and W. D. Woggon, *Angew. Chem. Int. Ed.*, 2000, **39**, 1267.
36. R. R. French, Ph. Holzer, M. Leuenberger, M. C. Nold, and W. D. Woggon, *J. Inorg. Biochem.*, 2002, **88**, 295.
37. A. G. Dedov, S. M. Volkov, S. Yu. Narin, and E. A. Karakhanov, *Vestn. MGU*, *Ser. 2*, *Khim.*, 1985, 521 [*Vestn. Mosk. Univ.*, *Ser. Khim.*, 1985, 521 (Engl. Transl.)].
38. E. A. Karakhanov, S. Yu. Narin, V. A. Artemov, T. Yu. Filippova, and A. G. Dedov, *Neftekhimiya*, 1988, 352 [*Petroleum Chemistry*, 1988, 352 (Engl. Transl.)].
39. A. G. Dedov, V. A. Sergeev, E. V. Leonova, A. V. Malkov, T. Yu. Filippova, and E. A. Karakhanov, *Metalloorg. Khim.*, 1988, 1354 [*Organomet. Chem. USSR*, 1988, 1354 (Engl. Transl.)].
40. E. A. Karakhanov, A. G. Dedov, and S. Yu. Narin, *Catal. Lett.*, 1989, No. 3, 31.
41. E. A. Karakhanov, S. Yu. Narin, T. Yu. Filippova, and A. G. Dedov, *Dokl. Akad. Nauk SSSR*, 1987, **292**, 1387 [*Dokl. Chem.*, 1987, **292** (Engl. Transl.)].
42. E. A. Karakhanov, E. A. Ivanova, S. Yu. Narin, and A. G. Dedov, *Vestn. MGU*, *Ser 2*, *Khim.*, 1989, **30**, 521 [*Vestn. Mosk. Univ.*, *Ser. Khim.*, 1989, **30**, 510 (Engl. Transl.)].
43. E. A. Karakhanov, S. Yu. Narin, and A. G. Dedov, *Appl. Organomet. Chem.*, 1991, **5**, 445.
44. A. L. Maksimov, E. A. Ivanova, and E. A. Karakhanov, *Neftekhimiya*, 2004, 466 [*Petroleum Chemistry*, 2004, 432 (Engl. Transl.)].
45. W. P. Weber and G. V. Gokel, *Phase Transfer Catalysis in Organic Synthesis*, Springer-Verlag, Berlin—Heidelberg, 1977.
46. M. N. Khan, *Micellar Catalysis*, Taylor and Francis, New York, 2006, 482 pp.
47. Y. Shijo, *Bull. Chem. Soc. Jpn*, 1975, **48**, 2793.
48. V. N. Tikhonov, *Zh. Anal. Khim.*, 1977, **32**, 1435 [*J. Anal. Chem. USSR*, 1977, **32**, 1435].
49. C. J. Suckling, *Ind. Eng. Chem. Prod. Res. Dev.*, 1981, **20**, 434.
50. *Surfactants and Polymers in Aqueous Solution*, Eds K. Holmberg, B. Jonsson, B. Kronberg, and B. Lindman, John Wiley and Sons, New York, 2002.
51. F. H. Quina, P. M. Nassar, J. B. S. Bonilha, and B. L. Bales, *J. Phys. Chem.*, 1995, **99**, 17028.
52. K. N. Panchal, A. Desai, and T. Nagar, *J. Disp. Sci. Techn.*, 2006, **27**, 963.
53. Ch. R. Pulippurasseril, T. Yu. Filippova, A. G. Dedov, and E. A. Karakhanov, *Vestn. MGU*, *Ser. 2. Khim.*, 1991, 418 [*Vestn. Mosk. Univ.*, *Ser. Khim.*, 1991, 418 (Engl. Transl.)].
54. E. A. Karakhanov, Ch. R. Pulippurasseril, T. Yu. Filippova, S. V. Egazar´yants, and A. G. Dedov, *Neftekhimiya*, 1992, **32**, 159 [*Petroleum Chemistry*, 1992, **32**, 159 (Engl. Transl.)].
55. M. S. Khan, *Adv. Colloid Interface Sci.*, 2006, **123—126**, 75.
56. N. Derkaouia, S. Saidb, Y. Grohensb, R. Oliera, and M. Privata, *J. Colloid Interface Sci.*, 2007, **305**, 330.
57. E. A. Karakhanov, S. Yu. Narin, T. Yu. Filippova, E. A. Ivanova, S. M. Volkov, and A. G. Dedov, *Neftekhimiya*, 1987, **27**, 791[*Petroleum Chemistry*, 1987, **27**, 791 (Engl. Transl.)].
58. T. Tahamuku, M. Tabata, A. Yamaguchi, J. Nishimoto, M. Kumamoto, S. Wakita, and T. Yamaguchi, *J. Phys. Chem. B*, 1998, **102**, 8880.
59. C. Olidiges, K. Wittler, T. Tonsing, and A. Alijan, *J. Phys. Chem. B*, 2002, **106**, 7147.
60. J. Laland and I. F. Hakem, *Eur. Phys. J.*, 2004, **E15**, 217.
61. E. A. Karakhanov, Yu. S. Kardasheva, A. L. Maksimov, V. V. Predeina, and E. A. Runova, *J. Mol. Cat. A. Chem.*, 1996, **107**, 235.
62. E. A. Karkahanov, A. L. Maximov, V. V. Predeina, T. Yu. Filippova, and A. A. Utukin, *Macromol. Symp.*, 1996, **105**, 67.
63. E. A. Karakhanov, Yu. S. Kardasheva, A. L. Maksimov, and E. A. Runova, *Ross. Khim. Zh*, 2000, No. 2, 53 [*Mendeleev Chem. J.*, 2000, No. 2, 48 (Engl. Transl.)].
64. E. A. Karakhanov, A. L. Maximov, V. V. Predeina, T. Yu. Filippova, S. A. Martynova, and I. N. Topchieva, *Catal. Today*, 1998, **44**, 189.
65. E. A. Karakhanov, A. L. Maximov, P. Poloznicova, and K. Suslov, *Stud. Surf. Sci. Catal.*, 1998, **121**, 127.
66. *Cyclodextrins and Their Complexes. Chemistry. Analytical Methods*, *Application*, Ed. H. Dodziuk, Wiley-VCH, 2006.
67. A. L. Maksimov, D. A. Sakharov, T. Yu. Filippova, A. Ya. Zhuchkova, and E. A. Karakhanov, *Ind. Eng. Chem. Res.*, 2005, **44**, 644.
68. J. S. Wu and K. Toda, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 365.
69. E. Karakhanov, A. Kirillov, and A. Maksimov, *J. Mol. Cat. A. Chem.*, 2000, **157**, 25.
70. E. Karakhanov, T. Buchneva, A. Maximov, and M. Zavertyaeva, *J. Mol. Cat. A. Chem.*, 2002, **184**, 11.
71. E. A. Karakhanov, A. Ya. Zhuchkova, T. Yu. Filippova, and A. L. Maksimov, *Neftekhimiya*, 2003, **43**, 309 [*Petroleum Chemistry*, 2003, **43**, 302 (Engl. Transl.)].
72. Th. Mathivet, C. Meliet, Y. Castanet, A. Mortreux, L. Caron, S. Tilloy, and E. Monflier, *J. Mol. Cat. A. Chem.*, 2001, **176**, 105.
73. M. T. Reetz and S. R. Waldwogel, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 865.
74. M. Komiyama, T. Takeuchi, T. Mukawa, and H. Asanuma *Molecular Imprinting: from Fundamentals to Applications*, New York, Wiley, 2003.
75. E. A. Karakhanov, A. L. Maksimov, A. Ya. Zhuchkova, T. Yu. Filippova, and L. M. Karapetyan, *Neftekhimiya*, 2005, **45**, 97 [*Petroleum Chemistry*, 2005, **45**, 79 (Engl. Transl.)].

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