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Thermodynamic Simulation for Interaction of Polychlorinated Biphenyls with Potassium Hydroxide in Polyalkanolamines

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Abstract—The interaction of congeners of technical mixtures of polychlorobiphenyls (brands Trichlorobiphenyl, Sovol) with potassium hydroxide in polyalkanolamine medium [diethanolamine, triethanolamine, 2-(*N,N*-dimethylamino)ethanol, 3-(*N,N*-dimethylamino)-1-propylene, *N*-methyldiethanolamine] was studied. It was found that diethanolamine and triethanolamine are the most effective solvents affording the maximum conversion of the initial congeners of mixtures of polychlorinated biphenyls at a temperature of 200°C under conditions of nucleophilic substitution.

Keywords: polychlorinated biphenyls, nucleophilic substitution, thermodynamic modeling, polyalkanolamines

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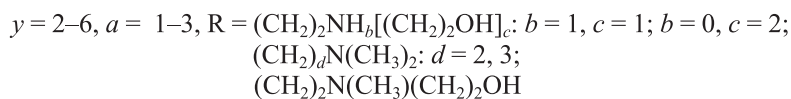
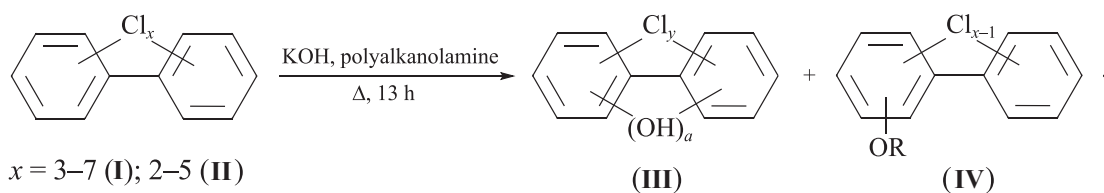
Polychlorinated biphenyls (PCBs) are ecotoxicants and are subject to mandatory destruction [1, 2]. The combustion method does not solve the problem of PCB destruction, since during the thermal treatment of chloroarenes, even more toxic phosgene, polychlorodibenzodioxins and dibenzofurans, chlorine oxides, etc. are released as products [3].

It is possible to completely suppress or minimize the formation of harmful emissions during the thermolysis of PCBs if the congeners of PCB mixtures are preliminarily prepared by chemical modification, namely, by their interaction with nucleophiles (S_N). As a result of nucleophilic substitution, a partial exchange of chlorine atoms for hydrocarbon groups occurs. Unfortunately, numerous experimental studies have shown that it is practically impossible to carry out an exhaustive replacement of chlorine atoms for other functional groups [4]. Nevertheless, the pretreatment of polychlorinated biphenyls with partial replacement of halogen atoms with other functional groups makes it possible to produce polychlorinated biphenyl derivatives with a reduced chlorine content and, during thermolysis, to minimize the risk of formation of more hazardous organochlorine compounds [5, 6].

Due to the multicomponent composition of technical PCB mixtures containing several dozen congeners with different physicochemical properties, the experimental selection of the conditions for nucleophilic replacement is long and challenging [7]. Previously, the method of thermodynamic modeling of chemical interactions was successfully used to select the conditions for nucleophilic replacement (temperature, composition of the starting components, etc.) [8]. Thus, using modeling, the conditions for the interaction of a mixture of Sovol polychlorinated biphenyls with potassium hydroxide in a 2-aminoethanol medium [8] were selected, which made it possible in practice to improve the conversion, as well as the content of hydroxy derivatives in the mixture of final products [aminoethoxy-, hydroxy-, and aminoethoxy(hydroxy) derivatives of polychlorinated biphenyls]. The last clarification concerning hydroxy derivatives of polychlorinated biphenyls is essential, since during thermal oxidation proceeding by a radical mechanism, the hydroxy group is converted into water.

It was previously shown that the use of various polyalkanolamines for the synthesis of hydroxy derivatives of polychlorobiphenyls [diethanolamine (DEA), triethanolamine (TEA), 2-(*N,N*-dimethylamino)-

Scheme 1.



ethanol (DMAE), 3-(*N,N*-dimethylamino)-1-propanol (DMAP), *N*-methyldiethanolamine (MDEA)] as a medium in the interactions of congeners of mixtures of polychlorinated biphenyls Sovol and Trichlorobiphenyl with potassium hydroxide is less effective (Scheme 1) [9] compared with the use of 2-aminoethanol [8]. In addition, in a medium of 2-(*N,N*-dimethylamino)-ethanol and 3-(*N,N*-dimethylamino)-1-propanol upon the interaction of the mixture of polychlorobiphenyls Sovol with potassium hydroxide, in addition to hydroxy derivatives, the products of nucleophilic replacement of chlorine atoms by the corresponding alkoxy groups were found derived from the applied polyalkanolamines. These facts are difficult to explain without calculation methods. They can be interpreted using thermodynamic simulation. Understanding the mechanism of nucleophilic replacement of chlorine atoms for hydroxy and alkoxy groups in a medium of various solvents will allow theoretically selecting not only the initial parameters (composition, temperature) of interactions, but also the reaction medium that affords the maximum possible conversion of PCB congeners.

This work is aimed at studying the effect of solvents from the series of polyalkanolamines on the behavior of the initial congeners of polychlorinated biphenyls of Sovol (I) and Trichlorobiphenyl (II) mixtures in reactions with potassium hydroxide using thermodynamic modeling.

RESULTS AND DISCUSSION

To simulate the replacement reactions of the technical mixtures under study, we employed the known thermochemical parameters of the compounds participating in the substitution reactions [standard enthalpy of formation (ΔH_{298}°), enthalpy increment from

0 to 298 K ($H_{298}^\circ - H_0^\circ$), standard heat capacity (C_{p298}°) and its dependence on temperature $C_p(T)$, entropy (S_{298}°), etc.] taken from the database of the software package for thermodynamic modeling HSC. The thermochemical characteristics for polyalkanolamines and derivatives of polychlorobiphenyls (IV) were calculated by the Joback group-contribution method [10] and compared with the known literature data from the HSC database. Earlier we calculated the thermochemical characteristics of hydroxy derivatives of polychlorinated biphenyls (III), formed on the basis of congeners included in the mixtures of Sovol (I) and Trichlorobiphenyl (II) [8].

Since the main contribution to the Sovol mixture (I) is made by PCBs, and in the Trichlorobiphenyl (II) mixture, by trichlorobiphenyls [8, 9], the thermochemical characteristics of products IV were calculated for derivatives based on penta- and trichlorobiphenyls, respectively (Table 1).

The thermochemical parameters which we calculated for DEA, TEA, DMAE, MDEA (Table 1), and those given in the database of the HSC software package agree satisfactorily.

The calculated values of thermochemical parameters for polyalkanolamines and derivatives of PCBs (IV) were entered into the database of the HSC software package and used in thermodynamic modeling (Equilibrium Composition module).

For selecting the conditions of the interaction of any reagents using thermodynamic simulation, models of an ideal solution and gas are widely used. These approximations have previously proven their effectiveness in many studies [8]. The simulation does not take into account the reaction rate. In this regard, the weights of the initial components and temperature

Table 1. Calculated thermochemical characteristics of polyalkanolamines and polychlorinated biphenyl derivatives

Compound	Standard enthalpy of formation ΔH_{298}° , kJ mol ⁻¹	Standard Gibbs energy ΔG_{298}° , kJ mol ⁻¹	Standard entropy S_{298}° , J mol ⁻¹ K ⁻¹	Enthalpy increment from 0 to 298 K $H_{298}^{\circ} - H_0^{\circ}$, kJ mol ⁻¹	Heat capacity $C_p = a + b \times 10^{-3}T + d \times 10^{-6}T^2 + c \times 10^5T^{-2}$, kJ mol ⁻¹ K ⁻¹				Standard heat capacity $C_{p,298}^{\circ}$, kJ mol ⁻¹ K ⁻¹
					<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	
Solvents									
3-(<i>N,N</i> -Dimethylamino)-1-propanol C ₅ H ₁₃ NO	-231.23 -383.46	-20.75 -171.64	415.61 466.39	22.56 24.38	34.873 101.18	523.21 364.88	-7.86 -35.38	-208.4 -111.38	151.34 163.51
<i>N</i> -methyldiethanolamine C ₅ H ₁₃ NO ₂	-379.91 ^a		469.00 ^a						160.26
2-(<i>N,N</i> -Dimethylamino)ethanol C ₄ H ₁₁ NO	-210.59 -201.95 ^a	-43.24	377.05 383.99 ^a	19.04	55.64	342.81	-19.50	-113.77	127.72 125.79
Triethanolamine C ₆ H ₁₅ NO ₃	-556.33 -561.95 ^a	-300.04	555.74 537.77 ^a	29.76	115.46	460.32	-38.31	-148.16	199.61 196.44
Diethanolamine C ₄ H ₁₁ NO ₂	-376.88 -364.91 ^a	-201.45	452.44 446.00 ^a	21.01	65.47	351.83	-17.55	-118.11	140.96 140.14
Derivatives of polychlorinated biphenyls									
(<i>N,N</i> -Dimethylaminoethoxy)- dichlorobiphenyl C ₁₂ H ₇ Cl ₂ [O(CH ₂) ₂ N(CH ₃) ₂]	-31.09 -85.51	261.69 218.57	635.59 687.87	47.28 52.11	58.33 101.65	1041.35 982.29	-11.65 -9.28	-434.24 -405.34	317.13 349.55
(<i>N,N</i> -Dimethylaminoethoxy)- tetrachlorobiphenyl C ₁₂ H ₅ Cl ₄ [O(CH ₂) ₂ N(CH ₃) ₂]									
(<i>N,N</i> -Dimethylaminopropoxy)- tetrachlorobiphenyl C ₁₂ H ₅ Cl ₄ [O(CH ₂) ₃ N(CH ₃) ₂]	-106.15	226.99	728.42	55.54	104.86	934.39	-10.16	-435.67	372.57
(<i>N,N</i> -Dimethylaminopropoxy)- dichlorobiphenyl C ₁₂ H ₇ Cl ₂ [O(CH ₂) ₃ N(CH ₃) ₂]	-57.13	270.11	674.14	51.02	61.56	1121.48	-12.54	-464.55	342.23
[2-(<i>N</i> -Methylethanolamino)- ethoxy] dichlorobiphenyl C ₁₂ H ₇ Cl ₂ [O(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ OH]	-203.96	133.29	724.93	52.74	73.71	1127.88	-14.01	-455.06	353.81
[2-(<i>N</i> -Methylethanolamino)ethoxy] tetrachlorobiphenyl C ₁₂ H ₅ Cl ₄ [O(CH ₂) ₂ N(CH ₃)(CH ₂) ₂ OH]	-258.38	90.17	779.21	57.24	113.58	1080.89	-10.90	-446.21	383.95
[2-(<i>N,N</i> -Diethanolamino)- ethoxy] tetrachlorobiphenyl C ₁₂ H ₅ Cl ₄ [O(CH ₂) ₂ N((CH ₂) ₂ OH) ₂]	-431.25	-38.23	868.55	62.35	125.51	1176.54	-12.52	-487.07	418.25
[2-(<i>N,N</i> -Diethanolamino)- ethoxy] dichlorobiphenyl C ₁₂ H ₇ Cl ₂ [O(CH ₂) ₂ N((CH ₂) ₂ OH) ₂]	-376.83	4.89	814.27	58.05	82.20	1240.36	-14.89	-515.97	389.43
[2-(<i>N</i> -Ethanolamino)ethoxy]- dichlorobiphenyl C ₁₂ H ₇ Cl ₂ [O(CH ₂) ₂ NH(CH ₂) ₂ OH]	-197.38	103.48	710.97	49.33	67.15	1053.40	-10.37	-435.26	330.89
[2-(<i>N</i> -Ethanolamino)ethoxy]- tetrachlorobiphenyl C ₁₂ H ₅ Cl ₄ [O(CH ₂) ₂ NH(CH ₂) ₂ OH]	-251.80	60.36	765.25	43.94	110.47	992.54	-8.00	-406.36	294.77

^a HSC software package database.

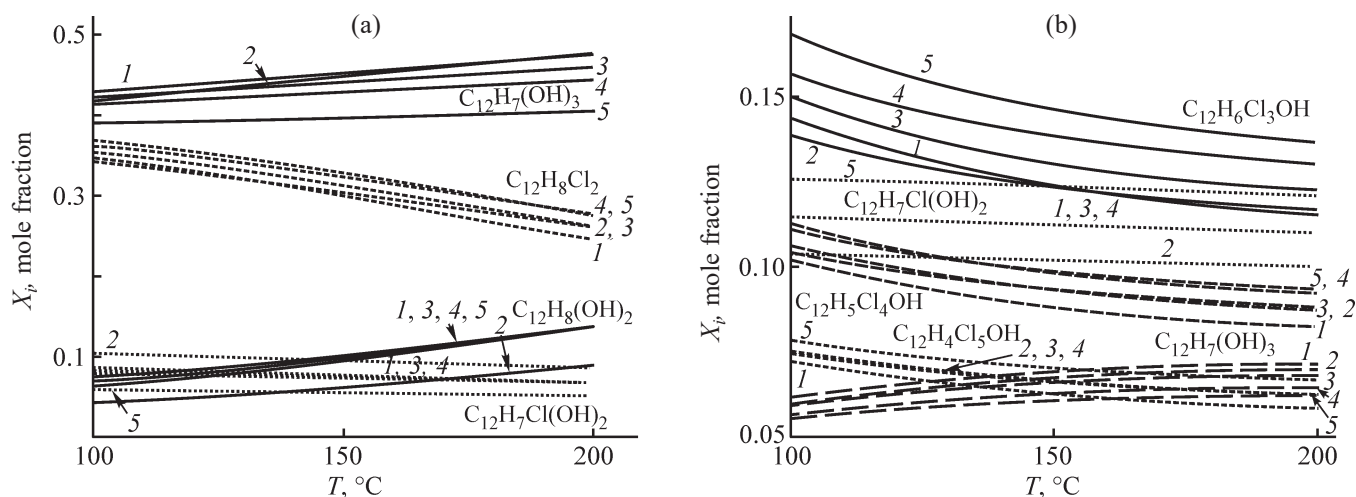


Fig. 1. The equilibrium composition of congeners and derivatives of polychlorinated biphenyls vs. temperature. Initial composition: 0.05 mol of a PCB mixture, 0.1 mol of potassium hydroxide, 0.3 mol of solvent, $P = 1$ atm. (a) Trichlorobiphenyl, (b) Sovol. Polyalkanolamine: (1) triethanolamine, (2) diethanolamine, (3) 2-(*N,N*-dimethylamino)ethanol, (4) *N*-methyldiethanolamine, (5) 3-(*N,N*-dimethylamino)-1-propanol. The graphs show compounds with a concentration of more than 0.05 mole fraction. The sum of the mole fractions of all congeners and polychlorinated biphenyl derivatives is 1.

indicators determined from the results of modeling should be considered as the maximum possible values.

In [9] the conditions for the experimental implementation of the nucleophilic substitution of chlorine atoms in the congeners of PCB mixtures of Trichlorobiphenyl (**II**) and Sovol (**I**) in the medium of polyalkanolamines under the action of potassium hydroxide were considered, under which, according to the calculated results, it was possible to achieve 100% conversion in the presence of solvent 2-aminoethanol [8]: 170°C, 6-fold molar excess of nucleophilic agent (potassium hydroxide) in relation to the PCB mixture. To substantiate the effect of polyalkanolamines on the conversion value of PCB congeners, it is incorrect to apply the above conditions for modeling. Provided that polyalkanolamines are also nucleophiles in the interaction of PCB mixtures with alkali, the mole fractions of potassium hydroxide and polyalkanolamines must be equated. However, in this case, polyalkanolamines will not be classified as solvents.

Using thermodynamic simulation and the HSC software package, we developed the model of the processes occurring in a medium of 0.3 mol polyalkanolamines (DEA, TEA, DMAP, DMAE, MDEA) between 0.05 mol of the mixture of polychlorobiphenyls Trichlorobiphenyl (**II**), Sovol (**I**), and 0.1 mol potassium hydroxide. The temperature range of 100–200°C was

considered, since the boiling point of some solvents is low [$T_b(\text{DMAE}) = 134^\circ\text{C}$, $T_b(\text{DMAP}) = 162\text{--}164^\circ\text{C}$], and at a process temperature of more than 200°C the formation of highly toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans is possible.

The initial considered composition (0.1 mol potassium hydroxide and 0.3 mol polyalkanolamine) is not optimal, since unreacted initial congeners, which are part of PCB mixtures, remain in the products.

When studying the effect of diethanolamine, triethanolamine, 2-(*N,N*-dimethylamino)ethanol, 3-(*N,N*-dimethylamino)-1-propanol, *N*-methyldiethanolamine on the behavior of PCB congeners in Sovol (**I**) and Trichlorobiphenyl (**II**) mixtures in interaction with potassium hydroxide, it is necessary to evaluate the calculated results (the reactivity of the congeners included in the initial mixtures of polychlorinated biphenyls, the effect of temperature on the conversion of the initial congeners of the mixtures of compounds **II** and **I**) and to identify the most effective solvent from the series of polyalkanolamines (Figs. 1a, 1b).

Reactivity of congeners of mixtures of polychlorobiphenyls Trichlorobiphenyl (II**) and Sovol (**I**).** When modeling the processes occurring in the polyalkanolamines medium between Trichlorobiphenyl and potassium hydroxide, the concentration of the initial congeners in the reaction products is several times higher than

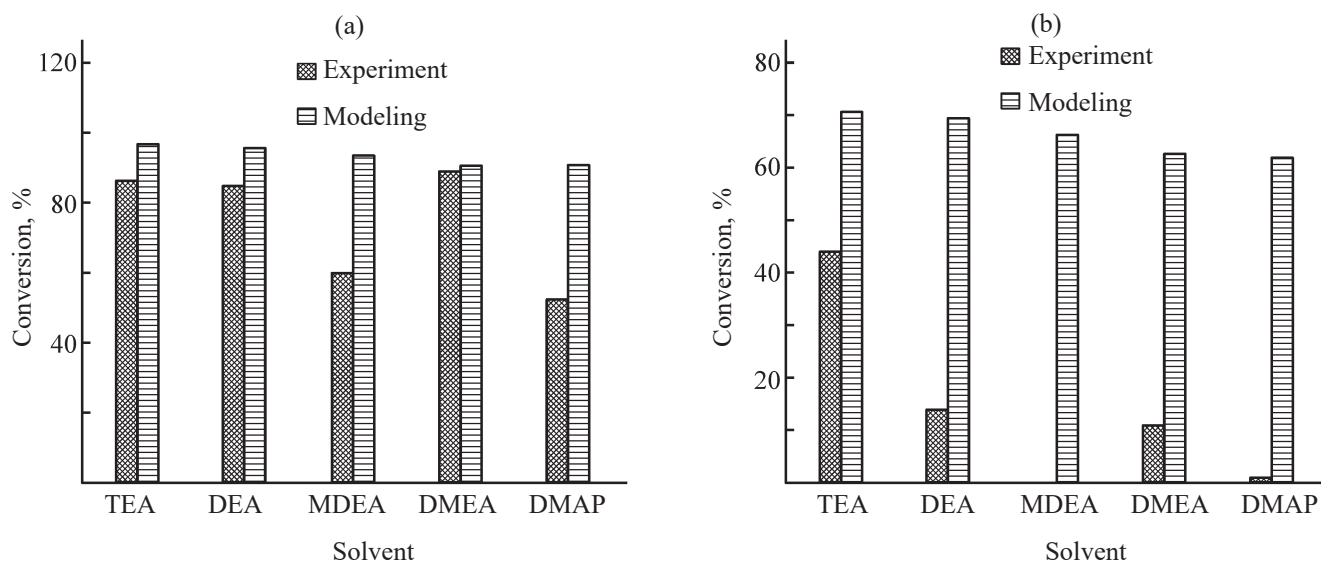


Fig. 2. Conversion of the starting PCB congeners of mixtures (a) Sovol and (b) Trichlorobiphenyl in the reaction with potassium hydroxide in diethanolamine (DEA), triethanolamine (TEA), 2-(*N,N*-dimethylamino)ethanol (DMAE), 3-(*N,N*-dimethylamino)-1-propanol (DMAP), *N*-methyl-diethanolamine (MDEA) according to the results of modeling ($T = 150^\circ\text{C}$) and experimental studies [13 h, $T = 170^\circ\text{C}$; for 2-(*N,N*-dimethylamino)-ethanol $T = 134^\circ\text{C}$, for 3-(*N,N*-dimethylamino)-1-propanol $T = 162^\circ\text{C}$] [10].

in the analogous interaction of Sovol. The simulation data are consistent with the earlier conclusions about the lower reactivity of the groups of PCB congeners included in the mixture of Trichlorobiphenyl, in comparison with the groups of congeners from Sovol [9]. Experimental studies of substitution processes between congeners of mixtures of PCBs and potassium hydroxide in the presence of polyalkanolamines also showed a lower conversion from the Trichlorobiphenyl mixture than from the Sovol mixture [9].

The main products in modeling the interaction of mixtures of polychlorobiphenyls **II** and **I** with potassium hydroxide are derivatives **III**, and derivatives **IV** are registered in a mixture of products at a concentration of less than 10–20 mole fraction. This fact allows a conclusion about the thermodynamic instability of derivatives **IV** and refers them to intermediate products, which further form derivatives **III** as a result of nucleophilic exchange of the alkoxy groups for hydroxy. Note that modeling does not take into account the rate of the reaction and, accordingly, does not give quantitative recommendations on the interaction time, which explains the differences between the results of thermodynamic modeling and experimental ones.

In view of the obtained modeling data, it can be predicted that polychlorinated biphenyl derivatives will be absent in mixtures of reaction products when nucleo-

philic substitution is carried out in a medium of 2-(*N,N*-dimethylamino)ethanol and 3-(*N,N*-dimethylamino)-1-propanol if the interaction time is increased comparing to that in [9].

Influence of temperature on the conversion of polychlorinated biphenyl congeners in mixtures of Trichlorobiphenyl and Sovol. With increasing the temperature, the conversion of the initial PCB congeners of the Trichlorobiphenyl and Sovol mixtures in the reaction with potassium hydroxide increases when diethanolamine, triethanolamine, 2-(*N,N*-dimethylamino)-ethanol, 3-(*N,N*-dimethylamino)-1-propanol, *N*-methyl-diethanolamine are used as a medium. In the reaction products, the concentration of the initial PCB congeners, as well as their hydroxy derivatives **III** as incomplete substitution products, decreases. In this case, the concentration of derivatives, which are products of the exhaustive substitution of chlorine atoms, rises. Therefore, it is advisable to carry out the process at the maximum possible temperature of 200°C . Since for some solvents the boiling point is less than 200°C [$T_b(\text{DMAE}) = 134^\circ\text{C}$, $T_b(\text{DMAP}) = 162\text{--}164^\circ\text{C}$], the interaction must be conducted at the boiling point of the reaction mixture, which was carried out experimentally in the case of 2-(*N,N*-dimethylamino)ethanol and 3-(*N,N*-dimethylamino)-1-propanol in [9].

Identification of the most effective solvents of diethanolamine, triethanolamine, 2-(*N,N*-dimethylamino)ethanol, 3-(*N,N*-dimethylamino)-1-propanol, *N*-methyldiethanolamine. When modeling the interaction in the medium of polyalkanolamines Trichlorobiphenyl and Sovol with potassium hydroxide, the conversion of the congeners of PCB mixtures has different values. In the reaction products, the concentration of derivatives **III** decreases in the series TEA → DMAP. Note that the results of calculation and experiment [9] regarding the efficiency of polyalkanolamines in substitution reactions of polychlorobiphenyl congeners in a mixture of **II** and **I** with potassium hydroxide are in satisfactory agreement (Fig. 2).

Differences in the simulation results when using diethanolamine and triethanolamine are observed in the temperature range 100–150°C (Fig. 1). At a higher reaction temperature, the concentrations of the obtained derivatives **III** are identical.

The lowest conversion under the applied conditions of substitution was obtained in the medium of 2-(*N,N*-dimethylamino)ethanol and 3-(*N,N*-dimethylamino)-1-propanol (Figs. 1, 2). At the boiling point of the reaction mixture (not more than 160°C), the content of the reaction products of the initial low-reactive congeners of polychlorobiphenyls (dichloro-, trichloro-) is significantly higher than at 200°C. Due to the low boiling point of 2-(*N,N*-dimethylamino)-ethanol and 3-(*N,N*-dimethylamino)-1-propanol, it is impossible to carry out the substitution process at higher temperatures without an autoclave. However, in the case of polychlorinated biphenyls, the use of closed vessels for carrying out chemical interactions is reasonably prohibited.

A clear pattern is observed when comparing the standard Gibbs energy (ΔG_{298}°) in the TEA → DMAP series (Table 1). According to the results of thermodynamic simulation the values of ΔG_{298}° of the most effective (reactive) solvents triethanolamine and diethanolamine are lower in comparison with less effective 2-(*N,N*-dimethylamino)ethanol and 3-(*N,N*-dimethylamino)-1-propanol, which is in complete agreement with the experimental data in [9]. The effectiveness of polyalkanolamines in the process under study is associated with proceeding the alcoholysis process, where solvents also simultaneously act as nucleophilic agents. In [9] it was reported that in the products there are polychlorobi-

phenyl (**IV**) derivatives when 2-(*N,N*-dimethylamino)ethanol and 3-(*N,N*-dimethylamino)-1-propanol were used, which is a consequence of the alcoholysis.

The use of the most reactive solvents results in a decrease in the ΔG_{298}° of the reaction and an increase in the rate of the direct displacement reaction compared to less reactive solvents.

In the reaction products of mixtures of polychlorobiphenyls Sovol (**I**), Trichlorobiphenyl (**II**) with potassium hydroxide in the medium of solvents triethanolamine and diethanolamine, there are no derivatives of polychlorobiphenyls **IV**, while in the medium of 2-(*N,N*-dimethylamino)ethanol, 3-(*N,N*-dimethylamino)-1-propanol they are present [9]. Probably, in the case of using triethanolamine and diethanolamine, derivatives **IV** can also be obtained if the process time is significantly reduced in comparison with a similar parameter from [9], but then the conversion of the initial congeners of polychlorinated biphenyls will be minimal.

CONCLUSIONS

Based on the simulation results, it was found that the substitution of chlorine atoms in the structure of polychlorinated biphenyls in the reaction with potassium hydroxide in the medium of polyalkanolamines is a complex multistage process characterized by the formation of both thermodynamically unstable derivatives **IV** and stable products **III**. An increase in the conversion of PCB congeners of commercial mixtures Sovol or Trichlorobiphenyl upon interaction with alkali in a polyalkanolamine medium comparing to the data from [9] is possible only if the temperature in the reaction zone is increased.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest requiring disclosure in this article.

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