MASS TRANSFER IN A LIQUID–LIQUID OZONATION PROCESS

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Abstract. A liquid–liquid phase ozonation process for the removal of phenolic compounds from an aqueous solution using fluorinated organic solvents as the ozone carrier was studied. The experimental results showed that the oxidation of phenolic compounds by ozone is a mass transfer process accompanied by a surface reaction in the boundary layer of both the aqueous and the organic phase, whose role depends on the distribution coefficients and concentrations of reactants. The interfacial mass transfer is enhanced by the chemical reaction. Mass transfer coefficients, enhancement factors, and distribution coefficients of phenol, 4-methylphenol, 4-chlorophenol, and ozone were determined.

Key words: ozonation, fluorinated solvent, mass transfer, phenol, 4-methylphenol, 4-chlorophenol.

INTRODUCTION

The conventional ozonation for the destruction of hazardous organic compounds in wastewater is usually realized in practice as a gas–liquid process. In order to enhance the selectivity of the ozonation process and reduce the ozone consumption both the liquid–liquid phase and gas–liquid–liquid phase processes have been proposed [1, 2]. In our previous work [3] a new liquid–liquid ozonation technique was applied for the removal of phenol, 4-methylphenol, and 4-chlorophenol from an aqueous solution. As ozone carriers perfluorodecalin and a completely fluorinated hydrocarbon solvent FC 40 were used. It was established that the liquid–liquid phase ozonation process may be described as a surface reaction occurring near the interfacial contact area. Nevertheless, the mechanism and kinetics of the process need more detailed investigation.

The aim of the present work was to investigate and describe mathematically the mechanism and kinetics of the liquid–liquid ozonation process, establishing

the relation of the chemical reaction and mass transfer and the role of both the phases in the process.

The oxidation reaction can occur in the boundary layer of both the aqueous and the organic phase. For establishing the role of these phases in the interfacial mass transfer it is necessary to use solvents with different distribution coefficients of phenolic compounds. Therefore, in this work freon F 113 was used as solvent besides FC 40 and perfluorodecalin. Freon F 113 has a high distribution coefficient for 4-methylphenol and 4-chlorophenol, but it cannot be recommended for practical use because of its insufficient O_3 stability. For establishing the role of physical mass transfer and its enhancement by a chemical reaction, mass transfer experiments with and without a chemical reaction were carried out.

EXPERIMENTAL

The ozonation process was carried out in a system consisting of a reactor and an absorber. In the reactor the aqueous phase containing a phenolic compound was contacted with the organic phase containing ozone. In the absorber the organic phase (ozone carrier) was saturated with ozone. The ozone carrier was circulated in the system by means of a peristaltic pump. The oxidation reaction occurred near the interfacial contact area, the water soluble reaction products going into the aqueous phase. During the experiment the concentration of ozone in the organic phase was kept roughly constant. The experimental equipment as well as the methods of experiments and analysis are described in our previous paper [3].

As the ozone carrier octadecafluorobicyclo[4,4,0]-decane, perfluorodecalin (Perftoran, Moscow), fluorinent FC 40 (Sigma Chemical), 1,1,2-trichlorotri-fluoroethane, and freon F 113 (Sigma Chemical) were used. When the organic and the aqueous phase were stirred with small paddle stirrers the interfacial contact area remained practically constant at the stirring speed used (up to 375 rpm) due to the high density of the organic solvent (1.95 g cm^{-3} for perfluorodecalin, 1.57 g cm^{-3} for freon F 113). In the case a turbine stirrer was used the interfacial area was significantly larger because of phase dispersion.

RESULTS AND DISCUSSION

The interfacial mass transfer of a phenolic compound in the aqueous phase without a chemical reaction can be described as

$$-\mathrm{d}C_{pw} = k^{*}_{m} f_{w}(C_{pw} - C^{*}_{pw})\mathrm{d}t, \qquad (1)$$

where k^{*}_{m} is the physical mass transfer coefficient, m s^{-1}; t is the process time, s; C_{pw} and C^{*}_{pw} are phenol concentrations respectively in the bulk and at the interfacial area of the aqueous phase, mol m^{-3}; and f_w is the specific interfacial area of the aqueous phase, m^{-1}.

At the solvent–water interface the following equilibrium is valid:

$$C^*_{ps} = k_p C^*_{pw}, \qquad (2)$$

where C^*_{ps} is phenol concentration at the interfacial area of the organic (solvent) phase, mol m^{-3}; and k_p is the distribution coefficient of the phenolic compound.

When perfluorodecalin was used as solvent the distribution coefficients of phenolic compounds were very low and the concentrations in the aqueous phase high enough to regard C_{pw}, C^*_{pw}, and C^*_{ps} as constants and $C_{pw} = C^*_{pw}$ during a mass transfer experiment. The physical mass transfer of a phenolic compound from the interfacial area to the bulk of the organic phase can be described as

$$dC_{ps} = k^*_m f_s (C^*_{ps} - C_{ps}) dt, \qquad (3)$$

where $C^*_{ps} = k_p C_{pw}$ and f_s is the specific interfacial area of the organic phase, m^{-1}. In that case the integration of Eq. 3 gives

$$\ln(C^*_{ps}/(C^*_{ps} - C_{ps})) = k^*_m f_s t. \qquad (4)$$

The values of C_{ps} are available from experimental data.

In Fig. 1 experimental data and linear plots of $\ln(C^*_{ps}/(C^*_{ps} - C_{ps}))$ versus time are shown at different stirring speeds of a paddle stirrer in both the phases. The experiments were provided with phenol in the perfluorodecalin–water system without ozone at a constant specific interfacial area $f_s = 35.8$ m^{-1}. As it can be seen the plots at $n = 200$ rpm and $n = 375$ rpm coincide. Therefore, we can conclude that the mass transfer depends on the stirring speed up to 200 rpm, while at higher speeds there is no significant dependence. From the slopes of the linear plots in Fig. 1 we can calculate the values of the mass transfer coefficients.
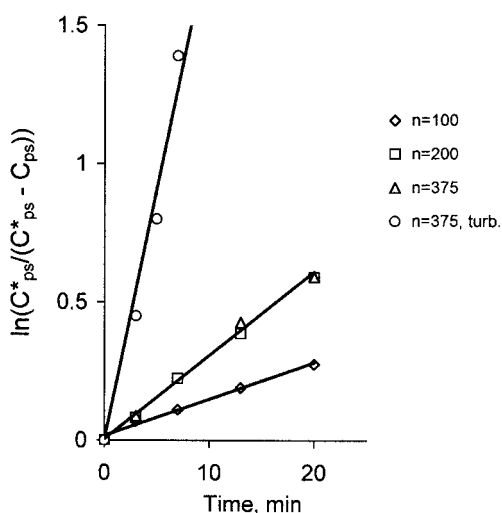

Fig. 1. Dependence of phenol concentration ratio on time at different stirring speeds. Perfluorodecalin carrier; paddle stirrer.

20

At the stirring speed $n = 375$ rpm the physical mass transfer coefficient of phenol $k^*_m = 1.3 \times 10^{-5}$ m s^{-1}. The distribution coefficients of phenolic compounds were estimated as limit values of C_{ps}/C_{pw} in our mass transfer experiments. They are in accordance with the results obtained by shaking organic and aqueous phases in a batch reactor. In the case perfluorodecalin was used as the organic solvent, the value of the distribution coefficient k_p at 18 °C was 0.00638 for phenol, 0.0142 for 4-methylphenol, and 0.0190 for 4-chlorophenol. When FC 40 was used the k_p value was 0.0105 for 4-methylphenol and 0.0131 for 4-chlorophenol. For comparison also the experimental data obtained using a turbine stirrer ($n = 375$ rpm) are shown in Fig. 1. As it seems, the slope of the linear plot, thus the value of $k^*_m f_s$ is significantly higher for the turbine stirrer than for the paddle stirrer due to the increasing interfacial area f_s by phase dispersion. This demonstrates that though the mass transfer rate is not influenced by the stirring speed it remains greatly dependant on the size of the interfacial area.

In the case freon F 113 was used as solvent the distribution coefficient of 4-methylphenol was high; therefore, we cannot regard C^*_{ps} and C_{pw} as constants. Despite that, dividing both the terms of Eq. 3 by C^*_{ps} we get

$$\mathrm{d}(C_{ps}/C^*_{ps}) = k^*_m f_s (1 - C_{ps}/C^*_{ps})\mathrm{d}t, \tag{5}$$

where $C^*_{ps} = k_p C^*_{pw}$, $C^*_{pw} \approx C_{pw}$, and C_{ps}/C^*_{ps} can be regarded as a new variable. The integration of Eq. 5 gives the same result as Eq. 4. The values of $\ln(C^*_{ps}/(C^*_{ps} - C_{ps}))$ calculated from experimental data of C_{ps} and C_{pw} are shown in Fig. 2. From the slope of the linear plot approximating the experimental data we can calculate the physical mass transfer coefficient of 4-methylphenol in the F 113–water system as $k^*_m = 2.73 \times 10^{-5}$ m s^{-1}.

The experimental value of the distribution coefficient of 4-methylphenol between the F 113 and aqueous phases depending on temperature is shown in Fig. 3. As it can be seen the distribution coefficient depends significantly on temperature, decreasing with increasing temperature.

As regards the mass transfer and distribution of phenol in the F 113–water system, our experiments showed phenol to be practically insoluble in F 113.

The mass transfer of ozone between the organic and aqueous phases was studied by the above-described method, but without a phenolic compound. As a result, the values of physical mass transfer coefficient $k^*_m = 5.4 \times 10^{-5}$ m s^{-1} and distribution coefficient $k_o = C^*_{os}/C^*_{ow} = 0.061$ were obtained for the F 113–water system at 17 °C. Here C^*_{os} and C^*_{ow} are ozone concentrations at the interfacial area in the organic and the aqueous phase, respectively, mol m^{-3}. For the perfluorodecalin–water system the value of the distribution coefficient of ozone $k_o = 0.15$, for FC 40–water system $k_o = 0.185$.

As to the mass transfer with a chemical reaction it should be noted that our previous work [3] demonstrated the absence of a phenolic compound in the organic phase as well as the absence of ozone in the aqueous phase during the main reaction period, that is $C_{ps} = 0$ and $C_{ow} = 0$. Thus the liquid–liquid
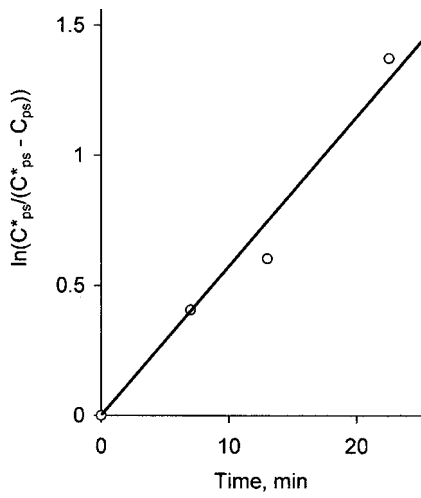
Fig. 2. Dependence of 4-methylphenol concentration ratio on time. F 113 carrier; paddle stirrer, $n = 375$ rpm; temperature 16 °C.
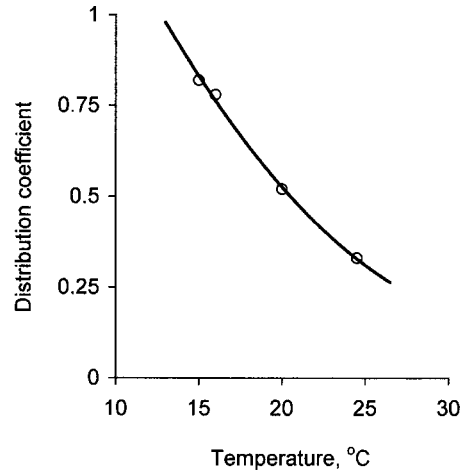
Fig. 3. Distribution coefficient of 4-methylphenol in F 113–water system depending on temperature.

ozonation occurs as a surface reaction near the interfacial area. The rate of the oxidation reaction is high enough to confine the reaction within the boundary layer, so the reactants cannot diffuse into the bulk of the opposite phase. The concentration profiles of reactants are shown in Fig. 4.
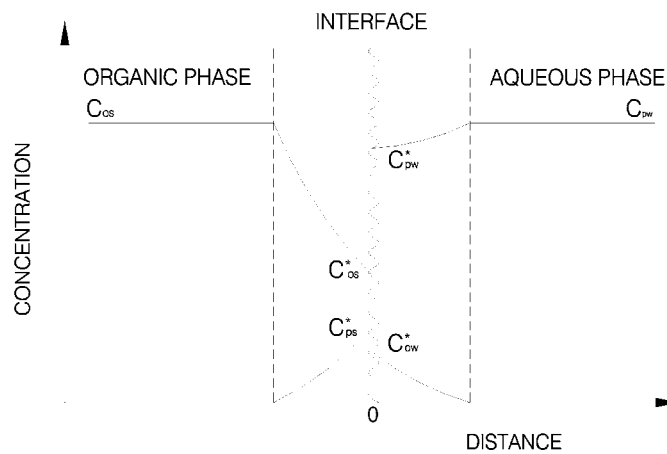

Fig. 4. Concentration profiles of ozone and a phenolic compound at liquid–liquid phase ozonation.

The material balances of ozone and a phenolic compound in both the boundary layers are:

$$C_{os} - C^*_{os} = k_s C^*_{ps} \tag{6}$$

and

$$k_s(C_{pw} - C^*_{pw}) = C^*_{ow}, \tag{7}$$

where C_{os} is ozone concentration in the bulk of the organic phase and k_s is stoichiometric factor, moles ozone per 1 mole of phenol.

At the solvent–water interface the following equilibria are valid:

$$C^*_{ow} = k_o C^*_{os} \tag{8}$$

and

$$C^*_{ps} = k_p C^*_{pw}. \tag{9}$$

Solving the system of Eqs. 6–9 we can get the values of C^*_{os}, C^*_{ps}, C^*_{ow}, and C^*_{pw} at given values of C_{os} and C_{pw}. The ratio of the phenolic compound reacting in the organic phase to that reacting in the aqueous phase can be calculated as

$$R_s/R_w = C^*_{ps}/(C_{pw} - C^*_{pw}). \tag{10}$$

The calculated values of C^*_{os}, C^*_{ow}, C^*_{ps}, C^*_{pw}, and R_s/R_w for phenol, 4-methylphenol, and 4-chlorophenol in perfluorodecalin–water, FC 40–water, and F 113–water systems are shown in Table 1. In the bulk of phases $C_{os} = 2.0$ mol m^{-3} and $C_{pw} = 1.0$ mol m^{-3}. The latter corresponds roughly to the state at half of the reaction period in our experiments. As it appears, at the oxidation of phenol in the F 113–water system the reaction occurs entirely in the aqueous phase. At the oxidation of 4-methylphenol in the F 113–water system, on the contrary, the reaction occurs only in the organic phase. In other cases the reaction takes place in both phases, although mostly in the aqueous phase.

Table 1. Interfacial concentrations of reagents

Phenol	Solvent	C^*_{os}	C^*_{ow}	C^*_{ps}	C^*_{pw}	R_s/R_w
Ph	PFD	1.983	0.297	0.0057	0.901	0.058
MPh	PFD	1.970	0.296	0.0125	0.877	0.101
CPh	PFD	1.968	0.295	0.0162	0.852	0.110
Ph	F 113	2.000	0.121	0	0.960	0
MPh	F 113	0.777	0.047	0.510	0.980	26.0
MPh	FC 40	1.979	0.366	0.0089	0.848	0.058
CPh	FC 40	1.979	0.366	0.0107	0.817	0.059

Ph, phenol; MPh, 4-methylphenol; CPh, 4-chlorophenol; PFD, perfluorodecalin.

If the reaction occurs in the organic phase only then practically $C_{pw} = C^*_{pw}$ and the mass transfer with the oxidation reaction of a phenolic compound can be described as

$$-dC_{pw}/dt = f_w \Phi k^*_m k_p C_{pw}, \tag{11}$$

where Φ is the enhancement factor (Hatta number), i.e. the ratio of the mass transfer coefficients with and without a chemical reaction,

$$\Phi = k_m/k^*_m. \tag{12}$$

By simplifying and integrating the equations describing diffusion and the chemical reaction in the boundary layer the following result was obtained [4]:

$$\Phi = M \operatorname{cth} M, \tag{13}$$

where

$$M = (k_2 \, C_{os} \, D_{ps} \, k^{*\,-2}_m)^{0.5}, \tag{14}$$

k_2 is the second order reaction rate constant of phenol oxidation, $m^3\, mol^{-1}\, s^{-1}$, and D_{ps} is the diffusion coefficient of a phenolic compound in the organic phase, $m^2\, s^{-1}$.

The integration of Eq. 11 gives

$$\ln(C^0_{pw}/C_{pw}) = f_w \Phi \, k^*_m k_p t, \tag{15}$$

where C^0_{pw} is the initial concentration of the phenolic compound in the aqueous phase.

Experimental data and a linear plot of $\ln(C^0_{pw}/C_{pw})$ versus time for the ozonation of 4-methylphenol in the F 113–water system at different temperatures are shown in Fig. 5. The concentration of ozone in the organic phase was kept roughly constant at $C_{os} = 1.2\, mol\, m^{-3}$. From the slope of the linear plot for 16°C we get the value of the mass transfer coefficient enhanced by the chemical reaction $k_m = 6.4 \times 10^{-5}\, m\, s^{-1}$. Taking into account the above value of the physical mass transfer coefficient we get $\Phi = 6.4/2.73 = 2.3$. If we calculate Φ by Eqs. 13 and 14, taking the second order reaction constant $k_2 = 2.2\, m^3\, mol^{-1}\, s^{-1}$ as in the case of ozonation in a CCl_4 solution [5], we will get $\Phi = 2.7$. The difference can be explained by the circumstance that the experimental data are connected with mass transfer in both the phases, the calculated value of Φ shows the enhancement of mass transfer in the organic phase only.

If the reaction occurs only in the aqueous phase, as in the case of phenol oxidation in the F 113–water system, then $C_{ow} = 0$, $C_{os} = $ const. (according to the conditions of the experiments), $C_{os} = C^*_{os}$, and the mass transfer rate is

$$-dC_{pw}/dt = f_w \, k_m \, k_s \, C^*_{ow}, \tag{16}$$

where $C^*_{ow} = k_o \, C_{os}$, $k_s = 3$ [5], and k_m can be taken as [4]

$$k_m = (D_{ow}\, k_2\, C_{pw})^{0.5}, \tag{17}$$

where D_{ow} is the diffusion coefficient of ozone in water, $m^2\ s^{-1}$.

The integration of Eqs. 16 and 17 gives a linear equation

$$C^0_{pw}{}^{0.5} - C_{pw}{}^{0.5} = 2f_w\, k_s\, k_o (k_2\, D_{ow})^{0.5}\, C_{os}\, t, \tag{18}$$

where C^0_{pw} is the initial concentration of the phenolic compound.

Figure 6 shows the experimental data and a linear plot of Eq. 18 for the ozonation of phenol in an F 113–water system. From the slope of the linear plot we get $(k_2\, D_{ow})^{0.5} = 0.6 \times 10^{-4}$, which is in accordance with the value calculated on the ground of literature data ($k_2 = 2.1\ m^3\ mol^{-1}\ s^{-1}$, $D_{ow} = 1.74 \times 10^{-9}\ m^2\ s^{-1}$) [6, 7].

If the chemical reaction occurs in both the phases, as in the case of the ozonation of a phenolic compound in the perfluorodecalin–water and FC 40–water systems, then the mass transfer rate is somewhat higher as Eq. 18 suggests, particularly at the beginning of the process. Nevertheless, in this case, considering the dominating role of the aqueous phase reaction, Eq. 18 would be more suitable. The plots of $C^0_{pw}{}^{0.5} - C_{pw}{}^{0.5}$ versus time for phenol, 4-chlorophenol, and 4-methylphenol in the perfluorodecalin–water system, shown in Fig. 7, also confirm the adequacy of the above mathematical description.
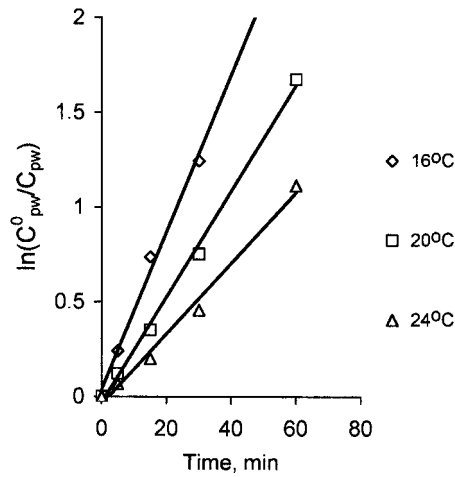

Fig. 5. Dependence of 4-methylphenol concentration ratio on time at different temperatures. F 113 carrier; paddle stirrer, $n = 375$ rpm.
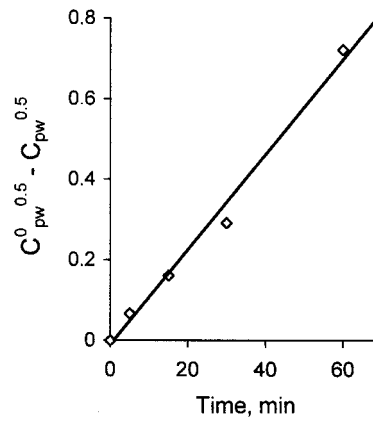
Fig. 6. Dependence of phenol concentration on time. F 113 carrier; paddle stirrer, $n = 375$ rpm.
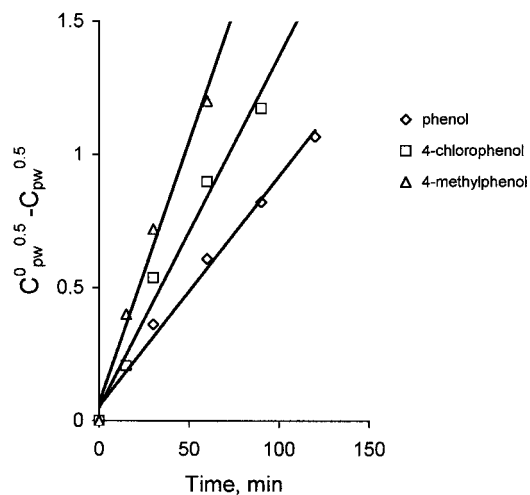
Fig. 7. Dependence of the concentration on time for different phenolic compounds. Perfluoro-decalin carrier; paddle stirrer, $n = 375$ rpm.

CONCLUSIONS

The liquid–liquid phase ozonation of phenol, 4-methylphenol, and 4-chloro-phenol in an aqueous solution with fluorinated organic solvents used as the ozone carrier is a mass transfer process accompanied by a chemical reaction. The reaction occurs in the boundary layer of both the aqueous and the organic phase, the reactants not diffusing into the bulk of the opposite phase. The role of the boundary layers differs, depending on the solvents and reactants used. In case of sufficient intraphasic mixing the mass transfer rate depends mainly on the size of the interfacial area and it is enhanced by the chemical reaction. The process rate and enhancement factor can be calculated by modified Hatta equations.

ACKNOWLEDGEMENT

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MASSIÜLEKANNE VEDELIK–VEDELIK OSOONIMISPROTSESSIS

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On uuritud fenoolsete ühendite lagundamiseks kasutatavat vedelik–vedelik-süsteemis toimuvat osoonimisprotsessi, milles osooni kanduriks on fluororgaanilised solvendid. Katsetulemustest nähtub, et fenoolsete ühendite oksüdatsioon osooni toimel on pindreaktsioon, mis kulgeb nii vee kui ka orgaanilise faasi pind-kihtides. Nende osatähtsus sõltub reagentide jaotuskoefitsientidest ja kontsentratsioonidest. Faasidevahelist massivahetust kiirendab keemiline reaktsioon. On määratud fenooli, 4-metüülfenooli, 4-klorofenooli ning osooni massiülekande koefitsient, kiirendustegur ja jaotuskoefitsient erinevate solventide puhul.