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46

MEASUREMENT OF THE OXYGEN MASS TRANSFER THROUGH THE AIR-WATER INTERFACE

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PRESS

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CONTENTS

1. LIST OF ORIGINAL PUBLICATIONS

The thesis consists of the review and the three original articles listed below. These are referred in the text by Roman numerals. The review summarizes and supplements the articles.

I. E. Mölder, T. Tenno, P. Nigu, "The influence of surfactants on oxygen mass-transfer through the air-water surface", *Crit Rev Anal Chem* **1998**, Vol 28–2, 75–80.

II. E. Mölder, T. Tenno, A. Mashirin, "The Effect of Surfactants on Oxygen Mass-Transfer Through the Air-Water Interface" *Environ Sci Pollut Res* **2002**, Special Issue 1, 39–42.

III. E. Mölder, A. Mashirin, T. Tenno, "Measurement of the Oxygen Mass Transfer Through the Air-Water Interface" *Environ Sci Pollut Res* **2004**, in press (DOI: http://dx.doi.org/10.1065/espr2004.11.223)

2. LIST OF SYMBOLS

c	analytical concentration of the surfactant in the solution [mol/m^3]
c_e	effective concentration of the oxygen in the chamber [J/m^3]
c_{es}	effective concentration of the oxygen in the liquid phase [J/m^3]
c_s	analytical concentration of the oxygen in liquid phase [mol/m^3]
D_s	diffusion coefficient of oxygen in the surface layer [m^2/s]
D_s / l_s	oxygen mass transfer coefficient in the surface layer [m/s]
E_p	activation energy of permeation [J/mol]
J_d	oxygen flow consumed by oxygen sensor [mol/s]
J_s	oxygen flow from the chamber into liquid through the interface [mol/s]
J_Σ	total oxygen flow from the chamber [mol/s]
j_f	density of the diffusional flow of gas through the surface free of surfactants [mol/m^{2}s]
j_o	density of the diffusional flow of gas through the surface covered with surfactant molecules [mol/m^{2}s]
K	the equilibrium constant of the adsorptional process
K'	reciprocal of the equilibrium constant of the adsorptional process
k_H	Henry`s constant [J/mol]
l_s	thickness of the diffusion layer of the liquid [m]
l_d	thickness of the membrane of the oxygen sensor [m]
m_{oth}	amount of the other gases in the chamber [mol]
m_{ox}	amount of the oxygen in the chamber [mol]
P_s	permeability of the diffusion layer of the liquid [mol/m·s·Pa]
P_d	permeability of the membrane of the oxygen sensor [mol/m·s·Pa]
p_a	atmospheric pressure [Pa]
p_{ox}	partial pressure of the oxygen in the chamber [Pa]
p_v	pressure of the gas mixture (air) in the chamber [Pa]
P_s / l_s	diffusion conductivity of the surface layer [mol/m^2·s·Pa]

P_d / l_d	diffusion conductivity of the membrane of the oxygen sensor [mol/m^2·s·Pa]
R	gas constant [J/mol·K]
s_f	surface area free of surfactant molecules [m^2]
s_o	surface area covered with surfactant molecules [m^2]
S_s	surface area of the liquid under the chamber[m^2]
S_d	area of the diffusion layer of the oxygen sensor [m^2]
T	temperature [K]
t	time [s]
V	volume of the chamber [m^3]
Γ	adsorption amount of the surfactant [mol/m^2]
Γ_∞	adsorption amount of the surfactant at maximum adsorption[mol/m^2]
Θ	surface coverage

Subscripts

o	initial value (at $t \to 0$)
i	current value of the parameter

2. INTRODUCTION

Gas mass transfer through the gas-liquid interface has enormous importance in various natural and industrial processes [1,2,].

When oxygen and other gases enter and leave a water body across the air-water interface, the transfer rate is controlled by the interaction of processes of molecular diffusion and the water turbulence structure near the interface [3–8]

Mass transfer of gases through the gas-liquid interface depends on the condition of the interface. Surfactants or insoluble compounds adsorbed onto interface will inhibit gas mass transfer [9–14] and also heat transfer [15,16] through the gas-liquid surface.

Investigation of the surfaces of natural water and sewage water is complicated because there are always multitudes of different surfactants on the air-water interface. Properties of the interfaces depend both on the amount of surfactants, structure their molecule and interactions between them [17–21]. Molecular interaction between different surfactants in mixed monolayers is described [22–24]. The effect of counterions on surface layer properties of anionic surfactants is also observed [25–27].

Various modern methods for study structural and topographical characteristics of monolayers [28–34] and orientation of molecules adsorbed in the air-water interface [35–39] is presented in the literature.

The oxygen transfer across the air-water interface is of great importance for many environmental applications such as the evaluation of the transport of pollutants and nutrients in the water environment. The understanding of geochemical cycling and the maintenance of satisfactory water quality in aquatic systems are also closely related to determining how the dissolved oxygen (DO) distributes across the water surface by maintaining adequate levels of dissolved oxygen in the water body [40–44]. Low DO levels have a negative impact on fisheries, hydropower discharges, and the drinking-water treatment processes [40]. In biological wastewater treatment, aerobic microbes need oxygen to survive and degrade the pollutants. The efficiency of the biological wastewater treatment process depends to a great extent on the DO levels in the aerotank [45].

Several oxygen transfer tests are used to determine the oxygen dissolution rates in bioreactors [46,47]. Modifications of the Winkler methods [48,49] and polarogrphic analysis with the dropping-mercury electrode [50,51] in the laboratory experiments is used [52,53]. Nowadays oxygen sensors with various construction hawe been designed. Clark-type amperometric oxygen sensors [54–56] but also other type of oxygen sensors [57,58] are used widely today. The rate of increase of DO concentration through aeration with bubble diffuser depends, in addition to the oxygen mass transfer through the liquid-air interface, also on intensity of the aeration, size of the air bubbles, turbulence in the reactor, etc. [59–65].

This study was motivated by the fact that it is difficult in some occasions in the biological wastewater treatment plants to maintain necessary DO concentration in the aeration tank. One reason of this situation may be high concentration of surfactants or insoluble compounds on the wastewater surface.

Consequently, if there are surfactants on the water surface there is a need to pump more oxygen into the aerotank in order to achieve the necessary oxygen concentration in the water phase. Additional air pumping consumes more energy and thus increases the operational costs of the treatment plant.

4. METHODS FOR MEASURING GAS MASS TRANSFER THROUGH THE GAS-LIQUID INTERFACE

At first, the studies of liquid surface layer permeability to gases were designed as extensions of the water evaporation experiments. Gases were dissolved in aqueous solution and the rates of evolution into the vapor phase were measured. For example, in 1927 Langmuir reported that monolayers of oleic acid lowered the rate of evaporation of ethyl ether from saturated solution in water to one-tenth its value.

By study of the effects on the evaporation of HCl, $CHCl_3$, and H_2S from aqueous solution through various monolayer it was found that monolayer resistance was due in large measure to nondiffusional factors and that the measured resistance could not be related to a permeability.

Archer and LaMer demonstrated in 1955, that specific resistance of the organic acid monolayer depends both on chain length and surface pressure of the organic acid. Increase of chain length and surface pressure cause the increase of the specific resistance of the monolayer.

In 1959 Blank studied the permeabilities of a variety of monolayers to carbon dioxide and oxygen. By careful examination of the experimental parameters, it was possible to choose conditions in which convection was absent and to demonstrate that the measurements led to an estimate of monolayer permeability. The apparatus used for these studies was a temperature-compensated differential manometer. The results of a number of studies indicated that the permeability of a monolayer to a gas depends upon the size of the permeant, that there were no solubility or partition effects in the monolayer and that there appeared to be interference effects between a permeating gas and another gaseous component of the system. The results also indicated that the effects of monolayer chain length and polar group were in line with those that had been observed in the case of water permeation.

Plevan and Quinn developed in 1966 an apparatus using a pressure transducer to allow the data to be recorded automatically, and their results were in line with those reported by Blank.

Hawke and co-workers, who studied the permeability of monolayers to H_2S and CO_2 with the aid of radioactive gases, measured values that are substantially in agreement with those reported earlier.

A measure of monolayer permeability to gases was obtained indirectly by measuring the gas transport through a soapstabilized bubble at the gas-solution interface. When drainage is complete and the top of the bubble consists of an equilibrium film composed of two monolayers and a thin layer of water in between, it is possible to measure the decrease in diameter of the bubble as gas diffuses out and to relate this to monolayer permeability [66].

Modern method to measure oxygen transfer through the gas-liquid interface is fluorescence oxygen visualization (FOV) method. This method is based on laser-induced fluorescence (LIF) technique. For example pyrenebutyric acid is used as a fluorescent indicator of oxygen, and an intensive charge coupled-device (ICCD) camera as an image detector. Dissolved oxygen concentration is measured through oxygen quenching of the fluorescence from dissolved pyrenebutyric acid [67,68].

Oxygen transfer rate from gas phase to liquid phase through surfactants layer on the surface was measured using electrochemical oxygen sensor. This approach uses an inverted ultramicroelectrode (UME), stationed in the water phase at micrometer distances from the air-water interface, to perturb the equilibrium distribution of oxygen between the two phases. The interface was established in a Langmuir trough, allowing the controlled compression of the 1-octadecanol monolayer. The reduction of oxygen at the UME creates a depleted region adjacent to the interface, which provides the thermodynamic force for the transfer oxygen from the air to the water phase. The steady-state current response, measured as a function of UME-surface separation at various 1-octadecanol monolayer compressions, demonstrates that the oxygen transfer rate is governed primarily by the accessible free area of the surface [69].

5. MEASURING TECHNIQUE

5.1. Description of measuring device

An original measurement cell was worked out for oxygen mass transfer rate measurements [I].

The most important part of the measurement cell is a chamber containing the electrochemical oxygen sensor inside it (Figure 1). The oxygen sensor "TriOximatic 300" and oxygen meter "Oxi 3000" (Wissenschaftlich-Tehnische Werkstätten GmbH) were used.

The volume of the chamber is filled with gas mixture containing oxygen and surrounded by the walls of the chamber and the surface of the liquid. The gas exchange between inside volume of the chamber and the external environment takes place only (excluding self-consumption of the oxygen sensor) through the investigated surface layer. Pressure of the gas mixture (air) in the chamber is equal to atmospheric pressure $(p_v = p_a)$.

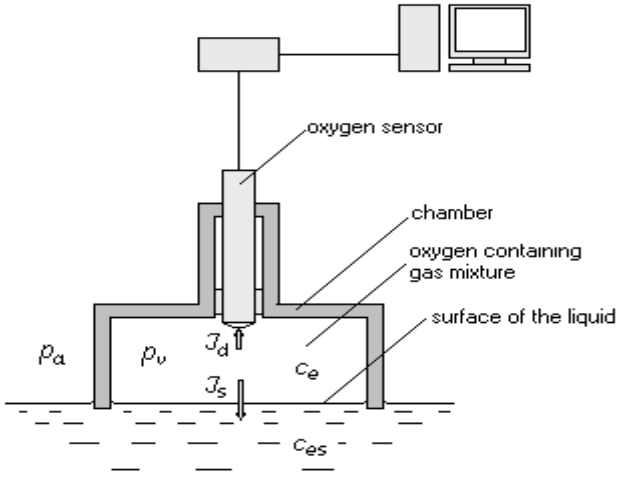

Figure 1. Schematic diagram of the device.

Oxygen is removed from the solution by adding Na_2SO_3, which triggers the oxygen mass transfer from the chamber through air-liquid interface into liquid phase.

Measuring device and investigated liquid were thermostated.

At the start of experiment deoxygenated investigated liquid was carefully raised up to touch horizontally placed lower border of the chamber (Figure 1).

5.2. Mathematical description of transient process of oxygen mass transfer

Total oxygen flow J_Σ from the chamber (Figure 1) can be written as follows:

$$J_\Sigma = J_d + J_s \ . \qquad (1)$$

Oxygen flow consumed by sensor can be expressed as $J_d = S_d * (P_d / l_d) * c_e$, where S_d is the area of the membrane of the oxygen sensor, P_d is permeability of the diffusion layer of the oxygen sensor, l_d is thickness of the diffusion layer of the membrane of the oxygen sensor, and c_e is effective concentration of the oxygen in the chamber [70]. Oxygen flow from the chamber into liquid through the interface can be expressed as $J_s = S_s * (P_s / l_s) * (c_e - c_{es})$, where S_s is surface area of the liquid under the chamber, P_s is permeability of the surface layer of the liquid, l_d is thickness of the surface layer of the liquid and c_{es} is effective concentration of the oxygen in the liquid phase.

Total oxygen flow can be represented as a function of the effective concentration of oxygen in the chamber and in the liquid phase:

$$J_\Sigma = \left[S_d (P_d / l_d) + S_s (P_s / l_s)\right] * c_e - S_s (P_s / l_s) * c_{es} \ . \qquad (2)$$

Effective concentration of the oxygen in chamber quantitatively equals to partial pressure of the oxygen in the chamber ($c_e = p_{ox}$).
According to this assumption and the ideal gas equation, the effective concentration of the oxygen is described by the equation:

$$c_e = m_{ox} * \frac{RT}{V} \ , \qquad (3)$$

where m_{ox} is the amount of the oxygen in the chamber, R is the gas constant, T is temperature and V is volume of the chamber.

Effective concentration of the oxygen in liquid phase is described by the equation:

$$c_{es} = k_H c_s \ , \tag{4}$$

where k_H is Henry`s constant, and c_s is analytical concentration of the oxygen in the liquid phase [70].

Taking into account that $p_v = p_a$ the volume of the gas mixture can be expressed as:

$$V = \left(m_{ox} + m_{oth}\right) * \frac{RT}{p_a} \ , \tag{5}$$

where m_{oth} is the amount of the other gases in the chamber.

The amount of the other gases in the chamber is constant. As the oxygen content is variable, the volume of the chamber is also variable.

Oxygen mass transfer occurs at conditions where effective concentration of the oxygen and volume of the gas mixture depend on the oxygen amount in the chamber. Oxygen sensor (Figure 1) measures directly the effective concentration of the oxygen in the chamber.

For current system, initial conditions of the process (at t = 0) could be described on the basis of equations (3) and (5) as follows:

$$c_{e,o} = m_{ox,o} * \frac{RT}{V_o} \ , \tag{6}$$

$$V_o = \left(m_{ox,o} + m_{oth}\right) * \frac{RT}{p_a} \ , \tag{7}$$

where $c_{e,o}$ is effective concentration of the oxygen at $t = 0$, $m_{ox,o}$ is the amount of oxygen in the chamber at $t = 0$, and V_o is volume in the chamber at $t = 0$.

Taking into account the equations (3,5,6 and 7), m_{ox} can be expressed by equation:

$$m_{ox} = \frac{V_o}{RT} * \frac{p_a - c_{e,o}}{p_a - c_e} * c_e \ . \qquad (8)$$

Total oxygen flow through the surface layer equals to the rate of change of the amount of oxygen in the chamber:

$$J_\Sigma = -\frac{dm_{ox}}{dt} \ . \qquad (9)$$

Differentiating the equation (8) and taking into account the equation (9), we can derive the expression for total oxygen flow:

$$J_\Sigma = -\frac{V_o p_a}{RT} * \frac{p_a - c_{e,o}}{(p_a - c_e)^2} * \frac{dc_e}{dt} \qquad (10)$$

Taking into account the equation (2), the equation (10) can be written in the following form, which describes oxygen transient process with the variables c_e and t:

$$\frac{dc_e}{dt} = -\frac{RT}{V_o} * \frac{(p_a - c_e)^2}{p_a(p_a - c_{e,o})} * \left[\left(S_d(P_d / l_d) + S_s(P_s / l_s)\right) * c_e - S_s(P_s / l_s) * c_{es}\right] \qquad (11)$$

After rearrangement equation (11) we can express equation (12) which enables calculating diffusion conductivity from experimentally measured effective oxygen concentration $c_{e,i}$ and derivative $(dc_e / dt)_i$ at any given time t_i during the process:

$$\left(\frac{P_s}{l_s}\right)_i = \frac{1}{S_s} * \left[\frac{V_o p_a}{RT} * \frac{p_a - c_{e,o}}{(p_a - c_{e,i})^2} * \left(-\frac{(dc_e / dt)_i}{c_{e,i} - c_{es}}\right) - \frac{S_d P_d}{l_d}\right] \qquad (12)$$

5.3. Calculation of the diffusion conductivity of the air-water interface

The effective concentration of oxygen, temperature and total air pressure were measured during the experiment.

Oxygen is removed from the solution by adding Na_2SO_3 ($c_{es} \approx 0$), which triggers the oxygen mass transfer from the chamber through liquid-air interface into liquid phase (Figure 1). Thus the amount of oxygen m_{ox} in the chamber decreases continuously (Figure 2) and the effective concentration of oxygen c_e also decreases in the chamber. The change rate of the oxygen concentration was measured as the percentage of the initial value of the concentration of the oxygen in the chamber. Concentration 100% is equal to the normal oxygen content in the air ($100\% = 0.2094 \cdot p_a$).

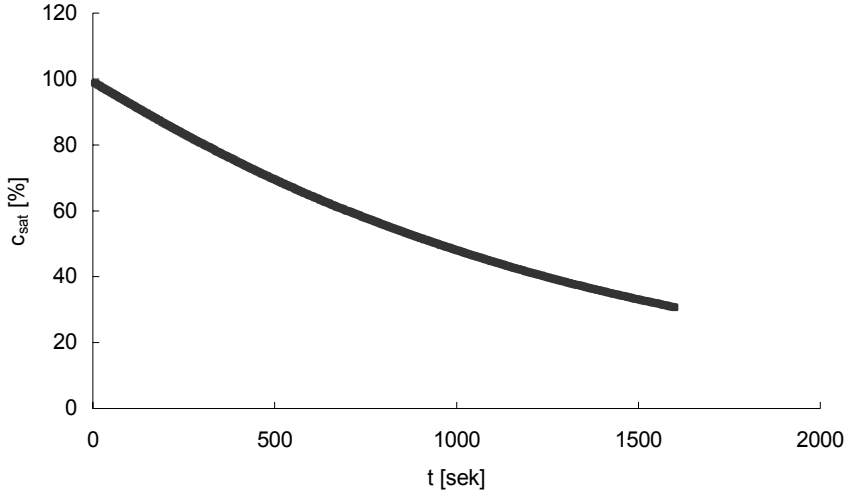

Figure 2. Decrease of the oxygen saturation in the chamber.

Oxygen sensor "TriOxmatic 300" (company WTW), with oxygen self-consumption 0.009 µg/h was used. Oxygen self-consumption of the sensor is small enough, compared with the flux of oxygen from chamber through the gas-liquid interface ($J_d << J_s$) and, thus, it is excluded from calculation. Based on the aforementioned considerations, the equation (11) can be presented in a simplified form:

$$\frac{dc_e}{dt} \cong -\frac{RT}{V_o} * \frac{(p_a - c_e)^2}{p_a(p_a - c_{e,o})} * S_s * (P_s / l_s) * c_e \ . \qquad (13)$$

The derivative dc_e / dt is found by using software that calculates from every point of the experimental curve $c_e = f(t)$ (Figure 2) the oxygen mass transfer rate at the specified time [71]. Figure 3 represents the decrease of the rate of oxygen mass transfer process during the experiment.

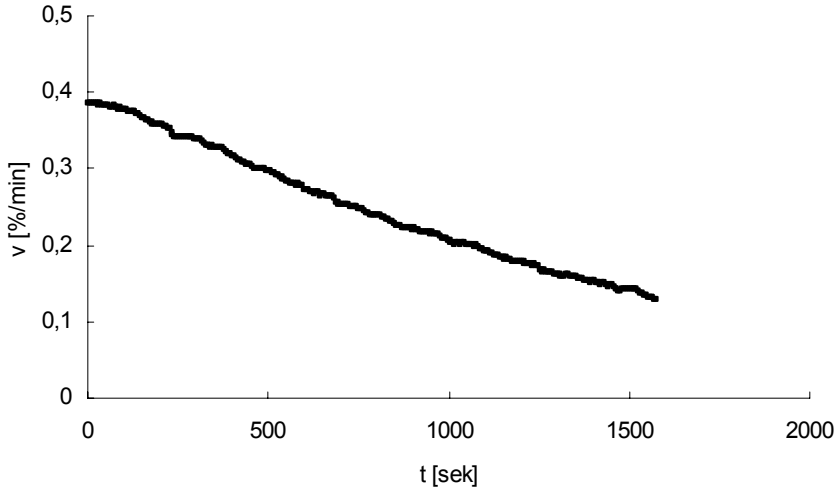

Figure 3. Decrease of the oxygen mass transfer rate through the investigated surface.

Using the equations (2) and (12), and taking into account the condition of the experiment ($J_d << J_s$ and $c_{es} \approx 0$), we can present an equation, which enables to calculate oxygen diffusion conductivity using the measured value c_e and derivative dc_e / dt:

$$\left(\frac{P_s}{l_s}\right)_i = \frac{V_o}{S_s} * \frac{p_a(p_a - c_{e,o})}{RT} * \frac{-(dc_e / dt)_i}{(p_a - c_{e,i})^2 * c_{e,i}} \ . \qquad (14)$$

We assume that oxygen permeability through the surface layer and thickness of the surface layer do not change during the experiment. Therefore, the parameter P / l should remain steady. This fact enables to use the mean value of oxygen diffusion conductivity to describe oxygen mass transfer through the air-water

interface. Figure 4 represents the value of oxygen diffusion conductivity during the experiment [III].

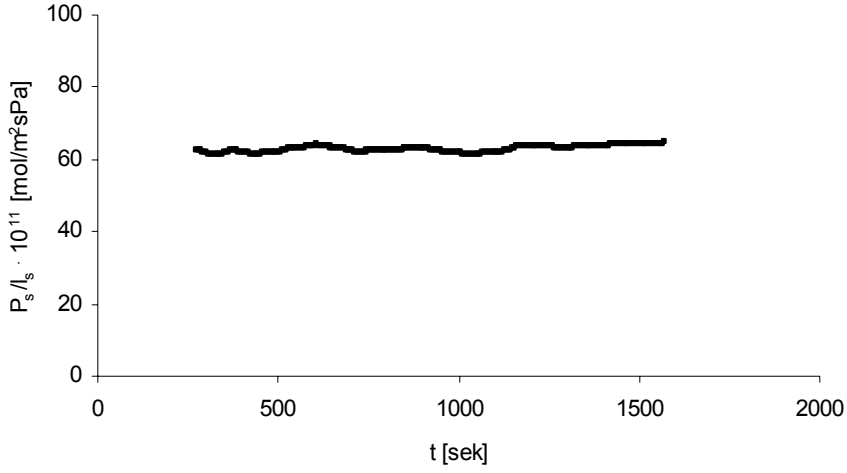

Figure 4. Oxygen diffusion conductivity of investigated surface vs. time.

6. MEASUREMENT OF SURFACE DIFFUSION PARAMETER

6.1. Diffusion conductivity of the air-water interface

At first diffusion conductivity of water surface layer using aforementioned method was measured.

Diffusion conductivity of the surface layer of the water without surfactants at temperature 20 C^{o} using effective concentration of oxygen is $P_s / l_s = 53{,}5 \cdot 10^{-11}\ \ mol/m^2 \cdot s \cdot Pa$ (standard deviation σ = 1,26) or using molar concentration of oxygen in the calculations the oxygen mass transfer coefficient is $D_s / l_s = 13 \cdot 10^{-5}\ \ cm/s$. Received value of oxygen mass transfer coefficient of water surface layer is in accordance with the data presented in literature [10,72–74].

This value is basis for comparing diffusion characteristic of different water solutions surfaces.

Temperature dependence of the oxygen diffusion conductivity through the air-water interface was compiled. It was assumed that it is induced from temperature dependence of the diffusion permeability, which ordinarily is in exponent form [75].

Therefore is dependence $P_s / l_s = f(T)$ given in exponential form to:

$$P_s / l_s = (P_s / l_s)_o * \exp\left[\frac{E_P}{R} * \frac{T - T_o}{T_o * T}\right], \qquad (15)$$

where $(P_s / l_s)_o$ is volume of P_s / l_s by $T = T_o$.

In our case $T_o = 293.16\ \ ^oK$ ($20.0\ \ ^oC$). If $|T - T_o| << T_o$ we can equation (15) represent in the following form:

$$P_s / l_s \cong (P_s / l_s)_o * \exp\left[\frac{E_P}{R} * \frac{T - T_o}{T_o^2}\right]. \qquad (16)$$

The same equation in logarithmic form:

$$\ln\left[P_s / l_s\right] \cong \ln\left[(P_s / l_s)_o\right] + \frac{E_P}{R} * \frac{T - T_o}{T_o^2} . \qquad (17)$$

By temperature $T_o = 293.16\ {}^oK$ ($20\ {}^oC$) equation (17) gives next value: $(P_s / l_s)_o = 54{,}3 \cdot 10^{-11}, mol/(m^2 \cdot s \cdot Pa)$ and $E_p = 14.75 \cdot 10^3\ J/mol$.

Table 1 shows the data of oxygen mass transfer coefficient and diffusion conductivity at variable temperatures measured by using aforementioned tehnique.

Table 1. Temperature dependence of oxygen mass transfer coefficient and diffusion conductivity of surfactant free water surface layer.

Temperature $T, {}^oC$	$\overline{D_s / l_s}$, $cm * s^{-1}$ $*10^5$	$\overline{P_s / l_s}$, $mol \cdot m^{-2} Pa^{-1} s^{-1}$ $*10^{11}$	Stdev. of $\overline{P_s / l_s}$ $mol \cdot m^{-2} Pa^{-1} s^{-1}$ $*10^{11}$
16,5	11,7	48,6	0,93
20,0	13,0	53,5	1,26
22,0	13,9	56,6	3,67
25,0	15,6	60,8	1,18

As we can see is difference with experimental data of diffusion conductivity (Table 1) and value of $(P_s / l_s)_o$ calculated from equation (17) at 20°C is $0{,}8 \cdot 10^{-11}\ mol/(m^2 \cdot s \cdot Pa)$ or $\approx 1{,}5\%$.

Figure 5 represents temperature dependence of diffusion conductivity of air-water interface calculated by using experimental data at investigated temperature interval.

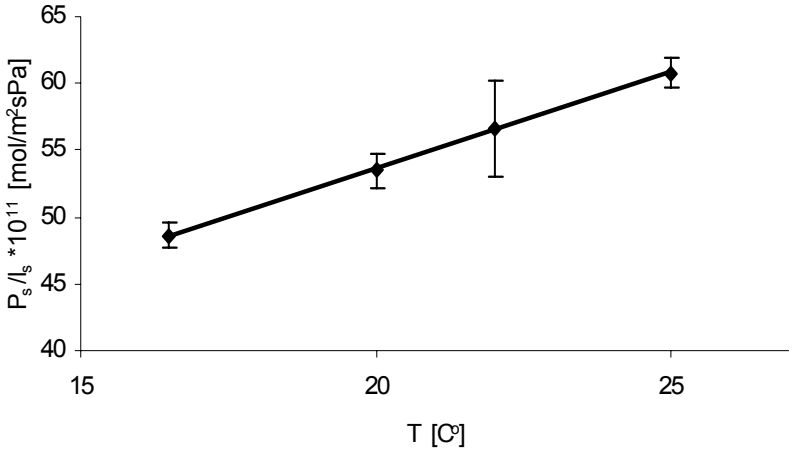

Figure 5. Temperature dependence of diffusion conductivity air-water interface.

6.2. Diffusion conductivity of butanol isomer surface layers

Short hydrocarbon chain alcohols as fast adsorbed and non-micellar surfactants for test-surfactants were selected [76,77].

The surfactants used in the current measurement were 1-butanol (n-butanol), 2-butanol (sec-butanol), 2-methyl-propanol (iso-butanol), and 2-methyl-2-propanol (tert-butanol).

Using the previously described technique, diffusion conductivites of butanol isomers were measured. Table 2–5 presents the values of diffusion conductivity of the solution surface layer by the different bulk concentration of the butanol isomers. In third column are given values of standard deviation at given measurements.

Table 2. Diffusion conductivity of 1-butanol

$c*10^5$, mol/l	$\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$	Stdev. of $\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$
0	52.01	3.88
2.55	43.07	2.53
5.1	39.57	3.65
10.2	31.56	2.43
20.04	23.98	4.46
30.24	20.84	3.44
40.07	17.51	2.26
61.93	14.44	2.50
80.14	12.03	1.37
98.36	13.41	3.26

Table 3. Diffusion conductivity of 2-butanol

$c*10^5$, mol/l	$\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$	Stdev. of $\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$
0	47.66	2.90
2.54	35.98	1.37
5.07	31.82	1.03
10.15	25.17	2.10
19.94	18.93	1.49
30.09	15.18	1.96
39.87	11.45	0.89
61.62	9.35	0.50
79.74	8.96	0.81
101.49	8.38	1.61

Table 4. Diffusion conductivity of 2-methyl-propanol

$c*10^5$, mol/l	$\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$	Stdev. of $\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$
0	48.94	3.70
2.53	39.65	2.67
5.06	35.89	2.30
10.11	29.14	1.16
19.86	24.21	1.60
29.97	20.32	1.90
39.72	16.87	2.81
61.39	13.69	1.21
79.45	13.58	0.47

Table 5. Diffusion conductivity of 2-methyl-2-propanol

$c*10^5$, mol/l	$\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$	Stdev. of $\overline{P_s/l_s}*10^{11}$ $mol\cdot m^{-2}Pa^{-1}s^{-1}$
0	54.47	2.94
2.47	51.85	2.51
4.95	48.18	3.43
9.9	46.25	3.51
30.05	42.59	3.35
60.09	41.24	2.81
81.3	38.09	4.20
98.97	33.80	3.50

Figure 6 shows diffusion conductivity for different concentrations of the butanol isomer solutions constructed using data Table 2–5.

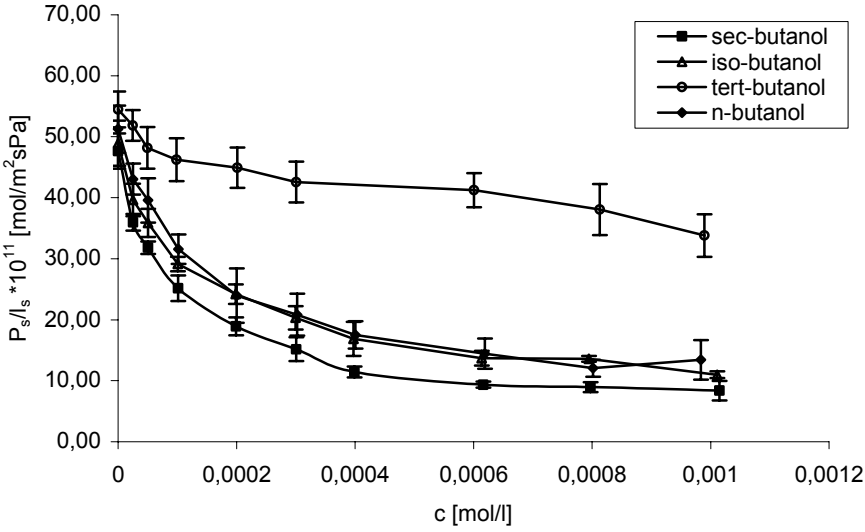

Figure 6. Diffusion conductivity of butanol isomers by their small bulk concentrations.

Based on data presented in the Figure 6 we can recognize that on the air-water interface adsorbed alcohol monolayer is significant impediment to the oxygen mass transfer already at very small bulk concentration of alcohol. This monolayer condition is called a two dimensional gas phase and characteristic for this condition is low surface concentration and large area per adsorbed molecule compared to maximum adsorption [78,79].

Further increase of surfactant bulk concentration does not have such substantial influence to the oxygen permeability through the surface layer.

6.3. Measuring of diffusion conductivity of the wastewater surface layer

The fact that the oxygen sensor is not in contact with the investigated liquid eliminates the possibility of damaging the operationality of the sensor and permits this technique to be used for investigating the different gas-liquid surfaces.

Diffusion conductivity of oxygen through wastewater surface layer was measured (Table 6) [III]. Wastewater may contain different surfactants and insoluble compounds that decrease oxygen permeability through the surface layer of wastewater.

Table 6. Diffusion conductivity of oxygen through selected wastewater surface layers.

Pollution source	Diffusion conductivity* $mol/m^2 \cdot s \cdot Pa$ $*10^{11}$	Stdev. $*10^{11}$
Municipal	9,03	0,19
Dairy	9,66	0,08
Dairy (diluted 1:5,5)	9,61	0,53
Production stage of dairy (diluted 1:50)	10,64	0,67
Production stage of dairy (diluted 1:200)	10,82	0,94
Meat industry	13,49	0,30
Cardboard factory	17,21	0,99

* – these values are derived from specific pollution sources and may be not characteristic of this category of wastewaters in general.

As we can see from Table 6, diffusion conductivity of the surface layers of different pollution sources differs about two times. The diffusion conductivity of different wastewaters was about 3 to 6 times less than in unpolluted water surface. It was observed that dilution of wastewater does not affect the oxygen diffusion conductivity trough the wastewater surface layer. We can explain this fact with the presence of very surface-active compounds in the wastewater which have significant influence on the oxygen permeability of the air-water interface even at very low bulk concentration [12,13].

7. MODELING OF DIFFUSION FLOW THROUGH THE GAS-LIQUID INTERFACE

7.1. Mathematical model of the diffusion flow through the gas-liquid interface

The amount of the surfactant in the gas-liquid interface as a function of the total concentration of the surfactant can be described by the Langmuir equation [80]:

$$\Gamma = \Gamma_{\infty} \frac{Kc}{1 + Kc} \qquad (18)$$

where: Γ is the number of surfactant moles per unitary area
Γ_{∞} is Γ value if $c \to \infty$
c is the molar concentration of the surfactant in the solution

K is the equilibrium constant of the adsorptional process, which is equal to the ratio of rate constants of adsorption and desorption.

The current study employs the model where the boundary layer of the solution consists of two parts. The unitary boundary layer can be represented so that part of the surface is covered with adsorbed surfactant molecules and part of the surface is free (Figure 7). The model is based on the idea that the surface area is covered with adsorbed surfactants molecules which are separated from each other by free surface.

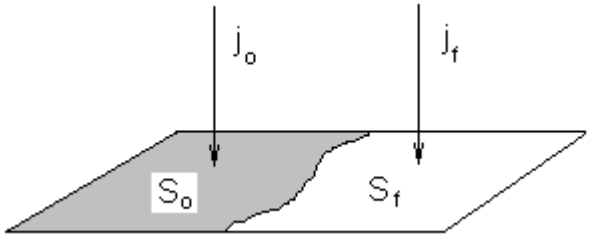

Figure 7. Boundary layer
s_f – surface area free of surfactant molecules
s_o – surface area covered with surfactant molecules

If s is the unitary surface area, then:

$$s = s_f + s_o \tag{19}$$

$$s_o = s \cdot \Theta \tag{20}$$

$$s_f = s - s_o = s \cdot (1 - \Theta) \tag{21}$$

Taking into account that surface coverage $\Theta = \Gamma/\Gamma_{max}$ and substituting constant K by its reciprocal $K' = 1/K$ in equation (18), we obtain a far more convenient equation for Θ interrelation to surfactant molar concentration c in the solution [2]:

$$\Theta = \frac{c}{K' + c} \tag{22}$$

Now we can using equations (21) and (22) represent the area of free surface s_f versus the concentration of the surfactant in solution c:

$$s_f = s \cdot \left(1 - \frac{c}{K' + c}\right) = s \cdot \frac{K'}{K' + c} \tag{23}$$

Similarly to equation (19) it is possible to express the density of diffusional flow of gas j through the gas-liquid interface as a sum of two components (Figure 7):

$$j = j_f + j_o \tag{24}$$

where: j_f is the density of the diffusion flow of gas through the surface free of surfactants and j_o is the density of the diffusion flow of gas through the surface covered with surfactant molecules

Correspondingly j_f and j_o can be expressed by using the maximum diffusion flow:

$$j_f = \frac{s_f}{s} \cdot j_{f,\max} \quad ; \quad j_o = \frac{s_o}{s} \cdot j_{o,\max} \tag{25,26}$$

where: $j_{f,\max} = k_f \cdot \Delta c_e$ is the density of the diffusion flow through the surface layer by a surfactant concentration of $c = 0$ in the solution.

$j_{o,\max} = k_o \cdot \Delta c_e$ is the density of the diffusion flow through the surface layer by maximum adsorption at given surfactant.

k_f is the diffusion constant of gas at the surface layer free of surfactants.

k_o is the diffusion constant of gas at the surface layer covered with surfactants.

Δc_e is the difference of concentrations of gas between two phases.

Combining equations (25,26) into equation (24) and taking into account equations (22,23) we obtain equation (27), which describes diffusion across the gas-liquid interface in the presence of the adsorptional layer:

$$j = j_{f,\max} \cdot \left[1 - \left(1 - \frac{k_o}{k_f} \right) \cdot \frac{c}{K^{/} + c} \right] \qquad (27)$$

7.2. Oxygen mass transfer through the air-alcohol solutions interface

The substances used in this experiment were methanol, ethanol, 1-propanol, 1-butanol and 1-penthanol. Oxygen mass-transfer rates for every solution investigated were compared with that for pure water surface.

Decrease of oxygen concentration in the cell (Figure 1) during time was measured at different surfactant concentrations. The slopes of the curves (Figure 2) characterize the rate of the diffusion of oxygen across the air-water interface.

Based on the knowledge that at the beginning of the experiment oxygen concentration inside the cell is equal to oxygen concentration in the air and know size of the measuring chamber (Figure 1) it is possible to calculate oxygen flow j through the boundary layer at a given surfactant concentration in the solution.

Figure 8 shows the values of total oxygen diffusion flow through the gas-liquid interface j at different surfactant bulk concentrations compared with the total diffusion flow for pure water surface $j_{\max}$.

As seen from Figure 8, oxygen flow through the boundary layer decreases especially steeply at very low concentrations of surfactants. It can be explained with the adsorption of surfactants on the surface. If the concentration of surfactants increases, the relative increase of the surface area covered with surfactants decreases. An increase of the surfactant concentration causes a decrease of oxygen flow through the boundary layer. Further increase of surfactant bulk concentration has much lower influence on the oxygen permeability through the investigated interface.

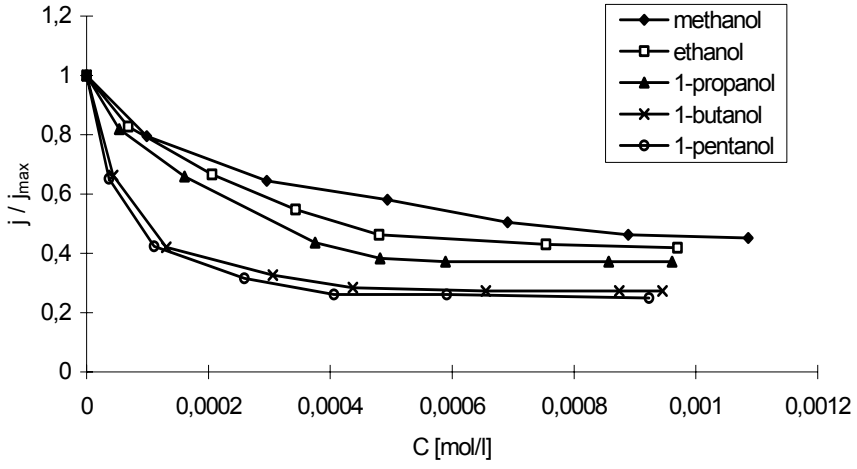

Figure 8. Relative value of the diffusion flow of oxygen depending on the surfactant concentration in the solution.

Equation (27), which describes the diffusion of gas through the surface layer, can be transformed to a more appropriate form to process the obtained experimental data:

$$\delta j = \frac{\delta k \cdot c}{K^{/} + c} \qquad (28)$$

where: $\delta j = 1 - \frac{j}{j_{f,\max}}$ is the relative decrease of the density of the diffusional flow of oxygen at given concentrations of the surfactant in the solution.

$\delta k = 1 - \frac{k_o}{k_f}$ is the relative value of the diffusional permeability of the surface layer at the maximum adsorption of surfactant molecules

The values of δj and c obtained from the experiment were inserted into equation (28) and by using the method of the least squares, constants δk and K' were gained. Constant K' is reciprocal equilibrium constant of the adsorptional process at a given surfactant. Constant δk characterizes the oxygen diffusional permeability of the air-water interface.

Every surfactant has its own characteristic value of δk and K' (Table 3).

Table 3. Values of constants δk and K' for different surfactants

Surfactant	K´	δk
methanol	26.3	0.680
ethanol	21.4	0.725
1-propanol	16.2	0.763
1-butanol	5.1	0.776
1-pentanol	4.5	0.798

Based on the data presented in Table 3, graphs were constructed (Figure 9 and 10). Those graphs show the values of constants δk and K' depending on the length of the carbon chain of homological alcohols used as surfactants.

As seen from Figure 9, an increase in the number of carbon atoms decreases constant K'. As K'=1/K, the increase of the carbon number of alcohol increases equilibrium constant K. That kind of dependence is in accordance with the data presented in literature [81, 82].

The increase of δk and the impediment of the boundary layer to oxygen mass transfer as the number of carbon atoms in alcohols increases, is also clear (Figure 10). As $\delta k = 1 - \frac{k_o}{k_f}$, it is easy to see that the decrease of oxygen

diffusion constant k_o through the surface covered with the surfactant increases δk. Consequently, the longer is the surfactant molecule, the stronger is the impediment to oxygen diffusion through the air-water surface [II].

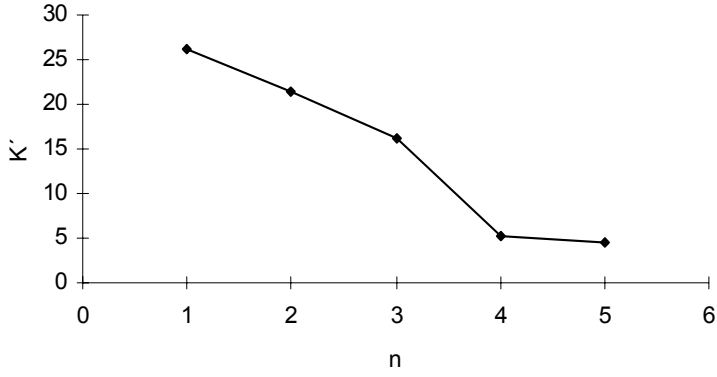

Figure 9. Values of adsorptional equilibrium constant $K^{/}$ versus the number of carbon atoms in aliphatic alcohols.

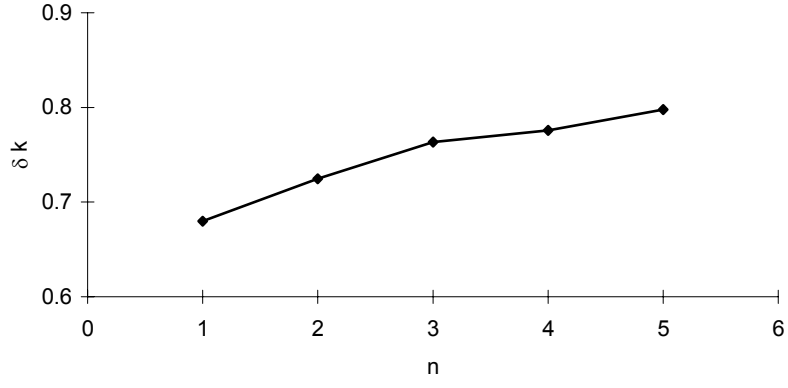

Figure 10. Values of relative diffusion permeability δk versus the number of carbon atoms in aliphatic alcohols.

8. CONCLUSIONS

Gas mass transfer through the gas-liquid interface has enormous importance in various natural and industrial processes. Surfactants or insoluble compounds adsorbed onto interface will inhibit gas mass transfer through the gas-liquid interface.

In this study, in principle novel technique for measuring the oxygen mass transfer through the air-water interface is presented. The measuring device, which is based on an electrochemical oxygen sensor, measures the decrease of oxygen concentration in the volume of the chamber that is in contact with deoxygenated liquid. Experimental data obtained with the device were incorporated into a novel mathematical model, which allowed calculating diffusion conductivity of liquid surface layer and oxygen mass transfer coefficient in the liquid surface layer.

These values of the parameters enable comparing resistances of the gas-liquid interface to oxygen mass transfer in the case of adsorption of different substances onto the liquid surface layer.

Oxygen mass transfer coefficient in the surface layer of the water without pollutants at temperature 20°C is measured $D/l = 13 \cdot 10^{-5}\ \ cm/s$.

Temperature dependence of the oxygen diffusional conductivity through the air-water interface was compiled.

The substances used in the current study were methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-butanol (sec-butanol), 2-methyl-propanol (iso-butanol), and 2-metyl-2-propanol (tert-butanol). The obtained results showed that the impediment to oxygen mass-transfer through the air-water interface depends on the concentration and molecule structure of the surfactant used.

A mathematical model was proposed, which allowed us to calculate the characteristic constants of surfactants – $K^{/}$ and δk starting from the experimental results. $K^{/}$ is the reciprocal equilibrium constant of the adsorptional process and δk characterizes the influence of the surfactant to oxygen mass transfer through the air-water interface.

The fact that the oxygen sensor is not in contact with the investigated liquid eliminates the possibility of damaging the operationality of the sensor and permits this technique to be used for investigating the different gas-liquid surfaces.

Diffusion conduction of oxygen through wastewater surface layer of selected pollution sources was measured.

Consequently we can recognize that by means of the developed device it is possible to measure the total impediment of the air-water interface to oxygen mass transfer.

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10. SUMMARY IN ESTONIAN

Hapniku massiülekande mõõtmine läbi õhk-vesi piirpinna

Gaaside massiülekandeprotsessid läbi õhk-vesi piirpinna on määravaks teguriks paljudes looduslikes ja tehnoloogilistes protsessides. Vees leiduvatele elusorganismidele on eriti tähtis lahustunud hapniku olemasolu vees. Fotosünteesi käigus veetaimedest eralduv hapnik kasutatakse osaliselt ära pimedal ajal taimede poolt. Samuti kulub palju hapnikku taimede lagundamiseks. Seega satub põhiline osa täiendavast hapnikust vette atmosfäärist, difundeerudes läbi õhk-vesi piirpinna.

On kindlaks tehtud, et õhk-vesi piirpinnale adsorbeerunud pindaktiivse aine või vees lahustumatu aine kile takistab hapniku massiülekandeprotsessi läbi piirpinna.

Käesolev uurimus sai alguse praktilisest vajadusest määrata reovee piirpinna takistust hapniku massiülekandele. Uuritavas reoveepuhastis esines olukordi, kus tekkis raskusi nõutava lahustunud hapniku taseme hoidmisega aktiivmuda basseinis.

Bioloogilise puhastusprotsessi aktiivmudabasseinis lahustunud hapniku hulgast sõltub otseselt puhastusprotsessi efektiivsus. Vajaliku hapniku kontsentratsiooni saavutamiseks reovees, mille pind omab suurt takistust hapniku massiülekandele tuleb kulutada rohkem energiat aeratsioonile ja seega reovee puhastuse hind tõuseb.

Õhk-vesi piirpinna summaarse takistuse mõõtmiseks hapniku massiülekandele töötati välja uudse lahendusega elektrokeemilisel hapnikuanduril põhinev mõõteseade.

Mõõteseadme tähtsaimaks osaks on mõõterakk, mis koosneb allapoole avanevast õhuga täidetud mõõtekambrist ja selles asuvast elektrokeemilisest hapnikuandurist. Katse algul viiakse uuritava lahuse pind vastu mõõtekambri alumist serva. Seega saab mõõtekambris olev gaas väljuda sealt ainult läbi uuritava lahuse pinna (hapnikuanduri omatarvet arvestamata). Selleks, et tekitada hapniku voogu läbi uuritava piirpinna on uuritavast lahusest lahustunud hapnik eemaldataud naatriumsulfiti lisamise teel.

Mõõtekamber ja uuritav lahus on termostateeritud.

Mõõtes hapniku kontsentratsiooni vähenemise kiiruse mõõtekambris, mis on võrdeline hapniku massiülekandekiirusega läbi uuritava piirpinna, temperatuuri ja õhurõhu ning teades mõõtekambri ruumala ja pindala saame arvutada uuritava piirpinna difusioonilisi parameetreid.

Välja on töötatud matemaatiline mudel ja selle põhjal on koostatud arvuti-programm, mis võimaldab lähtuvalt katsetingimustest ja mõõtmistulemustest arvutada uuritava piirpinna difusioonilise juhtivuse ja hapniku massiülekande koefitsendi antud tingimustel.

Kasutades kirjeldatud metoodikat mõõdeti adsorbaadi molekulidest vaba õhk-vesi piirpinna takistus hapniku massiülekandele, mis on võrdlusparameetriks kõigi vesilahuste jaoks. Puhta õhk-vesi piirpinna hapniku massiülekande koefitsendiks temperatuuril 20 ^{o}C saadi $D/l = 13 \cdot 10^{-5}\ cm/s$.

Koostati õhk-vesi piirpinna difusioonilise juhtivuse temperatuurisõltuvus temperatuuride vahemikus 16,5–25^{o}C.

Uuriti pindaktiivsete ainete mõju õhk-vesi piirpinna hapnikuläbilaskvusele. Uuritavate ainetena kasutati metanooli, etanooli, 1-propanooli, 1-butanooli ja 1-pentanooli ning butanooli isomeere 2-butanooli, 2-metüül-propanooli ja 2-metüül-2-propanooli. Näidati, et õhk-lahus piirpinna takistus hapniku massiülekandele sõltub pindaktiivse aine kontsentratsioonist lahuses ja pindaktiivse aine molekuli ehitusest.

Kuna katseseadmes kasutatav hapnikuandur ei ole otseses kontaktis uuritava lahusega siis on võimalik kirjeldatud seadmega uurida igasuguste lahuste

piirpindasid ilma, et need mõjutaksid hapnikuandurit ja seega ka saadavaid tulemusi. Seega saame kasutades antud metoodikat määrata ka reovee piirpinna takistust hapniku massiülekandele. Leiti, et mõõdetud reoveeproovide piirpinna difusiooniline juhtivus oli 3 – 6 korda väiksem kui puhta veepinna korral.

Töötati välja matemaatiline mudel, mis kirjeldab dfusiooniprotsessi läbi gaas-vedelik pindkihi.

Kokkuvõtteks võib öelda, et kirjeldatud mõõtmismetoodikat on võimalik kasutada vesi-õhk piirpinna summaarse takistuse mõõtmiseks hapniku massiülekandele.

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12. PUBLICATIONS

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2. **E.Mölder**, T.Tenno, A.Mashirin, "The Effect of Surfactants on Oxygen Mass-Transfer Through the Air-Water Interface" *Environ Sci Pollut Res* 2002, Special Issue 1, 39–42.
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