CHEMISTRY

Research of oxygen mass transfer through the air–water surface at low bulk concentrations of surfactants

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Abstract. Oxygen transfer from the gaseous to the liquid phase is often technologically a very energy-consuming process. We studied the influence of small alcohol molecules (1-butanol, 2-butanol, 2-methyl-propanol, and 2-methyl-2-propanol) as surfactants to oxygen permeability and addressed the importance of experimental methodology. The oxygen mass transfer rate in the air–water surface layer was calculated by using an original technique and the results were compared to the surface tension values obtained by the Du Nouy ring method. Our experiments revealed that oxygen permeability was inhibited already at very low surfactant concentrations (0.1–1 mmol/L), whereas a considerable increase in the surface tension was observed in a 1000-fold higher concentration range. These results demonstrate the importance of methodological considerations in the research of surface action of surfactants.

Key words: surface chemistry, air–water surface, oxygen permeability, surface tension, oxygen mass transfer.

INTRODUCTION

Gas mass transfer through the gas–liquid interface has an enormous importance in various natural and industrial processes, including wastewater treatment and fish farming. The aeration process is the most energy-consuming process in biological wastewater treatment, whereas impaired oxygen permeability caused by various chemicals at the air–water surface plays an important role in industrial wastewater treatment facilities. Thus, a thorough understanding of the inhibiting factors and estimation methodologies of gas transfer is of great importance.

The gas mass transfer rate through the gas–liquid surface is controlled by the interaction of processes of molecular diffusion and the water turbulence structure near the surface [1,2]. Surfactants and insoluble compounds can be adsorbed onto the surface and therefore inhibit gas mass transfer through the gas–liquid surface [3–5]. Properties of the surfaces depend on the amount of surfactants, their molecular structure, and interactions between them [6–8]. Therefore, detailed understanding of the particular surface properties and molecular structure is of crucial importance in revealing the gas transfer into different surfactant solutions.

Several oxygen transfer tests are used to determine the oxygen dissolution rates in bioreactors [9]. In bioreactors the rate of the increase of dissolved oxygen concentration through aeration with bubble diffuser depends, in addition to the oxygen mass transfer through the liquid–air surface, also on the intensity of the aeration, the size of the air bubbles, the turbulence in the reactor, the proportion of the reactor, etc. [10–13]. All these factors depend on the technological peculiarities of the particular process. Although these methods are suitable for describing the specific technological oxygen transfer processes, they are not applicable for the characterization of the effect of media on the oxygen transfer rate.

Various modern methods for studying structural and topographical characteristics of monolayers [14–17] and the orientation of molecules adsorbed in the air–water surface [18–19] are presented in the literature. One of the methods, which allows direct observation of oxygen transfer through the gas–liquid surface, is a fluorescence oxygen visualization method based on the laser-induced fluorescence technique [20,21]. Although these methods provide us an adequate insight into surface characteristics, they cannot be directly related to the gas mass

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transfer process. The oxygen transfer rate from the gas phase to the liquid phase through the surfactant layers on the surface was also measured using an electrochemical oxygen sensor. This approach uses an inverted ultra-microelectrode, stationed in the water phase at micrometre distances from the air–water surface, to perturb the equilibrium distribution of oxygen between the two phases. The surface was established in a Langmuir balance, allowing a controlled compression of the 1-octadecanol monolayer. This study demonstrates that the oxygen transfer rate through the gas–liquid interface is governed primarily by the accessible free area of the surface [22].

In the present study we investigated the effect of short-chain alcohol molecules on two distinct properties of the gas–liquid interface. We found that there was a dramatic difference in the bulk concentration of alcohol when the effect on the oxygen permeability or surface tension was observed.

METHODS

Oxygen mass transfer rate measurements

An original measurement cell was developed earlier for oxygen mass transfer rate measurements [23]. The most important part of the measurement cell is a chamber containing an electrochemical oxygen sensor (Fig. 1). An oxygen sensor 'TriOximatic 300' and an oxygen meter 'Oxi 3000' produced by Wissenschaftlich-Technische Werkstätten GmbH, Germany, are used. The volume of the chamber is filled with a gas mixture containing oxygen (air) and is surrounded by the walls of the chamber and the surface of the liquid. Gas exchange between the inside volume of the chamber and
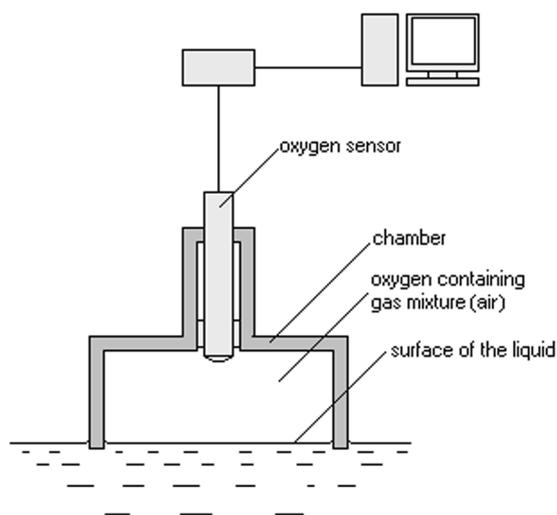

Fig. 1. Measuring device.

the external environment takes place only through the investigated surface layer.

The self-consumption of oxygen by the oxygen sensor is in this case inconsiderable and will not be taken into account. Oxygen is removed from the solution by adding Na_2SO_3, which triggers the oxygen mass transfer from the chamber through the air–liquid surface into the liquid phase.

The measuring device and the investigated liquid were thermostatted. At the start of the experiment deoxygenated investigated liquid was carefully raised to touch the horizontally placed lower border of the chamber (Fig. 1).

The measured effective concentration of the oxygen in the chamber c_e, air pressure p_a, temperature T, and time t were incorporated into a mathematical model, which allowed calculating parameter P_s/l_s in the liquid surface layer [23]:

$$\left(\frac{P_s}{l_s}\right)_i = \frac{V_0}{S_s} \cdot \frac{p_a(p_a - c_{e,0})}{RT} \cdot \frac{-(dc_e/dt)_i}{(p_a - c_{e,i})^2 \cdot c_{e,i}}, \quad (1)$$

where c_e – effective concentration of the oxygen in the chamber, J/m^3
l_s – thickness of the diffusion layer of the liquid, m
P_s – permeability of the diffusion layer of the liquid, mol/m·s·Pa
p_a – atmospheric pressure, Pa
R – gas constant, J/mol·K
S_s – surface area of the liquid, m^2
T – temperature, K
t – time, s
V – volume of the chamber, m^3.
Subscript
0 – initial value (at $t \rightarrow 0$)
i – current value of the parameter.

We assume that oxygen permeability through the surface layer P_s and the thickness of the surface layer l_s do not change during the experiment. Therefore, the parameter P/l should remain steady during the experiment. This fact permits us to use the mean value of parameter P_s/l_s to describe the oxygen mass transfer through the air–water interface. The dimension of parameter P/l according to Eq. (1) is $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$. By replacing the dimension of oxygen partial pressure in Pa by oxygen molar concentration in $mol \cdot m^{-3}$, the dimension of oxygen mass transfer rate K_L in $m \cdot s^{-1}$ is obtained.

Surface tension measurements

Surface tension of the sample solution was measured applying the conventional Du Nouy ring method. The experiments were preformed using tensiometer K8 (Krüss, Germany) with a 20 mm diameter platinum–

iridium ring. In this method, the Pt–Ir ring is lowered by the tensiometer onto the surface of the test liquid and then driven under the surface so that it is completely wetted. The ring is then progressively raised until contact with the liquid is broken. The maximum force exerted on the ring was measured. Using this measured force value and Eq. (2) the surface tension was calculated:

$$\gamma = \frac{F}{l}, \qquad (2)$$

where γ – surface tension, N/m
  F – maximum force exerted on the ring, N
  l – length of the edge, m.

RESULTS AND DISCUSSION

First we determined the oxygen mass transfer rate through the surface layer of water with the aforementioned method. The overall oxygen transfer rate in the liquid surface layer of $K_L = 1.3 \times 10^{-6}$ m/s was observed in the water surface layer without surfactants at a temperature of 20 °C [23]. This value is in accordance with the data presented in the literature with other methodological approaches used [24–26]. This value was taken as the basis for comparing diffusion characteristics of surfaces of different water solutions.

The short hydrocarbon chain alcohols are fast adsorbed and non-micellar surfactants [27,28]. In order to diminish the complications caused be adsorption kinetics, *n*-butanol (1-butanol), *sec*-butanol (2-butanol), isobutanol (2-methyl-propanol), and *tert*-butanol (2-methyl-2-propanol) were used as test surfactants in the current study.

Oxygen mass transfer rates were measured according to the above-described technique at different surfactant bulk concentrations. The data are presented in Fig. 2.
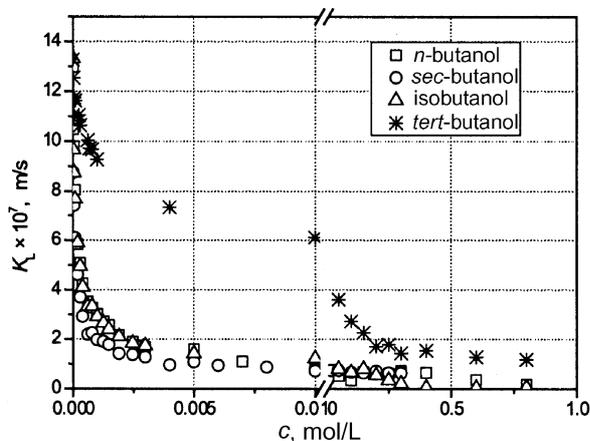
In order to compare the surface characteristics of the butanols by an alternative methodological approach, the same solutions of different alcohols were subjected to surface tension measurement according to the Du Nouy ring method. These data are shown in Fig. 3.

Based on the data presented in Fig. 2 we can demonstrate that on the air–water surface the adsorbed butanol monolayer has significant surface resistance to the oxygen mass transfer already at very small bulk concentrations of alcohol. However, a considerable decrease of surface tension was observed in about 1000-fold higher range of bulk concentration of butanols (Fig. 3). When an about 85% decrease in the oxygen permeability was achieved at the surfactant concentration of 0.002 mol/L, only about a 1% decrease of the initial surface tension was observed in this concentration range.

In order to uniformly evaluate the effect of the surfactant, we also calculated the bulk concentrations of butanols where a 50% maximum effect on oxygen mass transfer $(K_{L,\max/2})$ or surface tension $(\gamma_{\max/2})$ was achieved (Table 1). These values characterize the effect of the surfactant in a method-independent manner. As shown in Table 1, a 1200–1400-fold difference in the surfactant concentration was observed for *n*-, *sec*-, and isobutanol, whereas only a 70-fold difference was observed for *tert*-butanol.
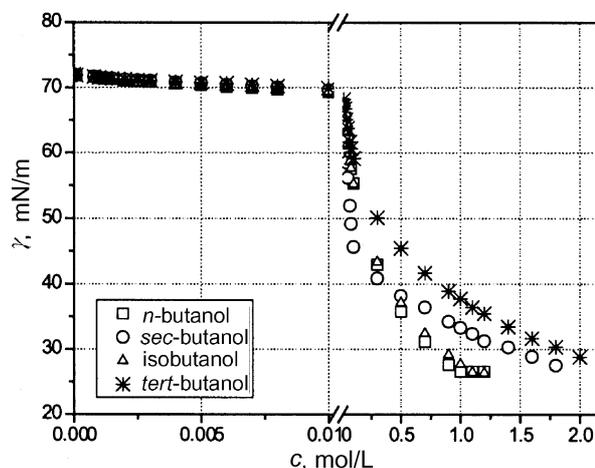

Fig. 3. Surface tension data of butanol aqueous solutions measured by the Du Nouy ring method.

Table 1. Bulk concentration of butanols when half of the maximum effect is achieved

Butanol	$c_{\gamma\,50\%}$, mol/L	$c_{\mathrm{KL}\,50\%}$, mol/L
n-Butanol (1-butanol)	0.20	1.7×10^{-4}
sec-Butanol (2-butanol)	0.13	9.6×10^{-5}
Isobutanol (2-methyl-propanol)	0.20	1.6×10^{-4}
tert-Butanol (2-methyl-2-propanol)	0.29	4.3×10^{-3}

Fig. 2. Oxygen mass transfer rates measured at different bulk concentrations of aqueous butanol solutions.

As the permeability and surface tension experiments were performed under equal experimental conditions, the surface concentration of alcohol molecules has to be equal. Thus, we propose that the mechanisms of the inhibition of oxygen permeability and surface tension have to be different for soluble, short hydrocarbon chain surfactants, whereas the gas permeability is already inhibited in the micromole concentration range. A very low bulk concentration of short-chain alcohol surfactants means also a low surface concentration. This surface monolayer condition is called a two-dimensional gas phase; and low surface concentration and large area per adsorbed molecule compared to maximum adsorption are characteristic of this condition [29,30].

In our experiments we observed no considerable differences between the oxygen mass transfer rates nor surface tension properties of the aqueous solutions of *n*-butanol, *sec*-butanol, and isobutanol. *tert*-Butanol was found to have a minor effect on the oxygen mass transfer rate at low concentrations; however, at higher concentrations equal effects on the mass transfer rates with the other alcohols were observed. Moreover, a reduction of the surface tension occurred also at higher concentrations of *tert*-butanol as compared to the other butanol isomers. The smaller decrease in its oxygen mass transfer rate can be explained by the significantly different molecular structure and thus, by different surface properties.

CONCLUSIONS

In this study we analysed surface properties of aqueous solutions of soluble short carbon chain alcohols. We used an original method for the assessment of the oxygen mass transfer through the gas–liquid surface and compared the permeability results to another important surface characteristic – surface tension. Although in both cases the effect of the surfactant on the surface characteristics was due to the bulk concentration of the surface active compound, the influence of the surfactant on the oxygen permeability at very low concentrations was much more significant than the effect on the surface tension.

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Õhu ja vee vahelise piirpinna uuringud pindaktiivse aine madalatel kontsentratsioonidel

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Kasutades originaalset metoodikat, mõõdeti õhu ja vee vahelise piirpinna takistust hapniku massiülekandele sõltuvalt eri pindaktiivsete ainete kontsentratsioonist lahuses. Pindaktiivsete ainetena kasutati butanooli isomeere. Saadud tulemusi on võrreldud uuritavate lahuste pindpinevuse andmetega. On näidatud, et oluline takistus piirpinna hapniku massiülekandele avaldub ligikaudu 1000 korda väiksematel pindaktiivse aine kontsentratsioonidel, kui toimub märgatav pindpinevuse vähenemine.