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# Gas separation ability of the liquid bubble film

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## ABSTRACT

The transport of carbon dioxide and methane through the liquid film of the bubble is studied. The liquid film is formed by blowing into a solution containing surfactants, sugar, glycerol and around 60% of weight of water, leading to formation of a bubble. Two methods were developed for the determination of the gas permeability in liquid film. The first one, denoted as a continuous inflow method, is based on measurements of a size of a bubble, to which the gas is permanently introduced. The second method, referred to as diminishing bubble method, is based on measurements of the decrease of size of a bubble, which has been previously filled by a certain volume of the testing gas. Bubbles were recorded by a camera and their size was determined by computer processing of recorded movie. Measured flux of carbon dioxide through the liquid film of the bubble corresponds to the calculated flux through the water film $J = 6.51 \times 10^{-2}\ \mathrm{mol\ m^{-2}\ s^{-1}}$ for the thickness of around 1 μm. Methane flux through bubble wall was almost negligible. Separation ability of the liquid film was tested by binary mixtures of 50 vol% of carbon dioxide and methane. The promising results, high carbon dioxide flux and separation factor were obtained.

## 1. Introduction

Transport between gas and liquid is often used for separation of mixtures of components with different physical properties. Arrangements of phase contact can be carried out in different ways; perhaps the most common arrangement is a column (either with or without fillings) into which the gas is injected through a distributor in its bottom and then flows upward, being in contact with the liquid flowing in the opposite direction.

When the volume of liquid is minimized, one obtains liquid films like soap bubbles that we all know from our childhood. The gas transport through such films could be described similarly as in the case of nonporous polymeric membranes, that is by a solution-diffusion model [1,2]. The films are therefore a powerful separation agent for gaseous mixtures, especially in the case when the components of gaseous mixture have very different solubility in used liquid (water). A typical case is carbon dioxide mixed with other non-acidic gases like methane, and this case is studied in this work. Similar separation properties can be expected also for mixtures involving hydrogen sulfide $H_2S$, sulfur dioxide $SO_2$ and ammonia $NH_3$.

The usage of liquid films as membranes for gas separation could exploit several major advantages when compared to traditional separation media: (i) their very low thickness, (ii) large difference in sorption of separated gases, (iii) very low cost and (iv) possibility to renew them easily just by forming new films. The first two properties lead to high separation efficiency, whereas the other two properties might be advantageous operational point of view.

The behavior of thin films (and foams) is reviewed e.g. by Pugh [3]. Theory about nature of the bubble structure was presented e.g. in [4,5]. For the purposes of this paper, it is sufficient to know that the bubble liquid films consist of two layers of adsorbed surfactant molecules that create boundaries of an aqueous core. Surfactants stabilize the liquid by preventing its drainage mostly via Marangoni stresses. The surfactant also decreases the water evaporation [4]. Farajzadeh et al. [4] reported that Fick's law is applicable for gas transport through soluble monolayers.

Most of studies (e.g. [6–8]) deal with the air permeation through the liquid film in situation, when a small pressure difference on opposite sides of the liquid film (in the range of tens of pascals) is the driving force of the gas transport, whereas the composition is the same on both sides of the film. Only a few papers have studied permeation of other gases than air through liquid films (an example is that by Ramanathan et al. [5] studying transport of pure nitrogen, argon and oxygen).

Papers dealing systematically with separation of mixtures containing carbon dioxide by using liquid films are not available. One of the rare investigations has been carried out by Farajzadeh et al. [9], who studied the diffusion of carbon dioxide to the liquid bulk.

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They observed that the initial permeation of carbon dioxide exceeded the estimations based on literature values of solubility and diffusivity, but the permeation flow was decreasing in time, dropping toward values lower by one order of magnitude than the initial permeation flux. Brown [6] studied the stability and permeability of different surfactant bubbles exposed to air. The drying and aging of bubble films and a decrease of flux were investigated for various surfactants.

Counter-current diffusion through an aqueous surfactant film was studied in papers [10–12]. The separation ability was investigated by observing the movement of the liquid film in a tube that was filled initially by two pure gases (each on the opposite side of the film). This experimental configuration, in which gases in the volumes on both sides of the liquid film are not mixed, has large influence of the boundary layer effect.

Gas separation using foam film has been also presented in a patent by Norman Li [13]. This device is, however, based on poly-layers foam in a column or vessel. Because of conditions quite different from those experienced by a single bubble, results from such a device cannot be used for a prediction of separation effectiveness of liquid films in another arrangement.

This contribution has two main purposes. One is the development of a reliable, easy and quick procedure for the study of the transport and separation properties of a liquid film in a wide range of application conditions. The second one is to provide data of real separation of a binary mixture of carbon dioxide and methane by the liquid film.

## 2. Experiments

### 2.1. Material

Bubble (with diameter between 20 and 30 mm) was formed from a solution for making "giant bubbles" [14], which assures stability (longevity) of thin film in range of minutes. This solution contains surfactants, sugar, glycerol and around 60% of weight of water. The measured properties of this solution are presented in Table 1.

### 2.2. Experimental methods for study of pure gases transport

Two methods were used for the study of the pure gas transport through the liquid film of the bubble.

The first one is denoted as **continuous inflow method** and to our knowledge; it has not been reported previously. This method is based on measurements of size of a bubble, to which a gas is permanently introduced. At the beginning, a constant gas flow is injected into the liquid and the bubble starts to grow. The gas permeation through the liquid film increases with the enlarging size of the bubble, i.e. with the increasing transport area. After a while, the permeation flow reaches the flow of injected gas and the bubble size then remains constant. At this instant, the feed flow rate divided by surface area of the bubble represents the gas flux through the liquid film. The change of bubble size in time during the measurement is depicted in Fig. 1.

The other method, referred to as **diminishing bubble method**, is based on the measurements of the decrease of size of a bubble, which has been previously filled by the testing gas. It is a variation of the diminishing bubble method (called also simple floating bubble method), previously described in papers [5–8], where a bubble rose from a capillary and then floated on the surface, where its shrinking was observed.

**Table 1**
Properties of solution S6.

| Temperature (°C) | 20 | 25 | 30 |
|---|---|---|---|
| Surface tension $\sigma$ (N/m) | $25.9 \times 10^{-3}$ | $25.7 \times 10^{-3}$ | $25.5 \times 10^{-3}$ |
| Dynamic viscosity $\mu$ (Pa s) | $2.34 \times 10^{-3}$ | $2.06 \times 10^{-3}$ | $1.84 \times 10^{-3}$ |
| Density $\rho$ (kg/m$^3$) | | $1.043 \times 10^{-3}$ | |

In our case, the bubble is created by manually submersing a needle that feeds the gas in a drop of solution placed on a flat glass support. The gas flow rate trough the flexible tube and needle is adjusted by a flow controller. After forming the bubble, the needle is removed. Owing to high flow rates used for this method, the bubble grew rapidly (in 1–5 s). The needle is then removed from the bubble, which starts to diminish in size (Fig. 2) due to gas permeation through the film. The permeation flux is evaluated using Eq. (1). In this arrangement, the bubble surface (that is transport area) decreases and also the thickness of the liquid film is changing. The thickness change is difficult to evaluate due to opposing effects of diminishing bubble size (thickening the film) and of film evaporation and drainage (thinning it).

The gas flux $J_i$ (ml cm$^{-2}$ s$^{-1}$) in time $t_i$ was calculated from Eq. (1) by (i) approximating the bubble shape by a hemisphere, (ii) by neglecting the counter-current permeation (of surrounding air into the bubble), and (iii) assuming constant thickness of the liquid film:

$$J_i(t_i) = -\frac{dV}{A_i dt} = -\frac{(V_i - V_{i-1})}{A_i(t_i - t_{i-1})} = -\sqrt[3]{\frac{2(V_i - V_{i-1})}{\pi d_i^2 (t_i - t_{i-1})}} \qquad (1)$$

$V_i$ is the bubble volume and $A_i$ is the surface area of bubble dome at time $t_i$.

In both experimental methods, the bubble was placed in an air stream (made using a fan) in order to remove the permeant from the environs of the bubble and hence prevent the formation of boundary layers, which decelerate the gas transport through the film.

In both methods, bubbles were recorded by a camera (Pulnix TM4200CL) in back-lit arrangement, which ensures sharp black contour. In the case of diminishing bubble method, the images were processed using a custom code written using Matlab's Image processing toolbox (see Fig. 3) and the bubble shape was integrated to evaluate the volume of gas enclosed in the bubble.

Similar evaluation was not possible for the continuous inflow method, in which the presence of filling tube hindered the identification of exact bubble boundaries by the software. The bubble volume was therefore evaluated manually with the use of ImageJ software by measuring the bubble diameter and by assuming hemispherical shape. The error of the manual evaluation was close to 5% of the total volume in most cases, but increasing toward 20% in the case of small bubbles (beginning of the bubble growth).

The continuous inflow method (compared to the diminishing bubble method) brings conditions closer to a steady-state and therefore might be more representative for some applications (e.g. a case when a long-life film is used to upgrading of biogas, as described in [15]).

### 2.3. Experimental test of separation of binary mixture

The transport of binary mixtures of gases (50 vol% of carbon dioxide and methane) was measured using the diminishing bubble method and the separation of mixture components was assessed by analyzing the composition of gas remaining in the bubble. The bubbles were created by injecting the binary gas mixture from a syringe (volume 3 ml) in a liquid drop and after varying time, the whole content of the bubble was taken off by the same syringe (that remained connected with the bubble). Glass balls in the syringe served for stirring the sample to ensure homogeneity of the gas mixture. A sample of the gas contained in the syringe was