

DETERMINATION OF SURFACTANT EFFECTIVE DIFFUSION COEFFICIENT USING INVERSE PROBLEM FOR WARD-TORDAI EQUATION

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Abstract: The main purpose of the study was to assess the usability of a new calculation algorithm for determining the surfactants effective diffusion coefficient. The adsorption of a mixture of non-ionic surfactants onto flat water-air interface was considered. Presented algorithm is composed of a two parts: Ward-Tordai equation solver based on Nyström method for integral equations and golden ratio optimization method used in inverse problem. In the investigation the Langmuir model of an isotherm was assumed. Presented algorithm was successfully used to determine the non-ionic surfactant - Nafol 810D (BRENNTAG) effective diffusion coefficient in the diffusion controlled adsorption process.

Keywords: DIFFUSION COEFFICIENT, DIFFUSION, ADSORPTION, INTEGRAL EQUATION, INVERSE PROBLEM

1. Introduction

In modelling of mass transport processes an important role plays the diffusion process, which describes the movement of molecules from a domain of higher concentration to a region of lower concentration. The mass flux is caused by a gradient of concentration of a particle in a solution.

Adsorption is defined as the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process, which is a consequence of surface energy, creates a film of the adsorbate on the surface of the adsorbent. In the systems with surfactants the monolayer is usually created, however the effects of electrostatic interactions are neglected [1]. Adsorption is usually described through the isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. These functions describes the relationship between the bulk concentration c $\left[\frac{\text{mol}}{\text{m}^3}\right]$ and surface excess Γ $\left[\frac{\text{mol}}{\text{m}^2}\right]$ of an adsorbed compound. Many models of isotherms were proposed in the literature. Their level of complexity depends on the phenomena according to the considered model. The easiest way to describe the above mentioned relation is the linear correlation called Henry isotherm and is given by eq. 1 [2].

$$\Gamma = K_H c \quad (1)$$

where K_H is a Henry constant. It is a huge simplification of the real problem because it doesn't include the finiteness of the surface. It might be useful for modelling the adsorption process in the terms of the low concentration of surfactant. More compatible with the real processes is the non-linear Langmuir isotherm given by eq. 2 [2].

$$\Gamma = \Gamma_\infty \frac{K_L c}{1 + K_L c} \quad (2)$$

where K_L is Langmuir constant and Γ_∞ $\left[\frac{\text{mol}}{\text{m}^2}\right]$ is a maximum surface excess. Both of the presented isotherms are connected with a dynamics of adsorption process. However the Gibbs isotherm, given by eq. 3, is useful to determine the equilibrium value of surface excess Γ_{eq} $\left[\frac{\text{mol}}{\text{m}^2}\right]$ of the considered system

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c} \quad (3)$$

where R $\left[\frac{\text{J}}{\text{mol K}}\right]$ is a gas constant, T [K] is a temperature of the system and γ $\left[\frac{\text{mN}}{\text{m}}\right]$ is a surface tension of the system [2].

Adsorption of non-ionic surfactants is characterized by two mechanisms – diffusion of molecules to the interface and adsorption on the surface (see fig. 1).

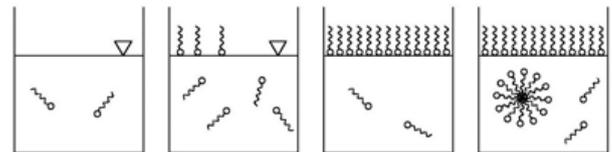


Fig.1. Diffusion and adsorption at the interface

When diffusion process is slower than adsorption process, what is a frequent situation in the real systems, one can say that the adsorption of surfactant is controlled by diffusion. This paper is focused on determination of surfactant effective diffusion coefficient which describes the rate of the whole process. The model of above presented process is given by one-dimensional

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (4)$$

diffusion partial differential eq. 4 [3,4].

$$D \frac{\partial c}{\partial x} \Big|_{x=0} = \frac{\partial \Gamma}{\partial t} \quad (5)$$

$$\lim_{x \rightarrow \infty} c(x, t) = c_b \quad (6)$$

with boundary conditions (5) and (6):

$$c(x, t) \Big|_{t=0} = c_b \quad (7)$$

for $t > 0$, where c_b is a bulk concentration, and initial condition (7):

The solution of diffusion model which describes dynamic of surfactant adsorption for a long time processes was given by Ward

$$\Gamma(t) = \sqrt{\frac{D}{\pi}} \left\{ 2c_b \sqrt{t} - \int_0^t \frac{c(\Gamma(\tau))}{\sqrt{t-\tau}} d\tau \right\} \quad (8)$$

and Tordai in 1946 by eq. 8 [5].

where D $\left[\frac{\text{m}^2}{\text{s}}\right]$ is a diffusion coefficient, $c(\Gamma(t))$ is the relations between concentration and surface excess and t is a time. Eq. 8 is a Volterra integral equation of the second kind. Linearity or non-linearity of this equation depends on chosen model of isotherm of adsorption. Linear case with Henry isotherm was solved

analytically by Sutherland [6]. In this paper the Langmuir isotherm will be used. The non-linear case doesn't have the analytical solution.

2. Results and discussion

The diffusion of the commercial surfactant was investigated (trade name Nafol 810D). The experimental data was given by the Du Nouy ring method [7]. The fig. 2 shows the change of surface tension during the experiment of the samples of different bulk concentration.

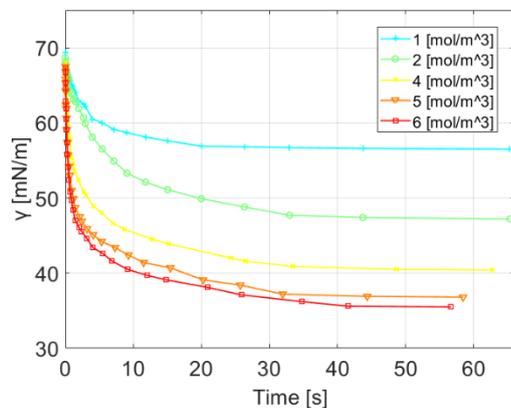


Fig.2. The change of surface tension during the experiment of the samples of different bulk concentration

The Szyszkowski isotherm, given by eq. 9 [8], was fitted to the experimental relation between the surface tension and the bulk concentration of the compound (fig. 3).

$$\gamma = \gamma_0 \left(1 - B_{sz} \ln \left(\frac{c}{A_{sz}} + 1 \right) \right) \quad (9)$$

where γ_0 is the water surface tension, γ is the surface tension associated with the surfactant concentration c , A_{sz} and B_{sz} are Szyszkowski constants, which have the physical meanings. A_{sz} describes the measure of tendency to interfacial adsorption and B_{sz} characterizes the orientation of the adsorbed molecule. Eq. 3 and 9 were used to determine the values of Γ_{eq} and Γ_{∞} of the considered system.

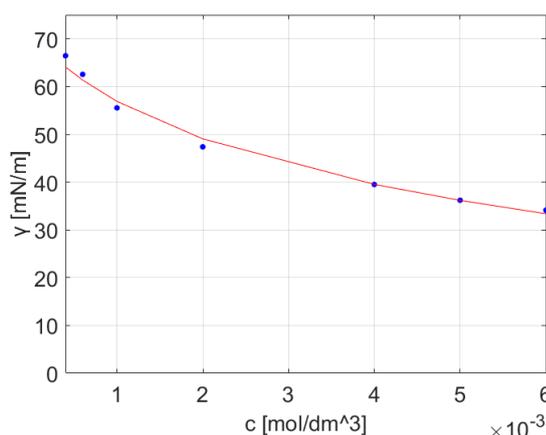


Fig.3. Experimental data of the equilibrium surface tension depending on the bulk concentration

The relation between surface excess and surface tension is given by eq. 10 [4,9]. It was used to determine the surface excess Γ as a function of time.

$$\Gamma(t) = \Gamma_{\infty} \left(1 - \exp \left(\frac{\gamma(t) - \gamma_0}{RT\Gamma_{\infty}} \right) \right) \quad (10)$$

The main purpose of the study was to assess the usability of a new calculation algorithm for determining the surfactants effective diffusion coefficient using the inverse problem for Ward-Tordai equation.

The diffusion coefficient was investigated in the interval $10^{-7} \div 10^{-16} \left[\frac{m^2}{s} \right]$. In order to solve the nonlinear Ward-Tordai integral equation associated with Langmuir isotherm the Nystrom method was used [10,11]. Nystrom method is a discrete method of solving integral equations. In short, the time interval is discretized into finite vector with constant time steps and the integral in eq. 8 is approximated by chosen quadrature. In a consider case the trapezium rule of integration was used. The final discretized form of eq. 8 is given by eq. 11 with initial step $\Gamma(0) = 0$, which means that any of surfactant molecule isn't adsorbed on the surface in the beginning of the diffusion process.

The golden ratio method was used in a optimization part of the inverse problem algorithm [12]. The aim function given by eq. 12 is the maximum norm of the subtraction of the experimental and numerical data vectors, respectively Γ_{num} and Γ_{exp} .

$$\Psi(D) = \|\Gamma_{num} - \Gamma_{exp}\|_{\infty} \quad (11)$$

The experimental data was compared with numerical data and error was minimized successfully in a numerical inverse problem algorithm for all considered samples. Fig. 4 shows the experimental and numerical data of the surface excess in the concentration bulk

$$\Gamma(t_i) = 2c_b \sqrt{\frac{Dt_i}{\pi}} - \frac{1}{K_L} \frac{D}{\pi} \sum_{j=1}^i A_j \frac{\Gamma(\tau_j)}{\sqrt{t_i - \tau_j} (\Gamma_{\infty} - \Gamma(\tau_j))} \quad (12)$$

5 $\frac{mol}{m^3}$ case.

for $i = 2, 3, \dots$

In every time iteration the nonlinear eq. 12 has to be solved. Eq. 12 can be reformulated into quadratic eq. which discriminant is a positive number. Only one solution of this eq. has a physical meaning.

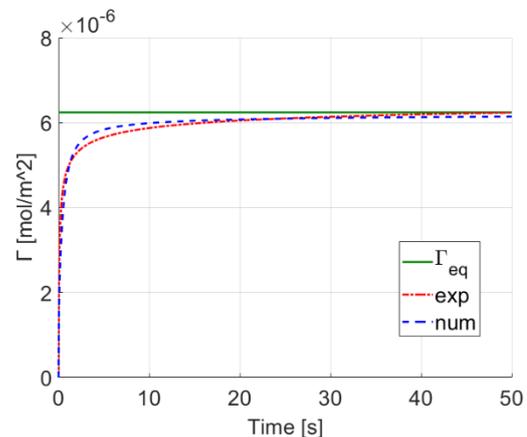


Fig.4. Experimental and numerical data of the surface excess in the bulk concentration 5 $\frac{mol}{m^3}$

Fig. 5 shows the minimization of the aim function during the optimization process. Fig. 6 shows reaching the optimal value of effective diffusion coefficient during the optimization process. Both figures are associated with the 5 $\frac{mol}{m^3}$ case as an example. The results of the first 15 iteration are showed. The optimal value for all investigated cases was reached after 30 \div 40 iterations.

The dependence between the effective diffusion coefficient and the concentration of the investigated compound is presented in the table 1.

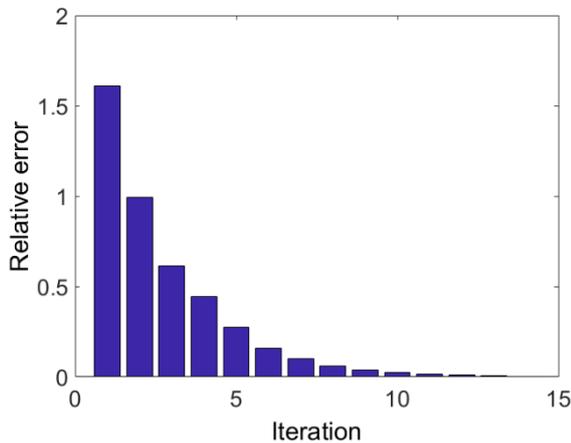


Fig.5. Experimental and numerical data of the surface excess in the bulk concentration $5 \frac{\text{mol}}{\text{m}^3}$

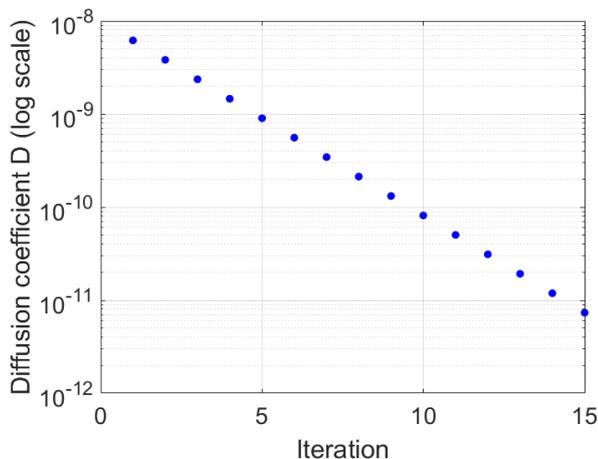


Fig.6. Experimental and numerical data of the surface excess in the bulk concentration $5 \frac{\text{mol}}{\text{m}^3}$

Table 1: Values of effective diffusion D coefficient for different bulk concentration c_b

Bulk concentration $c_b \frac{\text{mol}}{\text{m}^3}$	Effective diffusion coefficient $D \frac{\text{m}^2}{\text{s}}$
1	$2,87 \cdot 10^{-11}$
2	$3,34 \cdot 10^{-12}$
4	$1,62 \cdot 10^{-12}$
5	$1,68 \cdot 10^{-12}$
6	$1,14 \cdot 10^{-12}$

3. Conclusions

Above presented procedure was used to determine the effective diffusion coefficient of commercial surfactant Nafol 810D. In every case of the bulk concentration presented algorithm minimized the aim function and the inverse Ward-Tordai problem was solved. Result of the paper is the effective diffusion coefficient dependence on the bulk concentration of the surfactant.

Presented algorithm can be successfully use to determine the effective diffusion coefficient of amphiphilic surfactants based on the experimental data of dynamic of adsorption process.

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