



## A study on the method of short-time approximation – Criteria for applicability



Alvin Casandra<sup>a</sup>, Suryadi Ismadji<sup>b</sup>, Boris A. Noskov<sup>c</sup>, Libero Liggieri<sup>d</sup>, Shi-Yow Lin<sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, 43, Keelung Road, Sec. 4, Taipei 106, Taiwan

<sup>b</sup> Department of Chemical Engineering, Widya Mandala Catholic University, 37, Kalijudan, Surabaya, Indonesia

<sup>c</sup> Department of Colloid Chemistry, St. Petersburg State University, Universitetsky pr. 26, 198504 St. Petersburg, Russia

<sup>d</sup> CNR – Istituto per l'Energetica e le Interfasi IENI – UOS Genova, via De Marini, 6 Genova, Italy

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### ABSTRACT

Despite its widespread use in the determination of adsorption mechanisms and the estimation of surfactant diffusivity, the short-time approximation method, used for linearly fitting experimental dynamic surface tension data, should be validly applied only over a very specific range of time intervals or surface pressures. Therefore, the definition of general criteria for the applicability of this method and for error evaluation in diffusivity estimations is fundamental. In this work, a theoretical numerical simulation of the short-time approximation method was conducted, and general benchmarks for its accurate utilization were investigated. Specifically, for systems assuming planar gas–liquid surfaces, diffusion-controlled kinetics and a Langmuir adsorption isotherm, simple rules were developed in terms of limiting surface pressure ( $\pi_{\max}$ ) and dimensionless time ( $t_{\max}^*$ ) as a function of dimensionless surfactant concentration ( $C_0/a$ ). For values greater than the limiting (*maximal*) conditions, the dynamic surface tension curve deviates from the short-time approximation straight line, and thus, the corresponding linear fitting could lead to significant errors in evaluating the diffusivity. The simple criteria proposed in this study thus precisely define the range of applicability for the short-time approximation method.

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### 1. Introduction

Surfactants are essential agents in sundry practical applications and products, including detergents, inks, adhesives, pesticides, and cosmetics [1]. In recent years, the global market for surfactants has shown rapid growth, with a 3.8% annual increase: in 2012, the market value was estimated at approximately US\$26.8 billion, and it is expected to reach US\$31.1 billion by 2016 [2]. Because surfactant optimization depends on specific knowledge of their dynamic adsorption behavior [3], it is not surprising that this field of study has gained tremendous attention over the past two decades.

In 1946, Ward and Tordai introduced a general equation for interpreting the surfactant adsorption kinetics of planar gas–liquid surfaces [4]. In their model, the authors assumed that surfactant diffusion from the bulk to the sublayer is the limiting step compared to surfactant transfer from the sublayer to the surface. This *diffusion-controlled* approach has been observed to be valid for

the majority of small, pure surfactants and surfactant mixture systems [5] such that the equation describing their behavior is considered a fundamental starting point in numerous models used today.

However, the Ward–Tordai equation is rather complex, and its application has been hindered for decades by its complicated numerical calculations. Therefore, in 1959, Defay and Hommelen [6] and Hansen and Wallace [7] introduced a simplified form of the equation, assuming that surfactant backward diffusion from the sublayer to the bulk solution could be omitted for initial short time intervals. In 1979, van den Bogaent and Joos [8] coupled this simplified equation with the Gibb's adsorption equation and von Szyszkowski's equation, developing an *easy-to-use* linear approximation for the Ward–Tordai equation.

Due to its simplicity, this short-time linear approximation equation has been widely used to date [9–41]. Specifically, many researchers [10,14–17,19,20,22,23,25,27–32,34,35,37,38,40] have utilized the equation to evaluate surfactant diffusivities or determine the adsorption mechanism of various systems, linearly fitting dynamic surface tension data with the short-time linear approximation equation ( $\gamma$  vs.  $t^{1/2}$ ) for specific ranges of “short” time intervals (generally  $t^{1/2} = 0\text{--}5\text{s}^{1/2}$ , but up to  $t^{1/2} = 200\text{s}^{1/2}$  in [22]). A

\* Corresponding author. Tel.: +886 2 2737 6648; fax: +886 2 2737 6644.  
E-mail address: [sylin@mail.ntust.edu.tw](mailto:sylin@mail.ntust.edu.tw) (S.-Y. Lin).

detailed literature review of these diffusivities, estimated by using the short-time approximation method, is reported in Table 1.

Intuitively, because dynamic surface tension data can be accurately linearly fitted only for specific initial time intervals, an appropriate choice of the time range plays a crucial role in the correct evaluation of diffusivity. In fact, it has been reported [22,23,25,28] that quite diverse values of diffusivity have been observed when different time ranges were chosen. Ultimately, thus, certain general criteria for validly applying the short-time approximation method would be essential to guiding researchers in correctly estimating diffusivities.

Therefore, in this work, a theoretical numerical simulation of the short-time approximation method was conducted, and general benchmarks for its accurate utilization were investigated. All calculations were carried out for a diffusion-controlled adsorption process involving the mass transport of surfactant molecules from a uniform bulk phase to a freshly created air–water interface. The following conditions were applied: (1) a Langmuir adsorption isotherm, (2) a planar air–water interface, (3) room temperature 25 °C, and (4) a diffusivity of  $D_{\text{set}} = 5 \times 10^{-6} \text{ cm}^2/\text{s}$  for different dimensionless surfactant concentrations (the ratio between the bulk concentration and the surfactant activity)  $C_0/a$ . Additional simulations were conducted for different  $a$  values.

## 2. Theoretical framework

### 2.1. Ward–Tordai equation

In the case of one-dimensional diffusion and adsorption onto a planar surface from a bulk phase initially containing a uniform distribution of a surface active solute, the diffusion of the surfactant in the bulk continuous phase is described by Fick's law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} (z > 0, t > 0) \quad (1)$$

where  $z$  is the distance from the surface and  $C(z, t)$  is the bulk concentration of surfactant molecules. The boundary and initial conditions for Eq. (1) are as follows:

$$C(z, t) = C_0 (z > 0, t = 0) \quad (2)$$

$$C(z, t) = C_0 (z \rightarrow \infty, t > 0) \quad (3)$$

$$\frac{d\Gamma}{dt} = D \frac{\partial C}{\partial z} (z = 0, t > 0) \quad (4)$$

$$\Gamma(t) = 0 (t = 0) \quad (5)$$

**Table 1**

A literature review of experimental estimates of the diffusivity ( $D$ ) for different systems, predicted by using the short-time approximation method for different time intervals ( $t$ ).

Refs	Compound	$D$ ( $10^{-6} \text{ cm}^2/\text{s}$ )	$C_0$ ( $\text{mol}/\text{cm}^3$ )	$t^{1/2}$ ( $\text{s}^{1/2}$ )	$\pi^a$ (mN/m)	Model parameter <sup>e</sup>	
						$\Gamma_\infty$ ( $10^{-10} \text{ mol}/\text{cm}^2$ )	$a$ ( $10^{-10} \text{ mol}/\text{cm}^3$ )
13	Glu <sub>8</sub> -2-Glu <sub>8</sub>	1.5	$3.5 \times 10^{-6}$	0.1–0.3	6.0	3.99	4.23
	Glu <sub>12</sub> -2-Glu <sub>12</sub>	0.17		0.1–0.2	0.6	4.39	0.31
16	FluoroCarbon <sub>4</sub>	2.3	$1 \times 10^{-8}$	0–14	6.0	10.0	63.8
			$2 \times 10^{-8}$	0–14	13		
17	C <sub>9</sub> -TGE <sup>b</sup>	1.1	$2.6 \times 10^{-8}$	0–3	3.5	2.46	8.06
19	C <sub>12</sub> -Maltose ester	3.4	$0.8 \times 10^{-6}$	0–0.3	3.0	3.34	55.8
20	ANHG550 <sup>c</sup>	2.4	$0.32 \times 10^{-6}$	0–0.65	2.0	2.13	4.40
		2.6	$1.2 \times 10^{-6}$	0–0.2	10		
22	Pluronic F68	0.92	$0.17 \times 10^{-11}$	0–200	3.0	4.84	0.021
		0.92	$0.72 \times 10^{-11}$	0–30	4.0		
23	C <sub>10</sub> E <sub>6</sub>	57	$8 \times 10^{-8}$	0–0.4	22	2.30	10.8
25	di-C <sub>8</sub>	3.0	$2 \times 10^{-7}$	0–0.55	7.0	2.81	1.68
27	C <sub>8</sub> DMPO <sup>d</sup>	5.3	$4 \times 10^{-7}$	0–0.09	2.0	3.20	3830 <sup>e</sup>
			$20 \times 10^{-7}$	0–0.05	7.5		
			$2 \times 10^{-7}$	0–0.2	1.5	3.60	420 <sup>e</sup>
28	C <sub>10</sub> E <sub>4</sub>	4.9	$0.05 \times 10^{-6}$	0–0.05	17	3.18	25.7
			$0.6 \times 10^{-6}$	0–1.6	2.0		
			$5 \times 10^{-6}$	0–0.9	17		
29	b-lactoglobulin	4.9	$0.1 \times 10^{-9}$	0–30	0.5	1.88	2.02
			$5 \times 10^{-9}$	0–12	17		
			$0.1 \times 10^{-9}$	0–30	1.0	4.87	0.77
30	DPPC	4.9	$5 \times 10^{-9}$	0–30	14		
		12	$2 \times 10^{-9}$	0–19	5.8	2.79	2.71 <sup>e</sup>
		8	$10 \times 10^{-9}$	0–17	15		
31	Hexanol	1.5	$5 \times 10^{-6}$	0–0.07	9.0	6.86	52100
		0.39	$10 \times 10^{-6}$	0–0.03	12		
32	MTAB	13.4	$4 \times 10^{-8}$	0–1	5.9	2.80	3600 <sup>e</sup>
33	Triton X-405	0.7	$2.54 \times 10^{-8}$	0–0.21	0.1	0.92	0.22
			$7.63 \times 10^{-8}$	0–0.20	1.0		
34	TDSNa	2.0	$2 \times 10^{-6}$	0–0.09	14	9.24	4030 <sup>e</sup>
35	SDS	4.7	$0.5 \times 10^{-6}$	0–3	4.0	3.84	16000 <sup>e</sup>
		2.8	$2 \times 10^{-6}$	0–3.1	12		
37	Na-myristate + Na-Decanoate	1.1	$2.25 \times 10^{-7} + 1 \times 10^{-5}$	0–1	7.3	3.08	38800 <sup>e</sup>
38, 40	DC <sub>10</sub> PO	0.029	$0.29 \times 10^{-7}$	0–8	4.4	3.70	330 <sup>e</sup>
		0.011	$1.1 \times 10^{-7}$	0–6	11		
		0.4	$4.37 \times 10^{-8}$	0–10	7.2	4.20	280 <sup>e</sup>
	DC <sub>12</sub> AO		$17 \times 10^{-8}$	0–8	15		

<sup>a</sup> Surface pressure,  $\pi = \gamma_0 - \gamma$ .

<sup>b</sup> TGE = tryptophan glycerol ether surfactant.

<sup>c</sup> ANHG550 = heterogemisin surfactant of PEG with MW = 550.

<sup>d</sup> DMPO = dimethyl phosphine oxides.

<sup>e</sup> Parameters ( $\Gamma_\infty$  and  $a$ ; maximum surface concentration and surfactant activity) obtained from previous studies.

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