



ORIGINAL ARTICLE

# A unified nonlinear fractional equation of the diffusion-controlled surfactant adsorption: Reappraisal and new solution of the Ward–Tordai problem



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**Abstract** The article addresses a reappraisal of the famous Ward–Tordai equation describing the equilibrium of surfactants at air/liquid interfaces under diffusion control. The new derivation is entirely developed in the light of fractional calculus. The unified approach demonstrates that this equation can be clearly reformulated as a nonlinear ordinary time-fractional equation of order  $1/2$ . The work formulates versions with different isotherms. A simple solution of the case with the Henry's isotherm and a discussion of a Cauchy problem involving the Freundlich isotherm are provided.

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## 1. Introduction

Surfactants are broadly encountered in aqueous systems used as cleaning and wetting agents, dispersants stabilizers, lubricants, foam stabilizers, catalysts, as well as to stabilize pharmaceutical, cosmetic and agrochemical formulations, etc. (Davies and Rideal, 1963; Lenzi et al., 2005; Gaines, 1966; Gosh,

2009). In such systems molecules attempt to be at a position in the fluid where there are forces of attraction in as many directions as possible thus attaining local dynamic equilibria. For the molecules located at the surface, however, there exist forces directed inwards to the fluid which are not balanced outwards. As a result, the fluid attempts to minimize the free area due to resisting expansion. This cohesive feature of the fluid can be measured as a force per unit of length of the interface, and it is known as surface tension. The dynamics of the surface tension depends on the amount of molecules of surfactant accumulated (adsorbed) at the interface. The classical equation of Ward and Tordai (1946) describes the transient in the surface adsorption of surfactant when the supply of surfactant molecules is under diffusion control from the fluid to the fluid-air interface. This work stresses the attention on a unified

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re-formulation of the Ward–Tordai equation in a straightforward manner entirely in the light of the fractional calculus.

### 1.1. Physical background

The amount of surfactant adsorbed at an air/water interface is usually calculated indirectly from interfacial tension measurements (Dudnik and Lunkenheimer, 2000; Dannov et al., 2000). The surfactant concentration of the liquid bulk  $C_0$  and its equilibrium surface tension  $\sigma_e$  corresponds to the equilibrium amount at the interface  $G_\infty$  are interrelated by the Gibbs equation (Gaines, 1966).

$$d\sigma_{T,P} = -\sum_i G_{\infty i} d\gamma_i \quad (1)$$

where  $d\sigma$  is the change in surface tension of the solvent,  $G_{\infty i}$  is the surface excess of the  $i$ th component in the system and  $d\gamma_i$  is the change in chemical potential of the  $i$ th component. Commonly this quantity is denoted as  $\Gamma_\infty$  but the present analysis involves the Euler gamma function  $\Gamma(\bullet)$  and changing the symbol we avoid potential ambiguities. For solutions containing only one solute the Gibbs equation is often given in the form:

$$G = -\frac{1}{kRT} \left( \frac{d\sigma}{d \ln C} \right)_T \quad (2)$$

The factor  $k$  depends on the number of species constituting the surfactant and adsorbing at the interface: For a nonionic surfactant or a uni-univalent ionic surfactant with excess of electrolyte  $k = 1$ , while in the absence of electrolyte  $k = 2$ . If the surface tension is measured then Eq. (2) may be applied to obtain an equilibrium adsorption isotherm  $G(t)$ . There are many methods available for the determination of surface tension including force methods, among them (Davies and Rideal, 1963; Gaines, 1966; Frances et al., 1996): Wilhelmy plates (Kwok and Neumann, 1999; Gosh, 2009), du Nouy ring (Gosh, 2009), shape methods (pendant drop) (Saad et al., 2011), or pressure methods (maximum bubble pressure) (Christov et al., 2006). Depending on the adsorption isotherm at the interface the relationship between the surface tension and the amount of the adsorbed surfactant is given by a corresponding equation of state (Eastoe and Dalton, 2000); examples are summarized in Table 1.

Initially the surface is cleaned so that the initially adsorbed amount  $G_0 = 0$  at  $t = 0$  and the surface tension is that of the solvent  $\sigma_0$ . The system is out of equilibrium and will return to the equilibrium state. In this context, let us consider an aqueous surfactant solution in equilibrium with its air–water interface. The surfactant concentration is  $C_0$  and its

equilibrium surface tension  $\sigma_e$  corresponds to the equilibrium surfactant concentration denoted as  $G_\infty$ , interrelated by the Gibbs Eq. (2). The system is out of equilibrium and will return to the equilibrium state. Hence, the surfactant molecules will be transported to the surface by diffusion (Ward and Tordai, 1946; Baret, 1968; Mysels, 1982; Li et al., 1994; Campanelli and Wang, 1998; Liu and Messow, 2000; Liu et al., 2009).

### 1.2. Ward–Tordai equation: the common approach at a glance

Consider a process entirely controlled by the diffusion transport through the stagnant fluid (Ward and Tordai, 1946; Baret, 1968; Mysels, 1982; Borwankar and Wasan, 1983; Li et al., 1994, 2010; Campanelli and Wang, 1998; Liu and Messow, 2000; Liu et al., 2009) and instantaneous adsorption of the surfactant molecules at the interface. When the diffusion through the bulk of the liquid is linear, then the Fick’s second law describes the transfer of the surfactant to the surface, with initial and boundary conditions presented by the model.

$$\frac{\partial C}{\partial t} = D_0 \frac{\partial^2 C}{\partial x^2} \quad (3a)$$

$$C(x, t) \rightarrow C_0, \quad x \rightarrow \infty \quad C(0, t) = C_{s0} \quad (3b)$$

The problem at issue considers time-evolution of the surface concentration at  $x = 0$ , so the mass balance following from (3a) at  $x = 0$  reads:

$$\left. \frac{\partial C}{\partial t} \right|_{x=0} = D_0 \left. \frac{\partial C}{\partial x} \right|_{x=0} \Rightarrow \frac{\partial G}{\partial t} = D_0 \left. \frac{\partial C}{\partial x} \right|_{x=0}, \quad G(t) = C(0, t) \quad (4)$$

The final solution of the model (3) with help of (4) and the imposed boundary and initial conditions at  $t \rightarrow 0$  (short times) is (Ward and Tordai, 1946; Baret, 1968; Liu and Messow, 2000; Liu et al., 2009; Li et al., 2010).

$$G(t) = 2C_0 \frac{\sqrt{D}}{\sqrt{\pi}} \sqrt{t} - \frac{\sqrt{D}}{\sqrt{\pi}} \int_0^t \frac{C_{s0}(\tau)}{(t-\tau)^{1/2}} d\tau, \quad C_{s0}(t \rightarrow 0) \neq 0 \quad (5a)$$

Dividing both sides of (5a) by  $G_\infty$  we get the dimensionless form of the Ward–Tordai equation (Ward and Tordai, 1946).

$$\theta = 2 \frac{C_0}{G_\infty} \frac{\sqrt{D}}{\sqrt{\pi}} \sqrt{t} - \frac{1}{G_\infty} \frac{\sqrt{D}}{\sqrt{\pi}} \int_0^t \frac{C_{s0}(\tau)}{(t-\tau)^{1/2}} d\tau, \quad \theta = G(t)/G_\infty, \quad 0 \leq \theta \leq 1 \quad (5b)$$

The development of the Ward–Tordai equation (5a) is frequently referred to a solution of the model (3) by the Laplace transform (Hansen, 1960; Borwankar and Wasan, 1983; Chang and Frances, 1995; Kralchevsky et al., 2008) which

**Table 1** Principle isotherms and equations of states used in analysis of the dynamic surface tensions (in terms of the present article). In accordance with: Chang and Frances (1995), Eastoe and Dalton (2000) and Li et al., (2010).

	Isotherm	Equation of state
Henry	$G = K_H C_{s0}$	$\sigma - \sigma_0 = kRTG$
Langmuir	$G(t) = G_\infty \frac{aC_{s0}}{1+bC_{s0}}$	$\sigma - \sigma_0 = -kRTG_\infty \ln(1 - \frac{G}{G_\infty})$
Frumkin	$C_{s0} = \frac{1}{K_F} \frac{G(t)}{G(t)-G_\infty} \exp \left[ -\beta \left( \frac{G(t)}{G_\infty} \right) \right]$	$\sigma - \sigma_0 = -kRTG_\infty \ln(1 - \frac{G}{G_\infty}) - \frac{kRT}{2} G_\infty \left( \frac{G}{G_\infty} \right)^2$
Freundlich	$G(t) = k_f (C_{s0})^{1/n}$	$\sigma - \sigma_0 = kNRTG$
Volmer	$C_{s0} = K_V \left( \frac{G}{G_\infty - G} \right) \exp \left( \frac{G}{G_\infty - G} \right)$	$\sigma - \sigma_0 = kRT \left( \frac{G_\infty^2}{G_\infty - G} \right)$

differs from the original approach of [Ward and Tordai \(1946\)](#) and underlying solution of [Carslaw \(1921\)](#) using Green functions. Some specific point will be commented next.

In order to be correct, it is worthy to mention that [Ward and Tordai \(1946\)](#) have started the solution by directly applying the result developed by [Carslaw \(1921\)](#) for a problem in heat transfer analogous to the model (3) and involving a convolution integral (like that in (5a)). For the readers familiar with the book of [Carslaw and Jaeger \(1959\)](#), Ward and Tordai used the solution of problems 2.5 and 14.2, exactly equation (2) in section 14.2. Further, looking for an expression of the gradient of the subsurface concentration  $(\partial C/\partial x)_{x=0}$  from this solution Ward and Tordai applied Maclaurin's theorem. Consequently the subsurface gradient was expressed as:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = F(t) - \frac{1}{2\sqrt{\pi D}} \int_0^t \frac{\phi(z)}{\sqrt{t-z}} dz \quad (6a)$$

The function  $\phi(t)$  denotes the surface concentration in the terms used by Ward and Tordai.

Ward and Tordai represented the right-hand side of (6a) as  $F(t) = \Gamma(1/2)D^{-1/2}\phi(t)$  involving differentiation and integration of fractional order (sic!), without a reference source. Because the solution needed to find the time-derivative of  $F(t)$ , they applied the operator  $D^1 = d/dz$  (sic!) to  $F(t)$  that led to:

$$\begin{aligned} F'(t) &= \frac{d}{dt} \int_0^t \frac{\phi(z)}{\sqrt{t-z}} dz = \Gamma(1/2)D^1 D^{-1/2}\phi(t) \\ &= \Gamma(1/2)D^{1/2}\phi(t) = -(1/2) \int_0^t \frac{\phi(z)}{\sqrt{t-z}} dz \end{aligned} \quad (6b)$$

This step of their solution obviously uses the Riemann–Liouville fraction derivative (the Caputo derivative was invented about 25 years later). Hence, a small element of fractional calculus exists in the original work. We especially mention the point of the original solution with traces of fractional calculus because it is long and cumbersome, and to some extent unclear for people working on surfactants and surface tension problems without broad mathematical knowledge and skills. This personal statement is confirmed by the fact that all the works cited in this article (and the references therein) attack the problem with the tools of the conventional integer-order calculus resulting in intractable expressions and formulae. The situation has a simple explanation: even existing from about 300 years, the fractional calculus is most popular among the mathematicians rather than among the scholars working in the fields of chemical engineering where the Ward–Tordai equation is applied. To some extent, the presence of a convolution integral in the original Ward–Tordai equation is the principle obstacle in the solution procedures. In this context, for example, [Noskov \(1996\)](#) stated that *the equation is not sufficient for the calculation of the kinetic dependency of the adsorption because it contains an unknown function  $\tilde{c}(t - \tau)$*  (sic!). This indicates a misunderstanding of the role of the convolution integral which describes the reduction in time of the rate to transport surfactant to the interface.

The first independent solution of the model (3) has been developed by [Sutherland \(1952\)](#) with a linear relationship  $G = \bar{M}C$  where  $\bar{M}$  is average defined as  $\bar{M} = \frac{1}{C_\infty} \int_0^{C_\infty} (\frac{G}{C}) dc$   $G = \bar{M}C$  and considered independent of concentration. Then the boundary equation becomes:

$$\frac{\partial C_s}{\partial t} = \frac{D_0}{M} \frac{\partial C_s}{\partial x}, \quad x = 0, \quad t > 0 \quad (7)$$

with boundary and initial conditions:

$$C = 0, \quad x = 0, \quad t = 0, \quad C = C_0, \quad x > 0, \quad t = 0 \quad (8a, b)$$

The solution is simple ([Sutherland, 1952](#)) (sic!)

$$\left(\frac{C}{C_0}\right)_{x=0} = 1 - \exp\left(\frac{D_0 t}{M^2}\right) \operatorname{erfc}\left(\frac{\sqrt{D_0 t}}{M}\right) \quad (9)$$

Alternatively, a solution based on the reflection and linear superposition has been developed independently by [Mysels \(1982\)](#). Many attempts have been applied to develop the Ward–Tordai equation ([Petrov and Miller, 1977](#)) and to solve it for various adsorption isotherms (as well as to solve the original model (3)) among them: analytical solutions by series presentation of the convolution integral ([Hansen, 1960](#); [Petrov and Miller, 1977](#); [Ziller and Miller, 1986](#)), orthogonal collocation ([Ziller and Miller, 1986](#)) and numerically by an implicit difference method ([Miller, 1981](#); [Borwankar and Wasan, 1983](#); [Chang et al., 2006](#); [Li et al., 2010](#)), finite element method ([Fenandez and Muniz, 2011](#); [Fenandez et al., 2012a,b](#)). A comprehensive review of the existing models and possible analytical solutions is provided by [Chang and Frances \(1995\)](#).

The equation of Ward and Tordai is not enough to describe the adsorption process at the air–water interface because it relates two unknown functions  $G(t)$  and  $C_{s0}(t)$ . In fact,  $C_{s0}(t)$  is a function of  $\theta$  at the relationship depending on the equilibrium isotherm  $E_\theta(\theta)$  describing the process at the air–water interface (see [Table 1](#)).

Besides, Eq. (5b) cannot be considered as a simple Abel equation ([Linz, 1985](#)), because of the nonlinearity imposed by the function  $C_{s0}(t) = E_\theta(\theta)$ . The main problem in the solution of the Ward–Tordai equation and the proper evaluation of  $G(t)$  comes from the fact that  $C_{s0}$  is in a convolution integral with a weakly singular kernel and simultaneously depends on  $\theta$ . If the subsurface concentration is known independently through the adsorption process, then  $G(t)$  can be calculated immediately. In this context, [Johansen et al. \(1991\)](#), for instance, have suggested empirical forms of the subsurface concentration expressed by exponential functions:  $C(0, t) = C_0[1 - \exp(-\beta_1 t)]$  and  $C(0, t) = C_0[1 - \exp(-\beta_1 t) + \exp(-\beta_2 t)]$ . The parameters  $\beta_1$  and  $\beta_2$  are overall measures of the diffusion, adsorption, and desorption rates and are determined from the transients in equilibrium adsorption experiments.

### 1.3. Aim and article structure

This article presents a reappraisal of the model (3) in light of the fractional calculus that finally yields a nonlinear time-fractional ordinary equation of order 1/2. The article demonstrates an alternative derivation of the Ward–Tordai equation by using time fractional semi derivatives of Riemann–Liouville (Section 2). Further, the analysis in Section 3 allows developing a time-fractional nonlinear ODE analogous to the Ward–Tordai equation with a non-linear term depending on the type of the adsorption isotherm describing the equilibrium at the surface. Section 4 deals with the derived time-fractional equation in case of the Henry isotherm and analyses possible solutions. Section 5 addresses the general Cauchy problem pertinent to the formulated fractional ODE and the case of

the Freundlich isotherm. The discussion section analyzes the results developed and formulates new problems.

## 2. New development of the Ward–Tordai equation by time-fractional semiderivatives

Now, we present an alternative solution of the model (3) by the tools of the fractional calculus only, directly leading to the Ward–Tordai equation. The transport of the surfactant from the bulk to the surface is described by Eq. (3a) which can be represented as (Babenko, 1984):

$$\frac{\partial C}{\partial t} - D_0 \frac{\partial^2 C}{\partial x^2} = \left( \frac{\partial^{1/2} C}{\partial t^{1/2}} - \sqrt{D_0} \frac{\partial C}{\partial x} \right) \left( \frac{\partial^{1/2} C}{\partial t^{1/2}} + \sqrt{D_0} \frac{\partial C}{\partial x} \right) = 0 \quad (10)$$

$\frac{\partial^{1/2} C}{\partial t^{1/2}}$  is a fractional-time derivative of Riemann–Liouville sense (left RL derivative) of order 1/2, defined as:

$$\frac{\partial^{1/2} C(t)}{\partial t^{1/2}} = {}_{RL}D_t^{-1/2} C(t) = \frac{1}{\Gamma(1/2)} \frac{d}{dt} \int_0^t \frac{C(\tau)}{\sqrt{t-\tau}} d\tau, \quad \Gamma(1/2) = \sqrt{\pi} \quad (11a)$$

Hereafter we will use the notation  $\partial^{1/2} C / \partial t^{1/2}$  instead of  ${}_{RL}D_t^{-1/2} C(t)$  to avoid misunderstanding with the symbol of diffusivity  $D_0$ . Alternatively, the time-fractional Riemann–Liouville integral is defined as:

$$\frac{\partial^{-1/2} C(t)}{\partial t^{1/2}} = {}_{RL}D_t^{-1/2} C(t) = I^{1/2} C(t) = \frac{1}{\Gamma(1/2)} \int_0^t \frac{C(\tau)}{\sqrt{t-\tau}} d\tau \quad (11b)$$

In (10) only the second term has a physical reasoning  $x = 0$  (Oldham and Spanier, 1974) and, therefore, the diffusion in the fluid bulk can be described by the fractional (half-time) subdiffusion equation:

$$\frac{\partial^{1/2} C}{\partial t^{1/2}} = -\sqrt{D_0} \frac{\partial C}{\partial x} \quad (12)$$

Eq. (12) is equivalent to the integer-order counterpart close to the interface  $x = 0$  (Oldham and Spanier, 1974). Moreover, Eq. (12) relates the bulk concentration and the gradient at any point of the medium (Agrawal, 2004), and allows expressing it at  $x = 0$ , precisely expressing  $C(x \rightarrow 0) = C_{s0}$ , as:

$$\frac{\partial^{1/2} C_{s0}}{\partial t^{1/2}} = -\sqrt{D_0} \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (13)$$

Hence, we have two coupled Eqs. (14a,b) describing the process of surfactant accumulation at the surface, namely:

$$\frac{\partial^{1/2} C_{s0}}{\partial t^{1/2}} = -\sqrt{D_0} \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (14a)$$

$$\frac{\partial G}{\partial t} = D_0 \left( \frac{\partial C}{\partial x} \right)_{x=0} \quad (14b)$$

Eliminating the gradient  $(\partial C / \partial x)_{x=0}$  from (14a) and (14b) we get:

$$D_0 \left( \frac{\partial C}{\partial x} \right)_{x=0} = -\sqrt{D_0} \frac{\partial^{1/2} C_{s0}}{\partial t^{1/2}} \quad (15a)$$

Then, from (4) we read:

$$\frac{\partial G}{\partial t} = -\sqrt{D_0} \frac{\partial^{1/2} C_{s0}}{\partial t^{1/2}} \quad (15b)$$

Expressing the Riemann–Liouville fractional derivative in the RHS of (15b) through the fractional integral, we have:

$$\frac{\partial G}{\partial t} = -\frac{\sqrt{D_0}}{\sqrt{\pi}} \left[ \frac{d}{dt} \int_0^t \frac{C_{s0}(\tau)}{(t-\tau)^{1/2}} - \frac{C_0}{\sqrt{\pi t}} \right] \quad (16)$$

In (16) we take into account that the initialization (the lower limit in the convolution integral) in  ${}_{RL}D_t^{-1/2}$  is zero and the initial condition is  $C(0, t) = C_{s0}(t=0) = C_0$  (i.e., a uniform surfactant profile across the liquid layer). This is the principle equation describing the time evolution and the accumulation of the surfactant  $G(t)$  at the interface. Applying the operator  $D_t^{-1} = \int_0^t dt$  to both sides of (16) we get:

$$G(t) = 2 \frac{C_0 \sqrt{D_0}}{\sqrt{\pi}} \sqrt{t} - \sqrt{D_0} \frac{1}{\sqrt{\pi}} \int_0^t \frac{C_{s0}(\tau)}{(t-\tau)^{1/2}} d\tau \quad (17a)$$

This is the Ward–Tordai (WT) equation (1946). For  $t \rightarrow 0$  when  $C_{s0}(t) \approx 0$  the short-time solution (Kralchevsky et al., 2008) can be approximated as:

$$G(t)_{t \rightarrow 0} \approx 2 \frac{C_0 \sqrt{D_0}}{\sqrt{\pi}} \sqrt{t} \quad (17b)$$

The long-time solutions of (14a, b) as well as of (17a) with various non-linear relationships  $C_{s0}(t)$  are special, not straightforward solvable tasks, and some of them will be discussed next. However, a simplification for  $t \rightarrow \infty$  can be expressed as (Hansen, 1960; Daniel and Berg, 2001; Kralchevsky et al., 2008):

$$C_s = C_{s(t \rightarrow \infty)} = \frac{G_\infty - G_0}{\sqrt{\pi D t}} \quad (17c)$$

Certainly, the new approach to derive the Ward–Tordai equation presented in this section is straightforward, starts from the basic model (3) and does not use underlying solutions of similar problems taken from other sources. Moreover, it is entirely developed by the tools of the fractional calculus.

## 3. Formulation of a unified nonlinear fractional equation

Even though we have developed the Ward–Tordai equation in a simple manner, the equation of the adsorption isotherm has to be accounted for in order to accomplish the solution of the problem. Moreover, since we stress the attention on application of fractional calculus, this section demonstrates that it is possible to create a unified time-fractional equation describing the time evolution of the surfactant adsorbed at the interface. This equation is equivalent to the Ward–Tordai equation but now it is in a form which is “readable” by people solving fractional calculus models.

Now, starting from Eq. (17a) and taking into account that the relationship  $C_{s0}[G(t)] \Rightarrow C_{s0}(t) = f[G(t)]$  is the adsorption isotherm, we read:

$$G(t) = 2 \frac{C_0 \sqrt{D_0}}{\sqrt{\pi}} \sqrt{t} - \sqrt{D_0} {}_{RL}D_t^{-1/2} C_{s0} \quad (18)$$

For readers inexperienced in fractional calculus it is better to know some basic relationships with fractional semiderivatives:

**Table 2** Time-fractional differential equations in cases of various isotherms. Unified presentations in accordance with the general construction of Eq. (20a).

	Equations	Coefficients
Henry	$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{H0}\theta = A_{H0}$	$A_{H0} = A_0 = \left(\frac{C_0}{G_\infty}\right)\frac{\sqrt{D_0}}{\sqrt{\pi}}, B_{H0} = \frac{B_0}{K_H} = \frac{\sqrt{D_0}}{K_H}$
Langmuir	$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{L0}\frac{\theta}{1-\theta} = A_0$	$A_{L0} = A_0, B_{L0} = \frac{\sqrt{D_0}}{a}$ , for $a = b$
Frumkin	$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{F0}\frac{\theta}{1-\theta}\exp(-\beta\theta) = A_{F0}$	$A_{F0} = A_0, B_{F0} = \frac{\sqrt{D_0}}{K_F} = \frac{B_0}{K_F}$
Freundlich	$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{f0}\theta^{\frac{1}{m}} = A_{f0}$	$A_{f0} = A_0, B_{f0} = \frac{\sqrt{D_0}}{(k_f G_\infty)^m} = \frac{B_0}{(k_f G_\infty)^m}, m = \frac{1}{N}$
Volmer	$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{V0}\left(\frac{1}{1-\theta}\right)\exp\left(\frac{1}{1-\theta}\right) = A_{V0}$	$A_{V0} = A_0 B_{V0} = K_V \sqrt{D_0} = K_V B_0$

Common coefficients:  $A_0 = (C_0/G_\infty)(\sqrt{D_0}/\sqrt{\pi}) = \theta_0(\sqrt{D_0}/\sqrt{\pi}) [s^{-1/2}]$ ;  $B_0 = \sqrt{D_0} [m s^{-1/2}]$ .

${}_0D_t^{1/2}(1/\sqrt{t}) = 0$  and  ${}_0D_t^{1/2}(\sqrt{t}) = \sqrt{\pi}/2$ . Therefore, dividing both sides of (17a) by  $G_\infty$  (the saturation surface excess) and at the same time applying the operator  $D^{1/2}$  to both sides of (17a) we get:

$$\frac{\partial^{1/2}}{\partial t^{1/2}} \left[ \frac{G(t)}{G_\infty} \right] = \left( \frac{C_0}{G_\infty} \right) \sqrt{D_0} - \sqrt{D_0} \left[ \frac{C_{s0}(t)}{G(t)} \right] \left[ \frac{G(t)}{G_\infty} \right] \quad (19)$$

Denoting  $\theta = G(t)/G_\infty$  and  $E_\theta = [C_{s0}(t)/G(t)]\theta$  we may express (19) in a general form as:

$$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_0 E_\theta = A_0, \quad A_0 = \left( \frac{C_0}{G_\infty} \right) \sqrt{D_0}, \quad B_0 = \sqrt{D_0} \quad (20a, b, c)$$

The function  $E_\theta = C_{s0}[G(t)/G_\infty]$  depends on the adsorption isotherm used to describe the equilibrium. With different adsorption isotherms we obtain different fractional ODEs about  $\theta$  and Table 2 summarizes various versions of Eq. (20a). In this table only the Frumkin isotherm considers interaction between the adsorbed molecules that leads to a relation of the adsorption process instead of the assumption of the instantaneous adsorption. For  $\beta = 0$  this isotherm reduces to the Langmuir model.

## 4. Solution examples

### 4.1. The Henry isotherm

Even though this is the simplest case we will use it to demonstrate how the new developed time-fractional ordinary equation (20a) relates to existing solutions. With  $G = K_H C_{s0}$  and  $C = G/K_H$  we have  $E_\theta = (C_{s0}/G_\infty)\theta = \theta/K_H$  and  $\theta = (C_{s0}/G_\infty)K_H$  equation (20a) reads:

$$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{H0}\theta = A_{H0}, \quad A_{H0} = A_0, \quad B_{H0} = \frac{\sqrt{D_0}}{K_H} \quad (21)$$

#### 4.1.1. Zero initial condition

With initially clean interface, that is  $\theta_0 = 0$  and applying the Laplace transform to Eq. (21) we get:

$$\Theta(p) = \frac{A_{H0}}{p(\sqrt{p} + B_{H0})} \text{ and } L^{-1}[\Theta(p)] \Rightarrow \theta(t) = \frac{A_0}{B_{H0}} [1 - \exp(B_{H0}^2 t) \operatorname{erfc}(B_{H0} \sqrt{t})] \quad (22a, b)$$

Expressing  $A_{0H}$  and  $B_{0H}$  by the constants of the process and taking into account that  $G_0 = K_H C_0$  we have:

$$\theta(t) = \left( \frac{G_0}{G_\infty} \right) \left[ 1 - \exp\left( \frac{D_0}{K_H^2} t \right) \operatorname{erfc}\left( \frac{\sqrt{D_0}}{K_H} \sqrt{t} \right) \right] \quad (23)$$

Thus, we simply derived the first known solution of the Ward–Tordai equation (Sutherland, 1952), (see Eq. (9)):

$$\frac{G(t)}{G_0} = \left[ 1 - \exp\left( \frac{D_0}{K_H^2} t \right) \operatorname{erfc}\left( \frac{\sqrt{D_0}}{K_H} \sqrt{t} \right) \right] \quad (24)$$

Denoting  $\tau_D = K_H^2/D_0$  as a time scale, then Eq. (24) can be rewritten as:

$$\theta(t) = \left( \frac{G_0}{G_\infty} \right) \left[ 1 - \exp\left( \frac{t}{\tau_D} \right) \operatorname{erfc}\left( \sqrt{\frac{t}{\tau_D}} \right) \right] \quad (25)$$

#### 4.1.2. Non-zero initial condition

When an amount of surfactant  $\bar{G}_0 \ll G_\infty$  exists at the interface, then we have  $\theta(0) = \theta_0 = \bar{G}_0/G_\infty \neq 0$ . In that case, the semiderivative of surface excess of surfactant is  ${}_0D_t^{1/2}\theta - \theta_0/\sqrt{\pi t}$  (Oldham and Spanier, 1974) and we have:

$$\frac{\partial^{1/2}}{\partial t^{1/2}}\theta + B_{H0}\theta = A_{H0} + \frac{\theta_0}{\sqrt{\pi}} \frac{1}{\sqrt{t}} \quad (26)$$

The Laplace transform to (26) yields:

$$\Theta(p) = \frac{1}{[\sqrt{p} + B_{H0}]} \left( A_{H0} \frac{1}{p} + \frac{\theta_0}{\sqrt{p}} \right) \quad (27)$$

The inverse Laplace transform of (27) gives:

$$\theta(t) = \left( \frac{G_0}{G_\infty} \right) [1 - \exp(B_{H0}^2 t) \operatorname{erfc}(B_{H0} \sqrt{t})] + \theta_0 \exp(B_{H0}^2 t) \operatorname{erfc}(B_{H0} \sqrt{t}) \quad (28)$$

For  $\theta_0 = 0$  we get the solution (25). The second term in (28) is responsible for the contribution of  $\theta_0$  in short-time processes since it decays rapidly in time.

#### 4.1.3. Short time solution

The widely used short-time approximation of the Ward–Tordai equation is presented by (17b). Now, using the Laplace transform solution of the problem with zero initial condition (22a) we may develop an asymptotic series (restricted to 3 terms only for seek of simplicity of the analysis), namely:

$$\Theta(p)_{p \rightarrow \infty} \approx A_{H0} \left[ \left(\frac{1}{p}\right)^{3/2} - B_{H0} \frac{1}{p^2} + B_{H0}^2 \left(\frac{1}{p}\right)^{5/2} + O\left(\frac{1}{p^3}\right) \right] \quad (29a)$$

The inverse Laplace transform of (29a) gives the short-time approximation:

$$\theta(t)_{t \rightarrow 0} \approx 2A_{H0} \frac{\sqrt{t}}{\sqrt{\pi}} - B_{H0}t + \frac{4}{3\sqrt{\pi}} B_{H0}^2 t^{3/2} \quad (29b)$$

From (29b) it is clear that only the first term matches the expressions (17b). However, taking into account that  $B_{H0} = \sqrt{D_0}/K_H$  and  $D_0$  are commonly of order of magnitude  $10^{-10}$  to  $10^{-12}$  m<sup>2</sup>/s (Johansen et al., 1991), then reasonably only the first term of (29b) has a practical significance thus confirming the common rule to use the approximation (17b).

### 5. Formulation as a Cauchy problem and the case of the Freundlich isotherm

Certainly, the original Ward–Tordai equation (5a) is a Cauchy problem determining locally and uniquely the solution of the model (3). As commented by Baret (1968), the solution of (3a) and the Ward–Tordai equation (5a) are, in fact, the compatibility relations between the Cauchy's condition and the condition (3d).

Let us consider the linear fractional differential Eq. (20a) with the Freundlich isotherm expressed in the form:

$$\frac{\partial^{1/2}}{\partial t^{1/2}} \theta + B_{j0} \theta^m = A_{j0}, \quad A_{j0} = A_0, \quad B_{j0} = \frac{\sqrt{D_0}}{(k_f G_\infty)^m} = \frac{B_0}{(k_f G_\infty)^m}, \quad m = \frac{1}{N} \quad (30)$$

For  $N = 1$  we have the linear case solved in the previous section. Especially, for the Freundlich isotherm  $N > 1$  ( $m < 1$ ) we have convex isotherms, while for  $N < 1$  ( $m > 1$ ) the isotherms are concave in shape. Eq. (30) can be represented in a more general form (Kilbas et al., 2006) (example 3.3-p. 177 in this book) as:

$$D_{a+}^\mu \theta(t) = \lambda(t-a)^\beta [\theta(t)]^m, \quad t > a, \quad m > 0, \quad m \neq 1 \quad (31)$$

with real  $\lambda, \beta \in \mathbb{R} (\lambda \neq 0)$ .

It was proved by Kilbas et al. (2006) that if the condition:

$$\frac{\beta + \mu}{(1 - m)} > -1 \quad (32)$$

is satisfied, then Eq. (31) has an explicit solution

$$\theta(t) = \left[ \frac{\Gamma(\frac{\beta + \mu}{m-1} + 1)}{\lambda \Gamma(\frac{\beta + \mu m}{m-1} + 1)} \right]^{\frac{1}{m-1}} (t-a)^{\frac{\beta + \mu}{1-m}} \quad (33)$$

Denoting

$$\eta = \frac{\beta + \mu m}{m-1}, \quad \eta - \mu = \frac{\beta + \mu}{m-1} \quad (34b, c)$$

In the present case we have  $a = 0, \beta = 0$ . Therefore,  $\eta = \mu \frac{m}{m-1}$ ,  $\eta - \mu = \frac{\mu}{m-1}$  and Eq. (33) is simplified as:

$$\theta(t) = \left[ \frac{\Gamma(\eta - \mu + 1)}{\lambda \Gamma(\eta + 1)} \right]^{\frac{1}{m-1}} t^{-\frac{\mu}{m-1}} \quad (35)$$

The conditions imposed to the parameters when  $0 < \mu < 1$  (especially  $\mu = 1/2$  in the problem at issue) (Kilbas et al., 2006) are:

$$m > 1, \quad -m\mu < \beta < m - 1 - m\mu, \quad \text{that is} \\ -m/2 < 0 < m - 1 - m/2 \quad (36a)$$

$$0 < m < 1, \quad -1/2 \leq 0 < -m/2 \quad (36b)$$

For  $\mu = 1/2$  the condition  $(\beta + \mu)/(1 - m) > -1$  is valid since  $1/2(1 - m) > -1$  for  $m > 1$ , especially for  $m > 2$  ( $N < 0.5$ ).

In general, it is proved (Kilbas et al., 2006) that the condition (32) is equivalent to:

$$\beta < m - \mu - 1, \quad \text{for } m > 1; \quad \text{or } m - 1 - \mu < \beta \quad \text{for } 0 < m < 1 \quad (37a, b)$$

In the specific case with  $\mu = 1/2$  and  $\beta = 0$  we have from (37a) that  $0 < m - 3/2$  for  $m > 1$ , precisely for  $m > 3/2$ , that is for  $N < 2/3$ . Otherwise, for  $0 < m < 1$ , that is for  $N > 1$ , the condition (37b) is  $m - 3/2 < 0$ , precisely  $m < 3/2$  and  $N > 2/3$ . Then, the solution (35) can be expressed as:

$$\theta(t)_{\mu=1/2} = \left[ \frac{\Gamma(\eta + 1/2)}{\lambda \Gamma(\eta + 1)} \right]^{\frac{1}{m-1}} t^{\frac{1}{2(1-m)}}, \quad \eta = \frac{m}{2(m-1)} \quad (38a, b)$$

Equation excludes the case of  $m = 1$  as it is stated by (37b) due to a singularity in  $\eta$ , but this case corresponds to Henry's isotherm and the straightforward solution is presented by (25) and (28).

Moreover, for  $m = 2$ , for instance, that is  $N = 0.5$  representing a convex Freundlich isotherm, we have from (38b) that  $\eta = 1$  and then the solution (38a) is a simple square-root law of the time, namely

$$\theta(t)_{\mu=1/2, m=2} = \left[ \frac{\Gamma(3/2)}{\lambda \Gamma(2)} \right] t^{\frac{1}{2}} = \frac{1}{\lambda} \frac{\sqrt{\pi}}{2} \sqrt{t} \quad (39)$$

Further, for  $m = 0.5$ , for example, that is  $N = 2$  we have a concave Freundlich isotherm. Since for  $0 < m < 1$  (see 37b) the condition  $m - 1 - \mu < \beta$  is obeyed then for  $\mu = 1/2$  and  $\beta = 0$  (see the comments about Eqs. (34) and (35)) we get  $m - 1 - \mu = -1 < 0$ . However, in this case we have from (38b) that  $\eta = -1$  that leads to a singularity in the pre-factor of (38a) because  $\Gamma(-1 + 1) = 0$ . Therefore, the solution (38a) is adequate for convex isotherms ( $m > 1$  and  $N < 1$ ) such as the power-law Freundlich isotherm which is a specific case of the more general Langmuir equation for low  $\theta$ .

### 6. Conclusions

The article performed a reappraisal of the famous Ward–Tordai equation entirely developed in terms of fractional calculus. The unified approach demonstrates that Ward–Tordai equation can be clearly reformulated as a nonlinear ordinary time-fractional equation of order 1/2. In addition, the approach used allowed to formulate versions with different isotherms. The simple solution of the case with the Henry's isotherms is provided. The Cauchy problem involving an example with the Freundlich isotherm is discussed.

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