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Volterra integro-differential equation and the aging effect at a liquid interface

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The aging of a liquid surface is made evident through the surface-mass-density variation with time. By using the surface-mass conservation law together with the solution of the diffusion equation, we find, for dilute solutions, that surface-mass changes with time following a Volterra integro-differential equation of the second kind. The solution of this equation, for a semi-infinite fluid, together with the two-dimensional equation of state for a dilute gas, allows us to find the surface-tension variation with time. The result is compared with a recent experimental dynamic measurement of the liquid-vapor interfacial tension for aqueous solutions of a nonionic detergent.

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I. INTRODUCTION

Very little work has been done lately on understanding the aging problem of a liquid surface. Among the problems of surface fluid dynamics, this is an interesting one. It had been found earlier [1] that surface tension decreases with time in a drop formation. Recently, a complicated behavior of surface-tension variations with time [2] was observed, in complex systems undergoing a change of pressure. The aging effect has been also noticed in measurements of dynamic surface tension [3]. Different models have been proposed to explain this surface-tension diminution with time. One of these [4] was done by solving an *ad hoc* differential equation, where empirical formulations for concentration-dependent interfacial tension were coupled with various theoretical expressions for the concentration variation with time. Theories for time-surface mass variation, with and without a simultaneous loss of solute into the vapor phase, were also attempted [5,6]. These important approaches to the problem were developed on the basis of well-accepted physical laws (Gibbs adsorption equation, surface and bulk conservation laws, and a two-dimensional equation of state) that govern the phenomenon. In the present paper we also use the basic physical laws that govern this phenomenon. By pursuing an alternative line of research, we find that surface-mass changes with time follow a Volterra integro-differential equation of the second kind. The exact solution of this equation, for a unit source, shows that surface mass density or the surface tension depends not only on the initial amount of solute (e.g., see Ward and Tordai [5] and Hansen [6]), but on the position where this solute is placed. The result obtained by our present theoretical model is compared with the experiment.

II. SURFACE-TENSION TIME DEPENDENCE

When a solute is injected somewhere into a solvent, the structure of the interface changes. A surface-tension variation with time will be induced via a continous adsorption of solute at the interface. We will approach this problem by considering a simplified version of the surface-mass conservation law, the diffusion law, and the natural connection of both with the Gibbs adsorption equation. The solution of this set of equations provides and integro-differential equation for the surface-mass density. Then, by using a two-dimensional equation of state, we get the surface-tension variation with time.

On writing the surface-mass balance equation, we suppose that surface mass changes with time due to mass diffusion of solute (binary mixture) from the bulk to the adjacent interface. Under these restrictive assumptions, the surface-mass balance law reads

$$\frac{\partial \Gamma}{\partial t}=\left[\rho D\frac{\partial C}{\partial z}\right]_{z=0\,(\text{gas})}-\left[\rho D\frac{\partial C}{\partial z}\right]_{z=0\,(\text{liquid})}, \tag{1}$$

where $\Gamma=\int_{-\epsilon}^{+\epsilon}\rho(z)dz$ is the surface density of solute at the interface. $C=\rho_s/\rho$ is the mass fraction of solute, ρ_s and ρ are the solute density and total density (mass per unit volume). D is the binary diffusion coefficient. $z=0$ indicates the position of the interface, where the concentration gradients must be evaluated. This equation follows from the conservation-mass law, when the barycentric velocity vanishes. Equation (1) tells us that surface solute density changes with time as a result of changes produced in the concentration gradient of the solute at the interface. In the present problem, the solute is injected in the liquid phase and it will not have any effect upon the gas phase. The solute diffusion is governed by

$$\frac{\partial C}{\partial t}=D\nabla^2 C\ . \tag{2}$$

If the initial concentration is $f(z)$ and the concentration at the boundary $C(z=0,\,t)=C_s(t)$, the concentration for a semi-infinite fluid at $z>0$ will be [7]

$$C(z,t)=\frac{z}{2\sqrt{D\pi}}\int_0^t \frac{C(\tau)}{(t-\tau)^{3/2}}e^{-z^2/4D(t-\tau)}d\tau + \frac{1}{2\sqrt{D\pi t}}\int_0^\infty f(z')(e^{-(z-z')^2}/4Dt - e^{-(z+z')^2/4Dt})dz' \ . \qquad (3)$$

Let the concentration of solute $f(z')$ be zero in all spaces, except for an infinitely thin layer at $z'=L$, which is infinite in such a way that the total concentration $\int f(z')dz'$ is finite. The concentration $C_s(t)$ will change with time due to the diffusion of solute from the bulk towards the interface. The concentration at any z will be

$$C(z,t)=\frac{z}{2\sqrt{D\pi}}\int_0^t \frac{C(\tau)}{(t-\tau)^{3/2}}e^{-z^2/4D(t-\tau)}d\tau - \frac{Q}{2\sqrt{D\pi t}}e^{-(z-L)^2/4Dt} , \qquad (4)$$

where Q is the solute mass per unit area divided by the mass per unit volume at $z'(<0)=L$ and $t=0$. With the help of Eq. (4), Eq. (1) becomes

$$\frac{\partial\Gamma}{\partial t}+\frac{\rho}{2}\left[\frac{D}{\pi}\right]^{1/2}\int_0^t \frac{C(\tau)}{(t-\tau)^{3/2}}d\tau=\frac{\rho QL}{4(\pi D t^3)^{1/2}}e^{-L^2/4Dt} . \qquad (5)$$

Whenever a variation of mass fraction of solute, at the surface and an initial concentration of solute at L are given, the integro-differential Equation (5) shows how surface density changes with time. In order to solve this equation, an explicit relation between surface density and solute concentration must be given. For dilute solutions of an un-ionized solute, the only case that will be considered here, the surface density and the solute concentration are linked by

$$\Gamma=\alpha^{-1}C , \qquad (6)$$

where α is a constant. By substitution of Eq. (6) into Eq. (5) we have

$$\frac{\partial\Gamma}{\partial t}+\alpha\frac{\rho}{2}\left[\frac{D}{\pi}\right]^{1/2}\int_0^t \frac{\Gamma(\tau)}{(t-\tau)^{3/2}}d\tau = \frac{\rho QL}{4(\pi D t^3)^{1/2}}e^{-L^2/4Dt} . \qquad (7)$$

The solution of this Volterra integro-differential equation of the second kind is solved by a Laplace transform, and is written as

$$\Gamma(t)=\frac{\rho Q}{2}e^{-(\rho\alpha/\pi)L}e^{-(\rho\alpha/\pi)^2 Dt} \times \mathrm{erfc}[L/(2\sqrt{Dt})-(\rho\alpha/\pi)\sqrt{Dt}\,] . \qquad (8)$$

This equation predicts the growth of the solute at the interface with time. This growth depends on the solvent-solute nature, via the diffusion constant D, on the initial quantity of solute per unit area ρQ, and on the position L where the solute is placed.

We assume that surface density and surface tension are related by the following two-dimensional equation of state:

$$\sigma-\sigma_0=-RT\Gamma , \qquad (9)$$

where, here, σ and σ_0 indicate the surface tension of the solution and the pure solvent, respectively. This equation is analogous to the three-dimensional equation of state of a perfect gas. If the effect of cohesive forces in the film is taken into account, the following two-dimensional equation of state holds:

$$\sigma-\sigma_0=-E\ln(\Gamma/\Gamma_0) , \qquad (10)$$

where E is the modulus of surface elasticity and Γ_0 is the surface density when the surface tension is σ_0. As $1/E$ is the compressibility of the film, we could call the above equation the compressibility equation of state. It must be pointed out that, by writing Eq. (10) in the differential form ($d\sigma=-Ed\Gamma/\Gamma$) and considering the surface elasticity (Marangoni elasticity) E to be linearly related to surface density Γ, Eq. (10) becomes structurally similar to Eq. (9).

By substitution of Eq. (8) into Eqs. (9) and (10), we find that the surface-tension variation with time is

$$\xi(t)=\xi_0(t=0)-(RT/\sigma^E)\Gamma(t) \qquad (11)$$

and

$$\xi(t)=\xi_0-(E/\sigma^E)\ln[\Gamma(t)/\Gamma_0] , \qquad (12)$$

where σ^E is the equilibrium interfacial tension, $\xi(t)=\sigma(t)/\sigma^E$, and $\xi_0=\sigma_0/\sigma^E$. In order to test the present approach we compare (see Fig. 1) Eqs. (11) and (12) with data of dynamic measurements of interfacial tension of aqueous solutions of a nonionic detergent (Tween-80) [4].

To compute ξ from Eq. (11), we use the following values of the parameters σ_0(water)=73 dyn/cm, σ^E(solution)=57 dyn/cm, $T=303.2$ K, $D\cong 10^{-5}$ cm^2/sec, $\alpha\cong 1/10$ cm^2 mol, $L\cong 1/10$ cm, and $\rho Q=3$

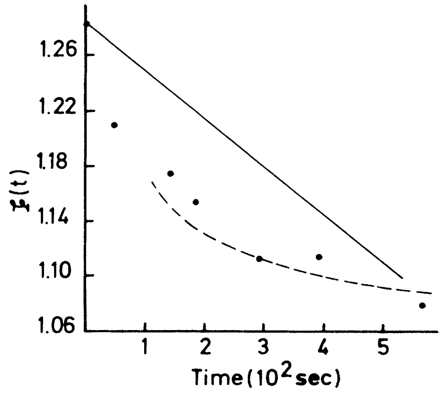

FIG. 1. Dimensionless liquid-vapor interfacial tension $\xi(t)$ as a function of time t, for a saline solution of a nonionic detergent (Tween-80). The circles indicate the experimental points. The solid and dashed lines represent Eqs. (11) and (12), respectively.

$\times 10^{-9}$ mol/cm^2. The constants used for evaluating ξ from Eq. (12) are $\sigma_0(t=290\ \text{sec})=67.6$ dyn/cm, $E=2$ dyn/cm, and $\Gamma_0(t=290\ \text{sec})\cong 7.7\times 10^{-9}$ mol/cm^2. Equation (12) cannot be used at $t=0$ because adsorption is null.

III. CONCLUSIONS

We present in this article a description of the aging of a liquid surface. The evolution in time of solute surface density is given by an integro-differential equation. When a crude linear relation between surface density and bulk mass fraction of solute [Eq. (6)] is assumed, this integro-differential equation [Eq. (5)] reduces to a Volterra-type equation of the second kind [Eq. (7)]. Under this restrictive hypothesis, low concentration, we find the surface density variation with time [Eq. (8)] by solving Eq. (7). The surface-tension variation with time [Eqs. (11) and (12)] is found with the help of two different equations of state [Eqs. (9) and (10)]. The two former equations and the experimental data of dynamic measurements of interfacial tension of aqueous solutions of a nonionic detergent (Tween-80) [4] are represented in Fig. 1. Equation (10) and consequently Eq. (12) seem to be more representative of the present experimental situation than Eqs. (9) and (11). It must be kept in mind that the solution of the aging problem given by Eqs. (11) and (12) corresponds to a seminfinite fluid system, while the symmetry associated with the experimental technique (pendant drop technique) [4] corresponds to a spherical symmetry.

The solution of the aging problem by a Volterra integro-differential equation is of importance because, at a low concentration of solute, an exact solution can be simply found. Furthermore, we show how the solution depends not only on the initial solute concentration[5,6] but also on where this solute is placed. When the initial solute concentration is far away from the interface, the aging process will be slow. This geometrical aspect of the problem, not considered before to the author's knowledge, is as important as the solute-solvent relation of the system (the diffuseness of the medium).

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