JOURNAL OF COLLOID AND INTERFACE SCIENCE 167, 320–331 (1994)

Dynamic Surface Tension of Solutions of Surfactant Mixtures

1. Diffusion-Convective-Controlled Adsorption

LEONID K. FILIPPOV

Lehigh University, Selley G. Mudd Building, 6 East Packer Avenue, Bethlehem, Pennsylvania 18015-3192

Received January 18, 1994; accepted April 6, 1994

A quantitative theory of the dynamic surface tension for 2 multicomponent mixture of surfactants obeying the Langmuir adsorption isotherms with constant diffusion coefficients in the bulk and in the adsorbed layer is developed for diffusion-controlled and diffusion-convective-controlled adsorption models. The effect of the mutual diffusion in the adsorbed layer and the effect of the convective transfer are estimated in an analytical form for the short-time and long-time approximations. It is concluded that the dynamic surface tension can be described by the diffusion-convective-controlled model. It is shown that the equation $F(\gamma(t)) = \log[(\gamma_0 - \gamma(t))/(\gamma(t) - \gamma_e)] = n \log(t/t_{\mathrm{rel}})$ is valid over a wide range of time for the multicomponent mixture of surfactants. Because the diffusion-controlled and diffusion-convective-controlled adsorption models are shown to be asymptotical, correlation n equals one-half. Simple formulae are derived to calculate the parameters n and t_{rel} and the dynamic surface tension over a wide range of time for adsorption isotherms of multicomponent mixtures obeying the Langmuir adsorption isotherms.

INTRODUCTION

Many important phenomena, such as interfacial turbulence, thin film stability, high wetting or foaming, and retardation of drop motion, are consequences of the fact that surface tension varies with surface concentration and time. In these processes equilibrium concentrations are not attained and dynamic processes play a major role.

Time-dependent surface tension, known as dynamic surface tension, has been investigated by many authors for the individual and mixture surfactants (1–31). The suggestion that surfactant diffusion to the surface is the cause of dynamic surface tension was first made by Milner (1) and described by Langmuir and Schaefer (3). Diffusion-controlled adsorption for an individual surfactant was first analyzed quantitatively by Ward and Tordai using an integral equation (5). Hansen (7) has found analytical solutions in the form of three terms for the short-time approximation and in the form of the first term for the systems obeying the Langmuir isotherms. A critical analysis of numerical solutions has been conducted by Borwankar and Wasan (19) for the individual surfactant and by Miller and co-workers (30) for multicomponent mixtures. These authors analyzed the different numerical schemes and showed that numerical solutions of the nonlinear equations may be obtained only by making sets of simplifying assumptions. The dynamic surface tension for a two-component mixture of surfactants has been studied experimentally by Joos and Van den Bogaert (11). As shown in (25, 26, 29), a relaxation equation, Eq. [1], may be used to describe surface tension over a wide range of time as a function of time and two adjustable parameters,

$$\log\{[\gamma_0 - \gamma(t)]/[\gamma(t) - \gamma_e]\} = n \log(t) - n \log(t_{\mathrm{rel}}), \quad [1]$$

where γ_0 is the solvent surface tension, $\gamma(t)$ is the surface tension at time t, γ_e is the equilibrium surface tension of the solution, and n (dimensionless) and t_{rel} (units of time) are constants. It is reasonable to analyze the theoretical foundations of the relaxation equation in terms of the diffusion-controlled adsorption and diffusion-convective-controlled models.

Forced convection decreases the adsorption at the surface of a drop or bubble relative to a static aging surface. The diffusion-convective model for growing drops and bubbles was first formulated by Ilkovic (32, 33). The approximate solution for this model was derived by Delahay *et al.* (34, 35). The convective transfer of surfactant from the bulk to the expanding surface is accounted for by a convective term in (36, 37). Application of the theory of diffusion-convective kinetics to experimental data is based on using the first term for the short-time approximation (16, 27, 29, 36). There is no first term for the long-time approximation of diffusion-convective kinetics.

We examine the analytical approaches and the simplifying assumptions of the earlier investigations. Despite several attempts, there is no treatment of the problem which achieves

0021-9797/94 $6.00

a general analytical approach for solving the nonlinear equations for multicomponent mixtures of surfactants, without making sets of simplifying assumptions (36). Therefore, we present a general formulation of the problem and a simple analytical scheme to solve the resulting nonlinear equations for both the diffusion-controlled and the diffusion-convective-controlled models of adsorption kinetics.

The purposes of this paper are (a) to develop a theory of the dynamic surface tension over a wide range of time for multicomponent mixtures of surfactants, (b) to estimate the effects of the mutual diffusion in the adsorbed layer and the convective transfer in an analytical form for the short-time and long-time approximations, (c) to justify theoretically that Eq. [1] may be useful to describe dynamic surface tension in a wide time range for multicomponent mixtures of surfactants, and (d) to derive simple formulae to calculate the parameters n and t_{rel} in the relaxation equation [1].

THEORY

Surface Tension Relations of Surfactant Mixtures for Langmuir Adsorption Isotherms

The change in the equilibrium surface tension is related to the adsorption by the Gibbs equation (Eq. [2]) (38)

$$d\gamma = -\sum_{k=1}^{n} \Gamma(c)d\mu_k \approx -\sum_{k=1}^{n} \Gamma_k(c_1, c_2, \ldots, c_n)RTdc_k/c_k, \quad 1 \leqslant k \leqslant n, \quad [2]$$

where Γ_k is the amount of adsorption for the kth mixture component, c_k is the concentration of the kth mixture component, n is the number of mixture components, R is the gas constant, and T is the absolute temperature.

For the Langmuir adsorption isotherm in the dimensional and dimensionless forms, respectively,

$$\Gamma_k(c) = \Gamma^0_{\mathrm{m}}K^{\mathrm{p}}_k c_k/[1 + V(c)], \; \Gamma_k(C) = (1 + V_0)C_k/[1 + V(C)], \quad C_k = c_k/c_{0k} \quad [3a]$$

$$\Gamma_k(C) = \Gamma_k(c)/\Gamma_{0k}, \; \Gamma_{0k} = \Gamma^0_{\mathrm{m}}b_k/(1 + V_0), \; V_0 = \sum_{k=1}^{n} b_k, \; V(c) = \sum_{k=1}^{n} K^{\mathrm{p}}_k c_k, \; V(C) = \sum_{k=1}^{n} b_k C_k \quad [3b]$$

$$b_k = K^{\mathrm{p}}_k c_{0k}, \; 0 \leqslant C_k, \; \Gamma_k \leqslant 1, \; 1 \leqslant k \leqslant n, \quad [3c]$$

where K^{p}_k is the equilibrium constant for the kth mixture component, Γ_m is the maximum adsorption, and c_{0k} is the concentration of the kth mixture component in the bulk.

Strictly the Gibbs equation should be applied only to equilibrium cases. However, if the reduction in surface tension is assumed to result only from the adsorption of surfactant, then the resulting surface tension relationships for each adsorption isotherm respectively can be written, with $\gamma(t)$ replacing γ_e,

$$\gamma(t) = \gamma_0 - RT\Gamma^0_{\mathrm{m}}\ln[1 + V(c(t))],$$
$$\gamma_0 - \gamma_e = RT\Gamma_{\mathrm{m}}\ln(1 + V_0). \quad [4]$$

The Diffusion-Controlled Model

The adsorption process takes place in a thin layer on a planar interface. In general this process is governed by the diffusion and mutual diffusion of molecules of the mixture components in the adsorption layer. Therefore, the adsorption processes on a planar surface may be described for the one-dimensional model as (38, 39)

$$\partial c_k(x, t)/\partial t = \sum_{j=1}^{n} \partial[D_{kj}(c_1, c_2, \ldots, c_n) \times \partial c_j(x, t)/\partial x]/\partial x, \quad 1 \leqslant k, j \leqslant n \quad [5]$$

$$\Gamma_k(t) = \int_0^{\infty} [c_k(x, t) - c_{0k}]dx, \quad 1 \leqslant k \leqslant n \quad [6]$$

with the initial [7] and boundary [8] conditions, respectively,

$$c_k(x > 0, 0) = c_{0k}, \; \Gamma_k(0) = 0, \; c_k(\infty, t) = c_{0k} \quad [7]$$

$$d\Gamma_k(t)/dt = \sum_{j=1}^{n} D_{kj}(c_1, c_2, \ldots, c_n)\partial c_j(0, t)/\partial x, \quad [8]$$

where $c_k(x, t)$ is the concentration of the kth mixture component at coordinate x normal to the surface ($x = 0$), $c_k(0, t)$ is the surface concentration of the kth mixture component on an interface, c_{0k} is the bulk concentration of the kth mixture component, $D_{kk}(c)$ and $D_{kj}(c)$ are the coefficients of diffusion ($k = j$) and mutual diffusion ($k \neq j$) of the kth and jth mixture components, and Γ_k is the adsorption of the kth mixture component on a planar interface. The diffusional transport of surfactant molecules in the bulk is described by Fick's second law in the form of Eq. [5]. For high adsorbate concentrations the diffusion coefficients, $D_{kj}(c_1, c_2, \ldots, c_{\mathrm{n}})$, depend on the adsorbate concentrations, c_k (38, 39). The boundary conditions Eq. [8] are drawn from Fick's first law, which describes the flux at a place $x = 0$. The adsorbed layer is not homogeneous, as the adsorbate concentrations, $c_k(x, t)$, depend on the distance x from the surface ($x = 0$). Therefore, the adsorbed amount per unit of surface, $\Gamma_k(t)$, for the kth mixture components, using the Gibbs convention (38), is given by Eq. [8], where $[c_k(0, t) - c_{0k}]$ is the excess concentration of the kth mixture component adsorbate in the adsorbed layer (mass per volume unit).

The inhomogeneous adsorption model in the form of Eqs. [5] through [8] is complex and it is reasonable to consider the simplified homogeneous adsorption model, which may be written (29, 40) as

$$\partial c_k(x,t)/\partial t = D^0_{kk}\partial^2 c_k(x,t)/\partial x^2, \quad 1 \leqslant k, j \leqslant n \qquad [9]$$

$$d\Gamma_k(t)/dt = \sum_{j=1}^{n} D^{\mathrm{ad}}_{kj}\partial c_j(0,t)/\partial x, \quad 1 \leqslant k, j \leqslant n, \qquad [10]$$

where D^0_{kk} are the diffusion coefficients of the kth mixture component in the bulk, and D^{ad}_{kj} are the diffusion coefficients of the kth mixture component in the adsorbed layer. This approach has been already introduced by Ravera and coworkers (40); the authors interpreted the diffusion coefficients, D^{ad}_{kk}, in the framework of an interfacial potential barrier in the adsorbed monolayer. For the simplified adsorption model the diffusion coefficients, D^0_{kk}, in the bulk are assumed to be constant. Inhomogeneity taking place within the adsorbed layer is assumed to be estimated by using the homogeneous model with constant diffusion coefficients, D^{ad}_{kj}, depending on the interaction between adsorbate molecules in the adsorbed layer and the architecture of the adsorbed layer. For low surfactant concentrations the mutual diffusion in the bulk can be neglected. The role of the mutual diffusion, D^{ad}_{kj} $(k \neq j)$, in the adsorbed layer can become important due to the interaction of surfactant molecules in the adsorbed layer.

The system of equations [9] and [10] may be reduced to a system of integral Volterra equations by using the Laplace transform (29, 35). By using the Laplace transform

$$\tilde{c}_k(x,p) = \int_0^{\infty} c_k(x,t)\exp(-pt)dt, \qquad [11]$$

where p is the parameter of the Laplace transform, the system of equations [6], [9], and [10] may be written as

$$\tilde{c}_k(0,p) = c_{0k}/p - \sum_{j=1}^{n} [(pD^0_{kk})^{1/2}(D^{\mathrm{ad}})^{-1}_{kj}]\tilde{\Gamma}_j(p),$$
$$1 \leqslant k, j \leqslant n, \qquad [12]$$

where $(D^{\mathrm{ad}})^{-1}_{kj}$ is the reciprocal matrix of D^{ad}_{kj}.

The inverse Laplace transform of Eqs. [11] and [12] may be reduced to the integral Volterra equations

$$\Gamma_k(t) = \sum_{j=1}^{n} 2[D^{\mathrm{ad}}_{kj}/(\pi D^0_{kk})^{1/2}]$$
$$\times\left[c_{0j}t^{1/2} - \int_0^t c_j(0, t-\rho)d\rho^{1/2}\right] \qquad [13]$$

$$c_k(0,t) = c_{0k} - \frac{d}{dt}\sum_{j=1}^{n}\int_0^t \Gamma_j(t-\rho)d\rho$$
$$\times[(D^0_{kk})^{1/2}(D^{\mathrm{ad}})^{-1}_{kj}]/(\pi\rho)^{1/2}, \quad 1 \leqslant k, j \leqslant n. \qquad [14]$$

As will be shown below, to describe the adsorption process over a wide range of times, it is reasonable to use the system of equations [13] for short times (see Eqs. [16]) and the system of equations [14] for long times (see Eqs. [21]). The solution of the system of equations [13] and [14] over a wide range of times may be found by using the relaxation function $F(t)$, which may be written in the form (25, 26, 29)

$$F(\gamma(t)) = \log[(\gamma_0 - \gamma(t))/(\gamma(t) - \gamma_e)]$$
$$= n\log(t/t_{\mathrm{rel}}), \qquad [15]$$

where t_{rel} is the relaxation time characterizing the rate of adsorption processes on the interface and in the adsorption layer, and n is the slope of the relaxation function $F(t)$ versus $\log(t)$. In fact, Eq. [15] is in a form similar to the Fourier transform of a correlation function, often used in relaxation theory (41, 42).

Arbitrary adsorption isotherms such as those of Langmuir, Volmer, and Van der Waals, excepting Freundlich adsorption isotherms, do not have the singularity at $C = 0$; i.e., $d\Gamma(C = 0)/dC$ is bounded. For these adsorption isotherms the solution of Eqs. [13] for short times ($t \rightarrow 0$) may be found in the form

$$\Gamma_k(t) = \sum_{j=1}^{\infty} a_{kj}t^{j/2}, \; c_k(0,\mathrm{t}) = \sum_{j=1}^{\infty} b_{kj}t^{j/2},$$
$$1 \leqslant k \leqslant n, j \geqslant 1. \qquad [16]$$

Substituting Eqs. [16] into Eq. [13] and establishing the coefficients in the power series by means of Eqs. [16], we find

$$a_{k1} = 2/\pi^{1/2}\sum_{j=1}^{n}(D^*_{kj})^{1/2}c_{0j}, \; D^*_{kj} = (D^{\mathrm{ad}}_{kj})^2/D^0_{kk},$$
$$1 \leqslant k, j \leqslant n \qquad [17a]$$

$$a_{k(s+1)} = -\sum_{j=1}^{n}(D^*_{kj})^{1/2}b_{js}\Gamma(1 + s/2)/\Gamma[(s+3)/2],$$
$$s \geqslant 1, 1 \leqslant k, j \leqslant n, \qquad [17b]$$

where $\Gamma(k)$ is the gamma function (41, 43).

For the Langmuir adsorption isotherms [3a] the coefficients in Eqs. [16] are equal to

$$a_{k1} = 2/\pi^{1/2}\sum_{j=1}^{n}(D^*_{kj})^{1/2}c_{0j}, \; b_{k1} = 2/(\pi^{1/2}\Gamma^0_{\mathrm{m}}K^{\mathrm{p}}_k)$$
$$\times\sum_{j=1}^{n}(D^*_{kj})^{1/2}c_{0j}, \quad 1 \leqslant k, j \leqslant n \qquad [18a]$$

$$a_{k2} = -\pi^{1/2}/2 \sum_{j=1}^{n} (D^{*}_{kj})^{1/2} b_{j1},\ b_{k2} = b_{k1}\Big(\sum_{s=1}^{n} K^{\mathrm{p}}_{s} b_{s1}\Big) - \pi^{1/2}/(2\Gamma^{0}_{\mathrm{m}} K^{\mathrm{p}}_{k}) \sum_{j=1}^{n} (D^{*}_{kj})^{1/2} b_{j1} \qquad [18b]$$

$$a_{k3} = -4/(3\pi^{1/2}) \sum_{j=1}^{n} (D^{*}_{kj})^{1/2} b_{j2} \qquad [18c]$$

$$b_{k3} = -4/(3\pi^{1/2}\Gamma^{0}_{\mathrm{m}} K^{\mathrm{p}}_{k}) \sum_{j=1}^{n} (D^{*}_{kj})^{1/2} b_{j2} + b_{k2} \sum_{s=1}^{n} K^{\mathrm{p}}_{s} b_{s1} + b_{k1}\Big[\sum_{r=1}^{n} K^{\mathrm{p}}_{r} b_{r2} - \Big(\sum_{s=1}^{n} K^{\mathrm{p}}_{j} b_{j1}\Big)^{2}\Big]. \qquad [18d]$$

From Eqs. [4] and [16] through [18], the dynamic surface tension for the Langmuir adsorption isotherms for short times ($t \to 0$) is given as

$$\gamma(t) = \gamma_0 - RT\Gamma^{0}_{\mathrm{m}} \ln[1 + V(t)],\ V(t) = \sum_{k=1}^{\infty} A_k t^{k/2},$$

$$A_k = \sum_{s=1}^{n} K^{\mathrm{p}}_{s} b_{sk}, \quad 1 \leqslant k, s \leqslant n. \qquad [19]$$

According to Eq. [19], for the Langmuir adsorption isotherms for short times Eqs. [4] and [15] reduce, respectively, to

$$[\gamma_0 - \gamma(t)]/(\gamma_0 - \gamma_e) \approx S_0 t^{1/2},$$

$$S_0 = 2/[\pi^{1/2}\ln(1 + V_0)] \sum_{k=1}^{n}\sum_{j=1}^{n} (D^{*}_{kj})^{1/2} c_{0j}/\Gamma^{0}_{\mathrm{m}} \qquad [20a]$$

$$F(\gamma(t)) = n_0 \log(t/t^{0}_{\mathrm{rel}}),\ n_0 = 0.5,$$

$$F(\gamma(t)) = 0.5 \log(t) + s_0 \qquad [20b]$$

$$t^{0}_{\mathrm{rel}} = 1/S^{2}_{0},\ s_0 = \log(S_0)\ \text{(short times)}, \qquad [20c]$$

where S_0 is the slope of the straight line $[\gamma_0 - \gamma(t)]/(\gamma_0 - \gamma_e)$ versus $t^{1/2}$ and s_0 is the shift of the straight line $F(\gamma(t))$ versus $\log(t)$ for short times.

As a first approximation for the Langmuir adsorption isotherms from Eq. [14] for long times ($t \to \infty$), we find

$$c_k(0, t) = c_{0k} - a^{\infty}_{k1}/t^{1/2},\ a^{\infty}_{k1} = \pi^{-1/2} \times \sum_{j=1}^{n} \Gamma_{0j}(D^{0}_{kk})^{1/2}(D^{\mathrm{ad}})^{-1}_{kj}, \quad 1 \leqslant k, j \leqslant n \qquad [21a]$$

$$\Gamma_k = \Gamma_{0k} - t^{-1/2} \sum_{j=1}^{n} a^{\infty}_{j1} \partial\Gamma_k(c_{01}, c_{02}, \ldots, c_{0n})/\partial c_j \qquad [21b]$$

$$[\gamma(t) - \gamma_e]/(\gamma_0 - \gamma_e) \approx S_{\infty} t^{-1/2},$$

$$S_{\infty} = \pi^{-1/2}/[(1 + V_0)\ln(1 + V_0)] \times \sum_{k=1}^{n}\sum_{j=1}^{n} K^{\mathrm{p}}_{k}\Gamma_{0j}(D^{0}_{kk})^{1/2}(D^{\mathrm{ad}})^{-1}_{kj} \qquad [21c]$$

$$F(\gamma(t)) = n_{\infty} \log(t/t^{\infty}_{\mathrm{rel}}),\ n_{\infty} = 0.5,$$

$$F(\gamma(t)) = 0.5 \log(t) + s_{\infty} \qquad [21d]$$

$$t^{\infty}_{\mathrm{rel}} = S^{2}_{\infty},\ s_{\infty} = -\log(S_{\infty})\ \text{(long times)}, \qquad [21e]$$

where S_{∞} is the slope of the straight line $[\gamma(t) - \gamma_e)]/(\gamma_0 - \gamma_e)$ versus $t^{-1/2}$ and s_{∞} is the shift of the straight line $F(\gamma(t))$ versus $\log(t)$ for long times.

The consistent time scale (CTS) approach may be used to find solutions of the system of equations [13] and [14] in the analytical form for arbitrary adsorption isotherms without the mutual diffusion in the adsorbed layer ($D^{\mathrm{ad}}_{kj} = 0$, $k \neq j$). The CTS approach is based on the preceding analysis and the following assumptions (44):

(A) The surface concentration of an individual adsorbate, $c_k(0, t)$, is described by using the function $g(t_k)$ in the form of Eq. [22]. As shown in (29), in the simplest case, when the equilibrium adsorption obeys the linear Henry law, from the inverse Laplace transform of Eq. [11], the adsorption in terms of the relative time $t_1 = t/t_{01}$ is

$$c_1(0, t)/c_{01} = \Gamma_1(t)/\Gamma_{01} = g(t_1),\ t_1 = t/t_{01} \qquad [22a]$$

$$t_{01} = (\Gamma_{01}/c_{01})^2/D^{*}_{11},\ D^{*}_{11} = (D^{\mathrm{ad}}_{11})^2/D^{0}_{11} \qquad [22b]$$

$$g(t_1) = 1 - \exp(t_1)\operatorname{erfc}(t_1^{1/2}) \qquad [22c]$$

$$\operatorname{erfc}(y) = 1 - \operatorname{erf}(y),\ \operatorname{erf}(y) = (2/\pi^{1/2}) \int_0^{\infty} \exp(-z^2)\,dz, \qquad [22d]$$

where $\operatorname{erf}(y)$ is the error function (37) and D^{*}_{11} is the effective diffusion coefficient, which was first introduced by Ravera and co-workers (40).

(B) The adsorption of the kth mixture component, $\Gamma_k(c_1, c_2, \ldots, c_n)$, and the consistent time scales, t_k and $\xi(t_k)$, according to the preceding relations and the CTS approach, may be written as

$$c_k(0, t) = c_{0k} g(\xi(t_k)), \quad 1 \leqslant k \leqslant n \qquad [23a]$$

$$\Gamma_k(c_1, c_2, \ldots, c_n) = \Gamma_k[c_{01} g(\xi(t_1)), c_{02} g(\xi(t_2)), \ldots, c_{0n} g(\xi(t_n))], \quad 1 \leqslant k \leqslant n \qquad [23b]$$

$$t_k = t/t_{0k},\ t_{0k} = (\Gamma_{0k}/c_{0k})^2 D^{0}_{kk}/(D^{\mathrm{ad}}_{kk})^2,\ 1 \leqslant k \leqslant n \qquad [23c]$$

$$\xi(t_k) = t_k\{c_{0k} g(t_k)/\Gamma_k[c_{01} g(t_1), c_{02} g(t_2), \ldots, c_{0n} g(t_n)]\}^2, \quad 1 \leqslant k \leqslant n. \qquad [23d]$$

The relations [23b] and [23c] made the time scales, $\xi(t_k)$, consistent with the local time scales, t_{0k}, because for any adsorption isotherms the local time scales depend on $(\Gamma_k/c_k)^2$ of mixture components in the form of $[\Gamma_k(g)/g(t_k)]^2$.

For the Langmuir adsorption isotherm [3] the solutions [23] reduce to

$$c_k(0, t) = c_{0k}g(\xi(t_k)), \quad 1 \leqslant k \leqslant n \qquad [24a]$$

$$\Gamma_k(t) = \Gamma_{\mathrm{m}}^0 K_k^{\mathrm{p}} c_{0k} g(\xi(t_k))/[1 + V(\xi)],$$

$$V(\xi) = \sum_{k=1}^{n} K_k^{\mathrm{p}} c_{0k} g(\xi(t_k)), \quad 1 \leqslant k \leqslant n \qquad [24b]$$

$$\gamma(t) = \gamma_0 - RT\Gamma_{\mathrm{m}}^0 \ln[1 + V(t)] \qquad [24c]$$

$$t_k = t/t_{0k},\ t_{0k} = [\Gamma_{\mathrm{m}}^0 K_k^{\mathrm{p}}/(1 + V_0)]^2 D_{kk}^0/(D_{kk}^{\mathrm{ad}})^2, \quad 1 \leqslant k \leqslant n \qquad [24d]$$

$$\xi(t_k) = t_k\{[1 + V(\xi)]/(1 + V_0)\}^2, \quad 1 \leqslant k \leqslant n. \qquad [24e]$$

The preceding equations may be used to describe the surface concentration, $c_k(0, t)$, the adsorption, $\Gamma_k(t)$, and the dynamic surface tension, $\gamma(t)$, over a wide range of time for the diffusion-controlled adsorption model without mutual diffusion in the adsorbed layer.

The Diffusion-Convective-Controlled Model

The surface age of a bubble or drop undergoing continuous surface expansion is less than the drop or bubble interval (16). Convective transfer of surfactant from the bulk to the surface is an additional mechanism of adsorption onto a drop or bubble surface. The concentration of surfactant at the expanding surface for the simplified homogeneous adsorption model is governed by the diffusion-convective equations (32–37)

$$\partial c_k(x, t)/\partial t - (2x/3t)\partial c(x, t)/\partial x = D_{kk}^0 \partial^2 c(x, t)/\partial x^2,\ c_k(x, 0) = c_k(\infty, t) = c_{0k} \qquad [25a]$$

$$\Gamma_k(0) = 0,\ d\Gamma_k/dt + (2/3t)\Gamma_k = \sum_{j=1}^{n} D_{kj}^{\mathrm{ad}} \partial C_j(0, t)/\partial x, \quad 1 \leqslant k, j \leqslant n. \qquad [25b]$$

By using Levich's transformation (36, 37) and the new variables $\tilde{x}$ and $\tilde{t}$, defined as

$$\tilde{x} = xt^{2/3}, \quad \tilde{t} = 3/7t^{7/3}, \qquad [26]$$

the diffusion-convective equations become

$$\partial c_k/\partial \tilde{t} = D_{kk}^0 \partial^2 c/\partial \tilde{x}^2,\ c_k(\tilde{x} > 0, 0) = c_k(\infty, \tilde{t}) = c_{0k}, \quad 1 \leqslant k \leqslant n \qquad [27a]$$

$$\Gamma_k(0) = 0,\ \sum_{k=1}^{n} D_{kj}^{\mathrm{ad}} \partial c_j(0, \tilde{t})/\partial \tilde{x} = dH_k(\tilde{t})/d\tilde{t},\ H_k(\tilde{t}) = (7/3)^{2/7}(\tilde{t}^{2/7}\Gamma_k). \qquad [27b]$$

The solution to Eqs. [27a] and [27b] may be found by the Laplace transform

$$\tilde{c}_k(\tilde{x}, \tilde{p}) = \int_0^\infty c_k(\tilde{x}, \tilde{t})\exp(-\tilde{p}\tilde{t})d\tilde{t}. \qquad [28]$$

The bounded solution for Eqs. [27a] and [27b] is

$$\tilde{c}_k(0, \tilde{p}) = c_{0k}/\tilde{p} - \sum_{j=1}^{n} [(\tilde{p}D_{kk}^0)^{1/2}(D^{\mathrm{ad}})_{kj}^{-1}]\tilde{H}_j(\tilde{p}), \quad 1 \leqslant k, j \leqslant n, \qquad [29a]$$

or in the equivalent form which is suitable for finding the solution at short times,

$$\tilde{H}_k(\tilde{p}) = \sum_{j=1}^{n} (D_{kj}^{*})^{1/2}[c_{0j}/\tilde{p}^{3/2} - \tilde{c}_j(0, \tilde{p})/\tilde{p}^{1/2}]. \qquad [29b]$$

With substitution of Eq. [26] into Eq. [29b], the solution becomes

$$\Gamma_k(t) = \sum_{j=1}^{n} 2[D_{kj}^{\mathrm{ad}}/(\pi D_{kk}^0)^{1/2}][c_{0j}(3/7t)^{1/2} - t^{-2/3} \times \int_0^{\tilde{t}} c_j(0, \tilde{t} - \rho)d\rho^{1/2}]. \qquad [30]$$

For arbitrary adsorption isotherms the solution of Eq. [30] for short times (t → 0) may be found in the form

$$\Gamma_k(t) = \sum_{s=1}^{\infty} a_{ks}^0 t^{s/2},\ c_k(0, t) = \sum_{k=1}^{\infty} b_{ks}^0 t^{s/2}, \quad 1 \leqslant k \leqslant n,\ s \geqslant 1. \qquad [31]$$

Substituting Eqs. [53] into Eq. [52] and establishing the coefficients in the power series by means of Eqs. [53], we find

$$a_{k1}^0 = \alpha_1 \sum_{j=1}^{n} (D_{kj}^{*})^{1/2} c_{0j},\ \alpha_1 = (12/7\pi)^{1/2} \approx 0.739, \quad 1 \leqslant k, j \leqslant n \qquad [32a]$$

$$a^0_{k(s+1)} = -\alpha_{(s+1)} \sum_{j=1}^{n} (D^*_{kj})^{1/2} b^0_{js},\ \alpha_{(s+1)}$$
$$= (3/7)^{1/2}\Gamma(1 + 3s/14)/\Gamma(3/2 + 3s/14),\ s \geqslant 1, \quad [32b]$$

where $\Gamma(x)$ is the gamma function (41, 43).

For the Langmuir adsorption isotherms [3a] the coefficients in Eqs. [31] are equal to

$$a^0_{k1} = \alpha_1 \sum_{j=1}^{n} (D^*_{kj})^{1/2} c_{0j},\ b^0_{k1} = \alpha_1/(\Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k)$$
$$\times \sum_{j=1}^{n} (D^*_{kj})^{1/2} c_{0j}, \quad 1 \leqslant k, j \leqslant n \quad [33a]$$

$$a^0_{k2} = -\alpha_2 \sum_{j=1}^{n} (D^*_{kj})^{1/2} b^0_{j1},\ b^0_{k2} = b^0_{k1}\Big(\sum_{s=1}^{n} K^{\mathrm{p}}_s b^0_{s1}\Big)$$
$$- \alpha_2/(\Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k) \sum_{j=1}^{n} (D^*_{kj})^{1/2} b^0_{j1} \quad [33b]$$

$$a^0_{k3} = -\alpha_3 \sum_{j=1}^{n} (D^*_{kj})^{1/2} b^0_{j2} \quad [33c]$$

$$b^0_{k3} = -\alpha_3/(\Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k) \sum_{j=1}^{n} (D^*_{kj})^{1/2} b^0_{j2} + b^0_{k2} \sum_{s=1}^{n} K^{\mathrm{p}}_s b^0_{s1}$$
$$+ b^0_{k1}\Big[\sum_{r=1}^{n} K^{\mathrm{p}}_r b^0_{r2} - \Big(\sum_{s=1}^{n} K^{\mathrm{p}}_j b^0_{j1}\Big)^2\Big]. \quad [33d]$$

From Eqs. [4] and [31] through [33], the dynamic surface tension for the Langmuir adsorption isotherms for short times (t → 0) is given as

$$\gamma(t) = \gamma_0 - RT\Gamma^0_{\mathrm{m}} \ln[1 + V(t)],\ V(t) = \sum_{k=1}^{\infty} A^*_k t^{k/2},$$
$$A^*_k = \sum_{s=1}^{n} K^{\mathrm{p}}_s b^0_{sk}, \quad 1 \leqslant k, s \leqslant n. \quad [34]$$

According to Eq. [34], for the Langmuir adsorption isotherms for short times Eqs. [4] and [15] reduce, respectively, to

$$[\gamma_0 - \gamma(t)]/(\gamma_0 - \gamma_e) \approx S^*_0 t^{1/2},\ S^*_0 = (12)^{1/2}/$$
$$[(7\pi)^{1/2} \ln(1 + V_0)] \sum_{k=1}^{n} \sum_{j=1}^{n} (D^*_{kj})^{1/2} c_{0j}/\Gamma^0_{\mathrm{m}} \quad [35a]$$
$$F(\gamma(t)) = n_0 \log(t/t^{*0}_{\mathrm{rel}}),\ n_0 = 0.5,$$
$$F(\gamma(t)) = 0.5 \log(t) + s^*_0 \quad [35b]$$
$$t^{*0}_{\mathrm{rel}} = 1/(S^*_0)^2,\ s^*_0 = \log(S^*_0)\ \text{(short times)}, \quad [35c]$$

where S^*_0 is the slope of the straight line $[\gamma_0 - \gamma(t)]/(\gamma_0 - \gamma_e)$ versus $t^{1/2}$ and s^*_0 is the shift of the straight line $F(\gamma(t))$ versus $\log(t)$ for short times.

Now we consider the solution of Eq. [29a] at long times ($t \to \infty$). Equation [29a] is reduced to Eq. [36], which is suitable for finding solutions at long times:

$$\Delta c_k(t) = c_{0k} - c_k(t),\ \Gamma_k(t) = \Gamma_{0k} - \Gamma_k(t),$$
$$1 \leqslant k \leqslant n \quad [36a]$$

$$\Delta c_k(t) = b^*_{k1}/t^{1/2} - \frac{d}{d\tilde{t}} \int_0^{\tilde{t}} \sum_{j=1}^{n} [(D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj}$$
$$\times \Delta H_j(\rho)[\pi(\tilde{t} - \rho)]^{-1/2} d\rho \quad [36b]$$

$$b^*_{k1} = \beta_1 \sum_{j=1}^{n} [(D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj}]\Gamma_{0j},$$
$$\beta_1 = (7/3)^{1/2}\Gamma(9/7)/\Gamma(11/14) \quad [36c]$$
$$\Delta H_k(\tilde{t}) = (7/3)^{2/7}[\tilde{t}^{2/7} \Delta\Gamma_k(\tilde{t})], \quad 1 \leqslant k \leqslant n. \quad [36d]$$

For arbitrary adsorption isotherms the solution of Eq. [36b] will be found in the form

$$\Delta\Gamma_k(t) = \sum_{k=1}^{\infty} a^*_{ks}/t^{s/2},\ \Delta c_k(t) = \sum_{s=1}^{\infty} b^*_{ks}/t^{s/2},$$
$$1 \leqslant k \leqslant n. \quad [37]$$

Substituting Eqs. [37] in Eqs. [36b] and establishing the coefficients in the power series by means of Eqs. [37], we find

$$b^*_{k1} = \beta_1 \sum_{j=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj} \Gamma_{0j},\ \beta_1$$
$$= (7/3)^{1/2}\Gamma(9/7)/\Gamma(11/14), \quad 1 \leqslant k, j \leqslant n \quad [38a]$$

$$b^*_{k(s+1)} = -\beta_{(s+1)} \sum_{j=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj} a^*_{js},$$
$$1 \leqslant k, j \leqslant n,\ s \geqslant 1 \quad [38b]$$

$$\beta_{(s+1)} = (3/7)^{1/2}[(11 - 3s)/14]$$
$$\times \Gamma[(18 - 3s)/14)]/\Gamma[(25 - 3s)/14] \quad [38c]$$
$$\beta_1 \approx 1.162,\ \beta_2 \approx 0.945,\ \beta_3 \approx 0.676,$$
$$\beta_4 \approx 0.326,\ \beta_5 \approx -0.214, \quad [38d]$$

where $\Gamma(x)$ is the gamma function (41, 43).

For the Langmuir adsorption isotherms [3a] the coefficients in Eqs. [37] are equal to

$$a^*_{k1} = \beta_1 \Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k (1 + V_0)^{-2} [c_{0k} \sum_{s=1}^{n} K^{\mathrm{p}}_s \sum_{j=1}^{n} (D^0_{ss})^{1/2} \times (D^{\mathrm{ad}})^{-1}_{sj} \Gamma_{0j} - (1 + V_0) \sum_{r=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kr} \Gamma_{0r}], \quad 1 \leqslant k, s, j, r \leqslant n \quad [39a]$$

$$a^*_{k2} = \Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k (1 + V_0)^{-2} \{ [(1 + V^0)^{-1} c_{0k} \sum_{s=1}^{n} K^{\mathrm{p}}_s b^*_{s1} - b^*_{k1}] \times \sum_{r=1}^{n} K^{\mathrm{p}}_r b^*_{r1} + c_{0k} \sum_{s=1}^{n} K^{\mathrm{p}}_s b^*_{s2} \} \quad [39b]$$

$$a^*_{k3} = \Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k (1 + V_0)^{-2} \{ c_{0k} \sum_{s=1}^{n} K^{\mathrm{p}}_s b^*_{s3} + (1 + V_0)^{-1} (\sum_{r=1}^{n} K^{\mathrm{p}}_r b^*_{r2})(\sum_{j=1}^{n} K^{\mathrm{p}}_j b^*_{j1}) + [c_{0k} \sum_{s=1}^{n} K^{\mathrm{p}}_s b^*_{s1} - (1 + V^0) b^*_{k1}][(1 + V_0)(\sum_{j=1}^{n} K^{\mathrm{p}}_j b^*_{j2}) + (\sum_{r=1}^{n} K^{\mathrm{p}}_r b^*_{r1})^2]/(1 + V_0)^2 \} \quad [39c]$$

$$b^*_{k1} = \beta_1 \sum_{j=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj} \Gamma_{0j}, \quad 1 \leqslant k, j \leqslant n \quad [39d]$$

$$b^*_{k(s+1)} = -\beta_{(s+1)} \sum_{j=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj} a^*_{js}, \quad 1 \leqslant k, j \leqslant n, s \geqslant 1. \quad [39e]$$

From Eqs. [4] and [37] through [39] the dynamic surface tension for the Lamgmuir adsorption isotherms for long times ($t \to \infty$) is given as

$$\gamma(t) = \gamma_0 - RT\Gamma^0_{\mathrm{m}} \ln[1 + V(t)], \; V(t) = V_0 - \sum_{k=1}^{\infty} A^{\infty}_k t^{-k/2}, \; A^{\infty}_k = \sum_{s=1}^{n} K^{\mathrm{p}}_s b^*_{sk}, \quad 1 \leqslant k, s \leqslant n. \quad [40]$$

According to Eqs. [40], for the Langmuir adsorption isotherms for long times Eqs. [4] and [15] reduce, respectively, to

$$[\gamma(t) - \gamma_e]/(\gamma_0 - \gamma_e) \approx S^*_{\infty} t^{-1/2}, \; S^*_{\infty} = \beta_1 / [(1 + V_0) \times \ln(1 + V_0)] \sum_{k=1}^{n} K^{\mathrm{p}}_k \sum_{j=1}^{n} (D^0_{kk})^{1/2} (D^{\mathrm{ad}})^{-1}_{kj} \Gamma_{0j} \quad [41a]$$

$$F(\gamma(t)) = n_{\infty} \log(t/t^{*\infty}_{\mathrm{rel}}), \; n_{\infty} = 0.5,$$

$$F(\gamma(t)) = 0.5 \log(t) + s^*_{\infty} \quad [41b]$$

$$t^{*\infty}_{\mathrm{rel}} = (S^*_{\infty})^2, \; s^*_{\infty} = -\log(S^*_{\infty}) \text{ (long times)}, \quad [41c]$$

where S^*_{∞} is the slope of the straight line $[\gamma(t) - \gamma_e]/(\gamma_0 - \gamma_e)$ versus $t^{-1/2}$ and s^*_{∞} is the shift of the straight line $F(\gamma(t))$ versus $\log(t)$ for long times.

For the diffusion-convective model the CTS approach may be used to find the solutions of the system of Eqs. [30] and [36a] in the analytical form for arbitrary adsorption isotherms without mutual diffusion in the adsorbed layer ($D^{\mathrm{ad}}_{kj} = 0$, $k \neq j$). The surface concentrations of individual surfactants, $c_k(0, t)$, are described using the function $h(t_k)$ in the form of Eq. [42]. As shown in (29), in the simplest case, when the equilibrium obeys the linear Henry law and $a^0_{ks} = b^0_{ks}$, $a^*_{ks} = b^*_{ks}$ ($1 \leqslant k \leqslant n$, $s \geqslant 1$), from Eqs. [31], [32], [37], and [38], for the diffusion-convective-controlled model the adsorption in terms of the relative time $t_1 = t/t_{01}$ may be written as

$$c_1(0, t)/c_{01} = \Gamma_1(t)/\Gamma_{01} = h(t_1), \quad t_1 = t/t_{01} \quad [42a]$$

$$t_{01} = (\Gamma_{01}/c_{01})^2 / D^*_{11}, \quad D^*_{11} = (D^{\mathrm{ad}}_{11})^2 / D^0_{11} \quad [42b]$$

$$h(t_1) = \begin{cases} h^0(t_1), & 0 \leqslant t_1 \leqslant 1 \\ h^{\infty}(t_1), & t_1 \geqslant 1 \end{cases} \quad [42c]$$

$$h^0(t_1) = \sum_{k=1}^{n} (-1)^{(k+1)} s^0_{\mathrm{k}} t_1^{k/2}, \; s^0_{\mathrm{k}} = \prod_{j=1}^{n} \alpha_j,$$

$$\alpha_{(j+1)} = (3/7)^{1/2} \Gamma(1 + 3j/14) / \Gamma(3/2 + 3j/14) \quad [42d]$$

$$s^0_1 \approx 0.739, \; s^0_2 \approx 0.483, \; s^0_3 \approx 0.287, \; s^0_4 \approx 0.158, \; s^0_5 \approx 0.04 \quad [42e]$$

$$h^{\infty}(t_1) = 1 - \sum_{k=1}^{n} (-1)^{(k+1)} s^{\infty}_k t_1^{-k/2}, \; s^{\infty}_k = \prod_{j=1}^{n} \beta_{\mathrm{j}} \quad [42f]$$

$$\beta_{(j+1)} = (3/7)^{1/2} \Gamma[(11 - 3\mathrm{j})/14)] / \Gamma[(25 - 3\mathrm{j})/14]$$

$$s^{\infty}_1 \approx 1.162, \; s^{\infty}_2 \approx 1.1, \; s^{\infty}_3 \approx 0.74, \; s^{\infty}_4 \approx 0.24, \; s^{\infty}_5 \approx -0.05. \quad [42g]$$

For the diffusion-convective-controlled adsorption model obeying the Langmuir adsorption isotherm [3] without mutual diffusion in the adsorbed layer ($D^{\mathrm{ad}}_{kj} = 0$, $k \neq j$), the solutions of Eqs. [30] and [36b] may be written as

$$c_k = c_{0k} h(t_k), \quad 1 \leqslant k \leqslant n \quad [43a]$$

$$\Gamma_k(t) = \Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k c_{0k} h(\xi(t_k)) / [1 + V(\xi)], \quad V(\xi) = \sum_{k=1}^{n} K^{\mathrm{p}}_k c_{0k} h(\xi(t_k)), \quad 1 \leqslant k \leqslant n \quad [43b]$$

$$\gamma(t) = \gamma_0 - RT\Gamma^0_{\mathrm{m}} \ln[1 + V(\xi)] \quad [43c]$$

$$t_k = t/t_{0k}, \; t_{0k} = [\Gamma^0_{\mathrm{m}} K^{\mathrm{p}}_k / (1 + V_0)]^2 D^0_{kk} / (D^{\mathrm{ad}}_{kk})^2, \quad 1 \leqslant k \leqslant n \quad [43d]$$

$$\xi(t_k) = t_k \{ [1 + V(\xi)] / (1 + V_0) \}^2, \quad 1 \leqslant k \leqslant n. \quad [43e]$$

The preceding equations may be used to describe the surface concentration, $c_k(0, t)$, the adsorption, $\Gamma_k(t)$, and the dynamic surface tension, $\gamma(t)$, over a wide range of time for the diffusion-convective-controlled adsorption model without mutual diffusion in the adsorbed layer.

DISCUSSION

We apply the theory of multicomponent adsorption kinetics to estimate the time dependence of dynamic surface tension over a wide range of time without and with the mutual diffusion in the adsorbed layer.

Below we consider in detail the multicomponent mixture for the Langmuir adsorption isotherms. For short times ($t \rightarrow 0$) from Eqs. [20a] and [35a] the relative dynamic surface tension is given as

$$[\gamma_0 - \gamma(t))]/(\gamma_0 - \gamma_e) \approx S_0 t^{1/2} \text{ (short times)} \quad [44a]$$

$$S_0 = \alpha_1^0 A_0,\ \alpha_1^0 = 2/[\pi^{1/2} \ln(1 + V_0)],$$

$$A_0 = \sum_{k=1}^{n} \sum_{j=1}^{n} (D_{kj}^*)^{1/2} c_{0j}/\Gamma_{\mathrm{m}}^0, \quad 1 \leqslant k, j \leqslant n \quad [44b]$$

$$S_0^- = \alpha_1^0 A_0^-,\ A_0^- = \sum_{k=1}^{n} (D_{kk}^*)^{1/2} c_{0k}/\Gamma_{\mathrm{m}}^0,\ 1 \leqslant k \leqslant n \quad [44c]$$

$$S_0^* = \alpha_1^* A_*,\ \alpha_1^* = 2/[(7/3\pi)^{1/2} \ln(1 + V_0)],$$

$$A_* = \sum_{k=1}^{n} \sum_{j=1}^{n} (D_{kj}^*)^{1/2} c_{0j}/\Gamma_{\mathrm{m}}^0, \quad 1 \leqslant k, j \leqslant n \quad [44d]$$

$$S_0^-{}^* = \alpha_1^* A_0^-{}^*,\ A_0^- = \sum_{k=1}^{n} (D_{kk}^*)^{1/2} c_{0k}/\Gamma_{\mathrm{m}}^0,$$

$$1 \leqslant k \leqslant n, \quad [44e]$$

where S_0 [44b], S_0^* [44d] and S_0^- [44c], $S_0^-{}^*$ [44e] are the slope of the straight line $[\gamma_0 - \gamma(t))]/(\gamma_0 - \gamma_e)$ versus $t^{1/2}$ for the diffusion-controlled and diffusion-convective-controlled models with and without mutual diffusion in the adsorbed layer, respectively.

From the preceding analysis it follows that for short times, due to mutual diffusion in the adsorbed layer, the rate of change of the dynamic surface tension increases because the following inequalities are valid:

$$S_0 > S_0^-, \quad S_0^* > S_0^-{}^* \text{ (short times).} \quad [45]$$

For long times ($t \rightarrow \infty$), from Eqs. [21c] and [41a], the relative dynamic surface tension is given as

$$[\gamma(t) - \gamma_e]/(\gamma_0 - \gamma_e) \approx S_\infty t^{-1/2} \text{ (long times)} \quad [46a]$$

$$S_\infty = \beta_1^0 B_\infty,\ \beta_1^0 = \pi^{-1/2} V_0/[(1 + V_0)\ln(1 + V_0)],$$

$$B_\infty = \sum_{k=1}^{n} \sum_{j=1}^{n} K_k^{\mathrm{p}} (D_{kk}^0)^{1/2} (D_{ad})_{kj}^{-1} \Gamma_{0j} \quad [46b]$$

$$S_\infty^- = \beta_1^0 B_\infty^-,\ B_\infty^- = \sum_{k=1}^{n} K_k^{\mathrm{p}} (D_{kk}^0)^{1/2} (D^{\mathrm{ad}})_{kk}^{-1} \Gamma_{0k},$$

$$1 \leqslant k \leqslant n \quad [46c]$$

$$S_\infty^* = \beta_1^* B_\infty^*,\ \beta_1^* = (7/3)^{1/2} V_0 \Gamma(9/7)/$$
$$[\Gamma(11/14)(1 + V_0)\ln(1 + V_0)],$$

$$B_\infty^* = \sum_{k=1}^{n} \sum_{j=1}^{n} K_k^{\mathrm{p}} (D_{kk}^0)^{1/2} (D^{\mathrm{ad}})_{kj}^{-1} \Gamma_{0j} \quad [46d]$$

$$S_\infty^-{}^* = \beta_1^* B_\infty^-{}^*,\ B_\infty^-{}^* = \sum_{k=1}^{n} K_k^{\mathrm{p}} (D_{kk}^0)^{1/2} (D^{\mathrm{ad}})_{kk}^{-1} \Gamma_{0k},$$

$$1 \leqslant k \leqslant n, \quad [46e]$$

where S_∞ [46b], S_∞^* [46d] and S_∞^- [46c], $S_\infty^-{}^*$ [46e] are the slope of the straight line $[\gamma(t) - \gamma_e]/(\gamma_0 - \gamma_e)$ versus $t^{-1/2}$ for the diffusion-controlled and diffusion-convective-controlled models with and without mutual diffusion in the adsorbed layer, respectively.

From the preceding analysis it follows that for long times, due to mutual diffusion in the adsorbed layer, the rate of change of the dynamic surface tension for the multicomponent mixture may decrease when the inequalities [47a] are valid, or increase when the inequalities [47b] are valid:

$$S_\infty < S_\infty^-, \quad S_\infty^* < S_\infty^-{}^* \text{ (long times)} \quad [47a]$$

$$S_\infty > S_\infty^-, \quad S_\infty^* > S_\infty^-{}^* \text{ (long times).} \quad [47b]$$

In particular, for the two-component mixture we have

$$B_\infty^-{}^* = K_1^{\mathrm{p}} (D_{11}^0)^{1/2}/D_{11}^{\mathrm{ad}} + K_2^{\mathrm{p}} (D_{22}^0)^{1/2}/D_{22}^{\mathrm{ad}} \quad [48a]$$

$$B_\infty^* = [K_1^{\mathrm{p}} (D_{11}^0)^{1/2} (D_{22}^{\mathrm{ad}} - D_{12}^{\mathrm{ad}}) + K_2^{\mathrm{p}}$$
$$\times (D_{22}^0)^{1/2} (D_{11}^{\mathrm{ad}} - D_{21}^{\mathrm{ad}})/(D_{11}^{\mathrm{ad}} D_{22}^{\mathrm{ad}} - D_{12}^{\mathrm{ad}} D_{21}^{\mathrm{ad}}). \quad [48b]$$

If $D_{12}^{\mathrm{ad}} = 0$, then

$$B_\infty^* = K_1^{\mathrm{p}} (D_{11}^0)^{1/2}/D_{11}^{\mathrm{ad}} + K_2^{\mathrm{p}} (D_{22}^0)^{1/2}$$
$$\times (D_{11}^{\mathrm{ad}} - D_{21}^{\mathrm{ad}})/(D_{11}^{\mathrm{ad}} D_{22}^{\mathrm{ad}}). \quad [48c]$$

From Eqs. [48a] and [48c] it follows that the inequalities [47a] are valid when $D_{11}^{\mathrm{ad}} < D_{21}^{\mathrm{ad}}$, and the inequalities [47b] are valid when $D_{11}^{\mathrm{ad}} > D_{21}^{\mathrm{ad}}$. Thus, for long times, the rate of

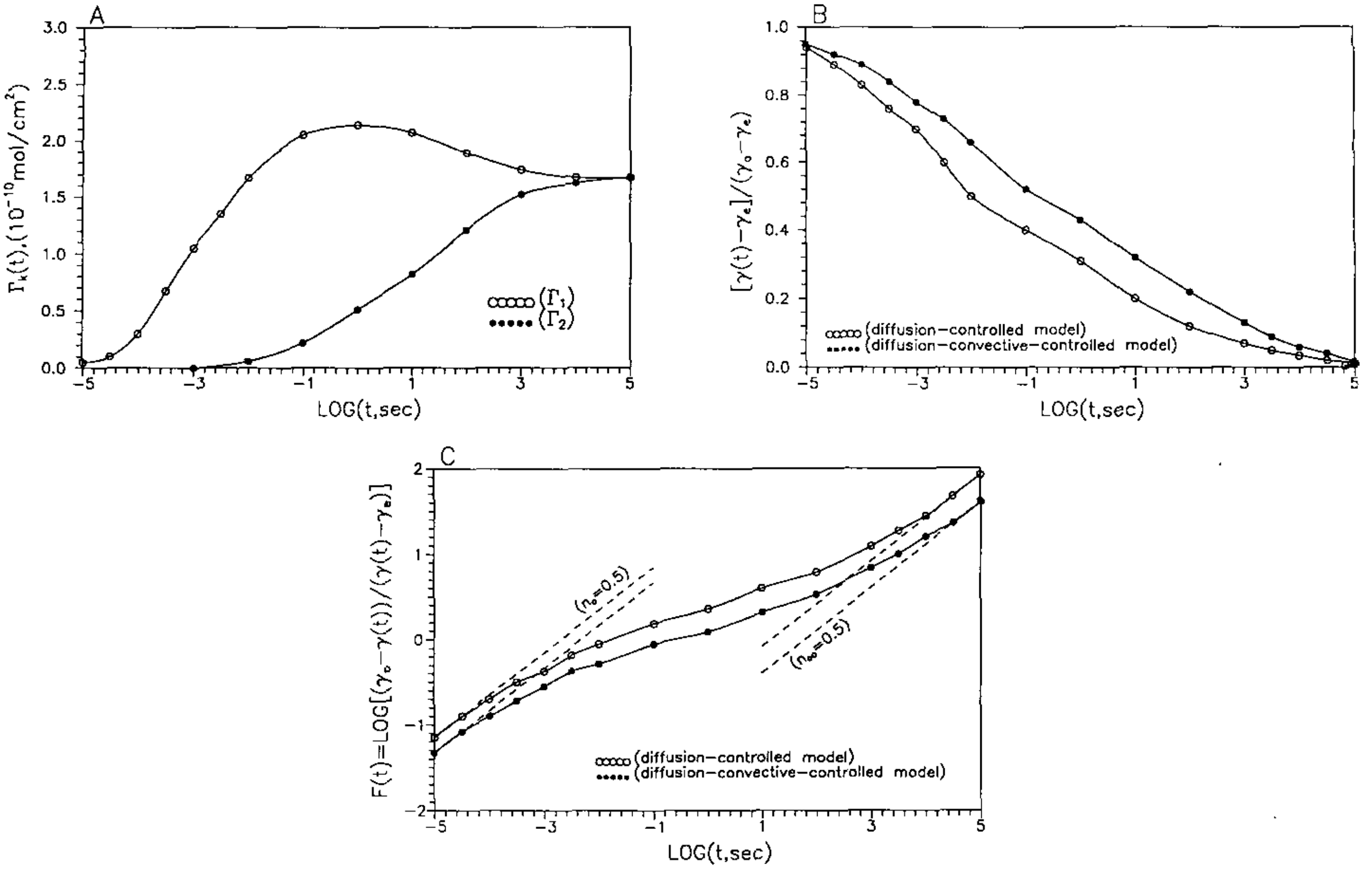

FIG. 1. Change of the relative adsorption (A), relative dynamic surface tension (B), and relaxation function (C) for the diffusion-controlled and diffusion-convective-controlled models with the parameters [49], according to Eqs. [16], [18], [19], [21], and [24] and [31], [33], [34], [37], [39], [40], and [43], for a two-component mixture of surfactants.

change of the dynamic surface tension depends on the values of the mutual diffusion coefficients in the adsorbed layer.

Equations [44] through [46] may be used to estimate the mutual diffusion coefficient, D^{ad}_{kj} $(k \neq j,\ 1 \leq k, j \leq 2)$, in the adsorbed layer for a two-component mixture. In this case the diffusion coefficients in the bulk, D^0_{kk} $(k = 1, 2)$, must be found first. The diffusion coefficient, D^{ad}_{kk} $(k = 1, 2)$, in the adsorbed layer for the individual surfactants must be found by using Eqs. [44] through [46] and experimental data for the dynamic surface tension for the individual surfactants.

Now we consider the dynamic surface tension for multicomponent mixtures obeying the Langmuir adsorption isotherms. Figures 1 and 2 show the adsorption, relative dynamic surface tension, and relaxation function for the diffusion-controlled and diffusion-convective-controlled models for the parameters

$$\Gamma^0_m = 5 \times 10^{-10}\ \text{mol/cm}^2,\ c_{01} = 10^{-6}\ \text{mol/cm}^3,\ c_{02} = 10^{-8}\ \text{mol/cm}^3 \qquad [49a]$$

$$D^0_{11} = D^0_{22} = 10^{-6}\ \text{cm}^2/\text{s},\ D^{ad}_{11} = D^{ad}_{22} = 2.24 \times 10^{-6}\ \text{cm}^2/\text{s}, \qquad [49b]$$

$$K^p_1 = 10^6\ \text{cm}^3/\text{mol},\ K^p_2 = 10^8\ \text{cm}^3/\text{mol},\ D^{ad}_{12} = D^{ad}_{21} = 0. \qquad [49c]$$

As shown in Fig. 1 the lightly adsorbed first component of the two-component mixture is displaced by the strongly adsorbed second component of the mixture. Therefore, the time dependence of adsorption for the lightly adsorbed first component is a nonmonotone function. The degree of the replacement depends on the ratio of adsorption of components. In case [48] this ratio is equal to $K^p_2/K^p_1 = 100$.

For the diffusion-controlled model without the mutual diffusion in the adsorbed layer the system of Eqs. [9] and [10] were integrated numerically by Miller and co-workers (30) with parameters [48]. However, it should be noted that computer analysis of the behavior of the dynamic surface tension over a wide range of time (four or more orders of magnitude) is a complex problem (15, 19, 30). As just men-

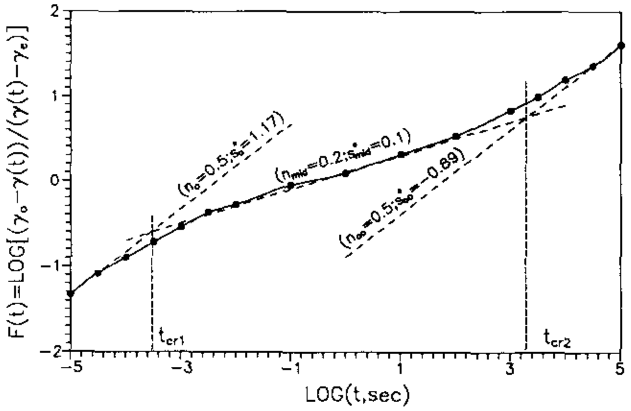

FIG. 2. Change of the relaxation function for the diffusion-convective-controlled models with the parameters [49], according to Eqs. [31], [33], [34], [37], [39], [40], [43], and [50], for a two-component mixture of surfactants.

tioned, the choice of mesh size, Δt, ΔC, and $\Delta\Gamma$ is important in the application of finite difference methods for the numerical integration of Eqs. [9], [10], and [27a], [27b] using a computer. Therefore, the correct numerical integration of nonlinear equations requires special mathematical analysis.

The role of convective transfer over a wide range of time may be estimated using Eqs. [19], [20], [34], [35], [40], [41], [44], and [46] and data shown in Figs. 1C and 2. According to Eqs. [1], [19], [20], [34], [35], [40], [41], [44], and [46], it follows that in the framework of diffusion-convective-controlled adsorption three linear equations in the form of Eq. [50a] may be used to describe the time dependence of dynamic surface tension over a wide range of times:

$$F(\gamma(t)) = \begin{cases} 0.5\log(t) + s_0^*, & 0 \leqslant t \leqslant t_{1\mathrm{cr}} \\ n_{\mathrm{mid}}\log(t) + s_{\mathrm{mid}}^*, & t_{1\mathrm{cr}} \leqslant t \leqslant t_{2\mathrm{cr}} \\ 0.5\log(t) + s_\infty^*, & t \geqslant t_{2\mathrm{cr}} \end{cases} \quad [50a]$$

$$\log(t_{1\mathrm{cr}}) = (s_{\mathrm{mid}}^* - s_0^*)/(0.5 - n_{\mathrm{mid}}) \quad [50b]$$

$$\log(t_{2\mathrm{cr}}) = (s_{\mathrm{mid}}^* - s_\infty^*)/(0.5 - n_{\mathrm{mid}}). \quad [50c]$$

The values of s_0^* and s_∞^* are found from Eqs. [35c] and [41c], respectively. According to Eqs. [1], [4], [34], [40], and [43], the values of n_{mid} and s_{mid}^* are given as

$$s_{\mathrm{mid}}^* = -0.5\log(t_{\mathrm{mid}}),\ n_{\mathrm{mid}} = dF(\gamma(t_{\mathrm{mid}}))/d\log(t),\ \gamma(t_{\mathrm{mid}}) = (\gamma_0 + \gamma_e)/2. \quad [51]$$

From the preceding analysis and Fig. 2 it follows that $n_0 = n_\infty = 0.5$, $n_{\mathrm{mid}} < 0.5$.

Diffusion-controlled and diffusion-convective-controlled adsorption are used in the literature to describe dynamic surface tension (16–30). Therefore, it is reasonable to compare these models and to estimate the effect of the convective transfer. In Fig. 2 the time dependence is shown for the dynamic surface tension of the diffusion-controlled adsorption and the diffusion-convective-controlled adsorption of the Langmuir adsorption isotherms over a wide range of time. According to Eq. [50a], the functions $F(\gamma(t))$ versus $\log(t)$ for the diffusion-controlled adsorption and diffusion-convective-controlled adsorption are the straight lines at short and long times. The shifts of Δs_0 and Δs_∞ between these lines at short and long times, respectively, characterize the effect of the convective transfer due to the growing surface during the formation of the bubbles or drops. From Eqs. [20a], [20c], [21c], [21e], [35a], [35c], [38a], [41a], and [41c], for multicomponent mixtures of surfactants, the values of shift, Δs_0 and Δs_∞, are equal to, respectively,

$$\Delta s_0 = \log(s_0/s_0^*) = 0.5\log(7/3) \approx 0.18 \quad [52a]$$

$$\Delta s_\infty = -\log(s_\infty/s_\infty^*) = \log[(7\pi/3)^{1/2}\Gamma(9/7)/\Gamma(11/14)] \approx 0.31. \quad [52b]$$

From Eqs. [50a], [52a], and [52b] and Fig. 2 it follows that the effect of the convective term for the multicomponent mixture of surfactants takes place over a wide range of times. Thus, to describe the experimental dynamic surface tension, diffusion-convective-controlled adsorption must be used. Equation [50a] may be useful to describe the dynamic surface tension for multicomponent mixtures of surfactants over a wide range of time.

Now we consider the dynamic surface tension for the three-component mixture obeying the Langmuir adsorption isotherms. Figure 3 shows the adsorption, relative dynamic surface tension, and relaxation function for the diffusion-controlled model for the parameters

$$\Gamma_m^0 = 5 \times 10^{-10}\ \mathrm{mol/cm^2},\ c_{01} = 10^{-6}\ \mathrm{mol/cm^3},$$

$$c_{02} = 10^{-7}\ \mathrm{mol/cm^3},\ c_{03} = 10^{-8}\ \mathrm{mol/cm^3} \quad [53a]$$

$$D_{11}^0 = D_{22}^0 = D_{33}^0 = 10^{-6}\ \mathrm{cm^2/s},$$

$$D_{11}^{\mathrm{ad}} = D_{22}^{\mathrm{ad}} = D_{33}^{\mathrm{ad}} = 2.24 \cdot 10^{-6}\ \mathrm{cm^2/s} \quad [53b]$$

$$K_1^{\mathrm{p}} = 10^6\ \mathrm{cm^3/mol},\ K_2^{\mathrm{p}} = 10^7\ \mathrm{cm^3/mol},$$

$$K_3^{\mathrm{p}} = 10^8\ \mathrm{cm^3/mol}. \quad [53c]$$

As shown in Fig. 3, the lightly adsorbed first and second components of the three-component mixture are displaced by the strongly adsorbed third component of the mixture. Therefore, the time-dependent adsorption for the light-adsorbed first and second components is a nonmonotone function. The degree of replacement depends on the ratio of adsorption of the components of the mixture.

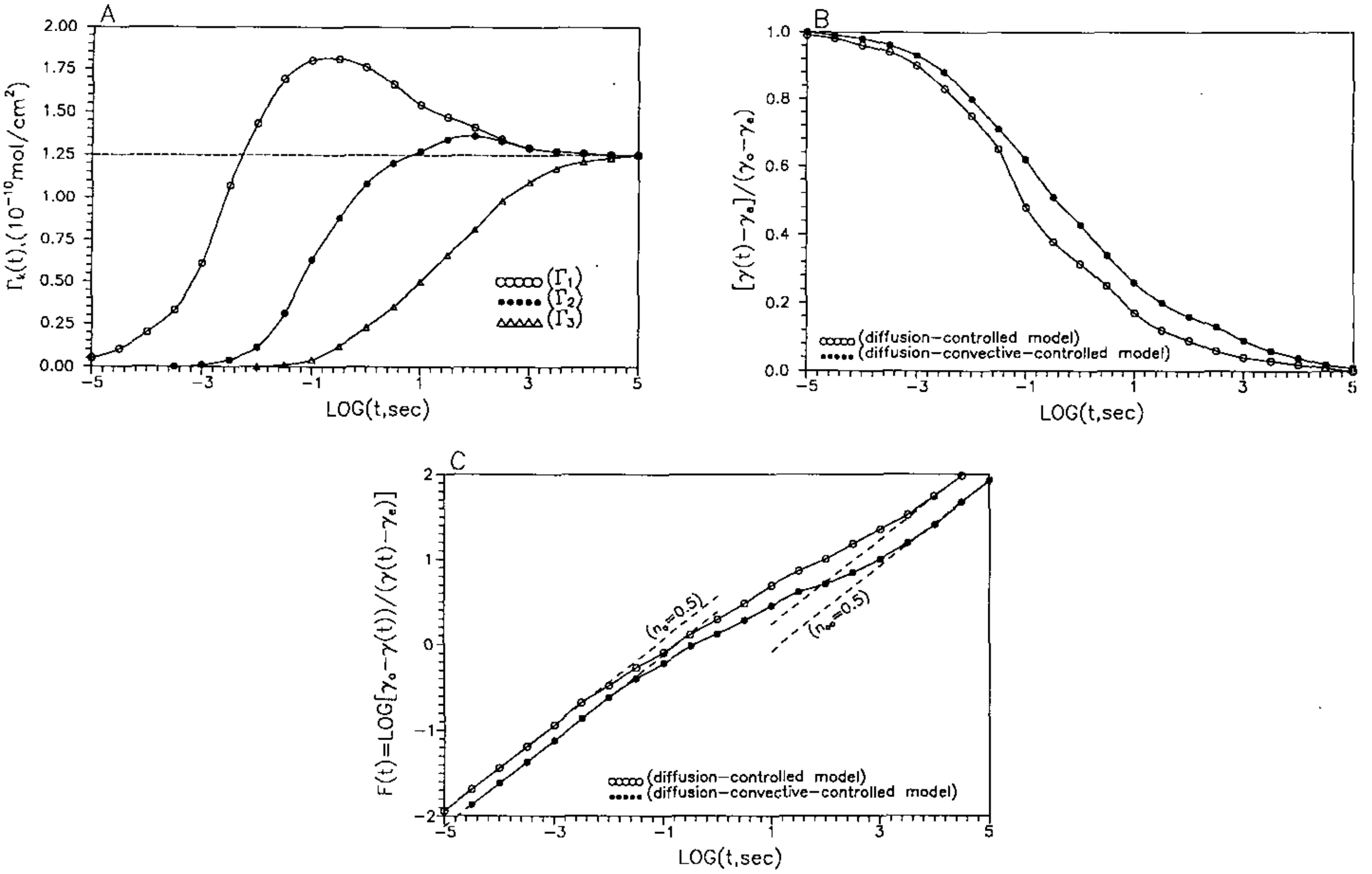

FIG. 3. Change of the relative adsorption (A), relative dynamic surface tension (B), and relaxation function (C) for a three-component mixture of surfactants for the diffusion-controlled model with the parameters [53], according to Eqs. [16], [18], [19], [21], and [24].

In conclusion, we note that in the framework of the diffusion-convective-controlled model with constant diffusion coefficients in the bulk and in the adsorbed layer, Eqs. [50] may be applied to predict the dynamic surface tension for multicomponent mixtures of different surfactants with and without mutual diffusion in the adsorbed layer over a wide range of times.

REFERENCES

1. Milner, S. R., *Philos. Mag.* **13,** 96 (1907).
2. Lottermoser, A., and Baumguret, B., *Trans. Faraday Soc.* **31,** 200 (1935).
3. Langmuir, I., and Schaefer, V. J., *J. Am. Chem. Soc.* **59,** 2400 (1937).
4. Tartar, H. V., Sivertz, V., and Reitmeir, R. E., *J. Am. Chem. Soc.* **62,** 2375 (1940).
5. Ward, A. F. G., and Tordai, L., *J. Chem. Phys.* **14,** 453 (1949).
6. Sutherland, K., *Aust. J. Sci. Res.* **A5,** 683 (1952).
7. Hansen, R. S., *J. Phys. Chem.* **64,** 637 (1960).
8. Hansen, R. S., *J. Colloid Sci.* **16,** 549 (1961).
9. Bendure, R. L., *J. Colloid Interface Sci.* **35,** 238 (1971).
10. Kloublek, J., *Colloid Polym. Sci.* **253,** 929 (1975).
11. Van den Bogaert, R., and Joos, P., *J. Phys. Chem.* **83,** 2244 (1979).
12. Petrov, J., and Miller, R., *Colloid Polym. Sci.,* **255,** 669 (1977).
13. Miller, R., *Colloid Polym. Sci.* **258,** 179 (1980).
14. Miller, R., and Kretzschmar, G., *Colloid Polym. Sci.,* **258,** 85 (1980).
15. Miller, R., *Colloid Polym. Sci.* **259,** 375 (1981).
16. Joos, P., and Rillaerts, E., *J. Colloid Interface Sci.* **79,** 96 (1981).
17. Loglio, G., Rillaerts, E., and Joos, P., *Colloid Polym. Sci.* **259,** 1221 (1981).
18. Rillaerts, E., and Joos, P., *J. Phys. Chem.* **86,** 3471 (1982).
19. Borwankar, R. P., and Wasan, D. T., *Chem. Eng. Sci.* **38,** 1637 (1983).
20. Van Havenbergh, J., and Joos, P., *J. Colloid Interface Sci.* **95,** 172 (1983).
21. Jho, C., and Burke, R., *J. Colloid Interface Sci.* **95,** 61 (1983).
22. Miller, R., and Schano, K. H., *Colloid Polym. Sci.* **264,** 277 (1986).
23. Balbaert, I., Bleyrs, G., and Joos, P., *J. Colloid Interface Sci.* **115,** 362 (1987).
24. Van Hunsel, J., and Joos, P., *Colloids Surf.* **24,** 139 (1987).
25. Hua, X. Y., and Rosen, M. J., *J. Colloid Interface Sci.* **124,** 652 (1988).
26. Hua, X. Y., and Rosen, M. J., *J. Colloid Interface Sci.* **141,** 180 (1991).
27. Joos, P., Fang, J. P., and Serrien, G., *J. Colloid Interface Sci.* **151,** 144 (1992).
28. Van Voorst Vader, F., Erkelens, Th., and van der Tempel, M., *Trans. Faraday. Soc.* **60,** 1170 (1964).
29. Filippov, L. K., *J. Colloid Interface Sci.* **163,** 49 (1994).
30. Miller, R., Lunkenheimer, K., and Kretzscmar, G., *Colloid Polym. Sci.* **257,** 1118 (1979).

31. MacLeod, C. A., and Radke, C. J., *J. Colloid Interface Sci.* **160,** 435 (1993).
32. Ilkovic, D., *Collect. Czech. Chem. Commun.* **6,** 498 (1934).
33. Ilkovic, D., *J. Chim. Phys. Physicochem. Biol.* **35,** 129 (1938).
34. Delahay, P., and Trachtenberg, I., *J. Am. Chem. Soc.* **79,** 2355 (1957).
35. Delahay, P., and Fike, C. T., *J. Am. Chem. Soc.* **80,** 2628 (1958).
36. Van den Bogaert, R., and Joos, P., *J. Phys. Chem.* **84,** 190 (1980).
37. Levich, V. G., "Physicochemical Hydrodynamics." Prentice–Hall, Englewood Cliffs, NJ, 1962.
38. Adamson, A. W., "Physical Chemistry of Surfaces." Interscience, New York, 1986.
39. Groot, S. P., and Mazur, P., "Non-equilibrium Thermodynamics." North-Holland, Amsterdam, 1962.
40. Ravera, F., Liggieri, L., and Steinchen, A., *J. Colloid Interface Sci.* **156,** 109 (1993).
41. Arfken, G., "Mathematical Methods for Physics." Academic Press, New York, 1970.
42. Atherton, N. M., "Electron Spin Resonance Theory and Applications." Halsted Press, New York, 1973.
43. Abramowitz, M., and Stegun, I., "Handbooks of Mathematical Functions with Formulas, Graphs and Mathematical Tables." National Bureau of Standards, Applied Mathematics Series, Washington, DC, 1964.
44. Filippov, L. K., and Filippova, I. V., *Russ. J. Phys. Chem.* **60,** 1834 (1986).