



Langmuir isotherm explains maximum foamability



Oscar Arciniega Saavedra, Jesús Gracia Fadrique*

Departamento de Físicoquímica, Facultad de Química, Universidad Nacional Autónoma de México, Ciudad de México 04510, Mexico

HIGHLIGHTS

- Foamability was evaluated as elasticity.
- Maximum foamability is found at the critical micelle concentration.
- Gibbs adsorption equation coupled with Langmuir equation explains foamability.
- Foamability. Cause: gradient in surface pressure; effect: maximum foamability at cmc.
- The results are valid too in transient foams behavior.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 November 2015
Received in revised form 8 February 2016
Accepted 9 February 2016
Available online 11 February 2016

Keywords:

Foam
Foamability
Surfactant
Elasticity
Surface

ABSTRACT

The relevant and promising empirical observation of M. Rosen regarding the maximum foam height in a column at the critical micelle concentration is explained using basic thermodynamic analysis. Elasticity determined isothermally from the equilibrium $\pi - A$ curve and Gibbs elasticity modulus, is evaluated by means of the Langmuir isotherm and the corresponding surface equation of state. Beyond surface tension, relevant variables on foam behavior were found on first and second derivatives of surface pressure in relation to bulk composition. This maximum foamability related to elasticity is predicted from the Gibbs elasticity modulus and it shows that the maximum foamability is reached in the vicinity of surface saturation conditions and therefore in the neighborhood of critical micelle concentration.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Foam height generally increases with increasing surfactant concentration, from highly dilute regions up to the critical micelle concentration. In the neighborhood of the critical micelle concentration foam height reaches a maximum value or increases slowly to a maximum value somewhat above the critical micelle concentration [1]. The present article shows, based on the Langmuir model, the theoretical fundamentals behind this experimental facts.

Permanent foams show a maximum foamability at critical micelle concentration [2]. This significant empirical observation made by M. Rosen, relative to the maximum foam height in a column at the critical micelle concentration is explained using basic thermodynamic analysis. The present theoretical approach concerns to the relationship among the maximum foam height and factors such as surfactant concentration, critical micelle concentration and surface tension. The theoretical results are in agreement with the factors which affect the initial foam height as determined by the Ross-Miles pour method [3].

At the present work, the Gibbs elasticity modulus is used as synonymous of foamability. The Gibbs elasticity is expressed throughout the Langmuir isotherm and the corresponding surface equation of state, which shows a divergence in surface coverage at the neighborhood of critical micelle concentration. Additionally,

* Corresponding author.

E-mail address: jgraciaf@unam.mx (J. Gracia Fadrique).

the Gibbs elasticity module can be expressed as a relation between the first and second derivative of surface pressure at any particular molar fraction; this quotient is independent of the surface equation of state proposed. In the vicinity of critical micelle concentration, $d\pi/d\ln x$ tends to the maximum value and the second derivative tends to zero, so the quotient shows maximum elasticity and hence maximum foamability.

This treatment is also valid for transient foams, where in the surroundings of saturation conditions, the foamability shows a lambda shape or divergence. The studies of S. Ross and G. Nishioaka about foamability of binary and ternary systems are pioneers in this field and are referenced to this behavior [4]. In our previous publication, we found the same lambda-type behavior at saturated conditions in phenol-water mixtures through the determination of transient foam stability [4]. Therefore, the observation and contribution of Milton Rosen [5] is also true in the case of transient foams of aqueous alcohol solutions [7] as 2-butoxyethanol-water. In our previous publication, we reported the behavior of the surface tension, composition and foaming capacity of the binary system butoxyethanol-water at three different temperatures (4 °C, 25 °C) and at the vicinity of the lower critical solution temperature 48 °C, the maximum foaming (lambda shape) occurs just at the critical micelle [6].

Maximum foamability is measured with a method that nowadays is ASTM procedure [3]. It is important to underline that this work provides thermodynamic fundamentals for this observation and it is described in an easy and simple way. Therefore, it is shown that an isotherm and equation of state derived from equilibrium conditions can be used. This is a crucial point of this analysis due to the possibility of linking isotherm equations to equations of state and elasticity modulus, leading to more stable and elastic films: when a surface is expanded, surfactant concentration on the surface decreases and surface tension increases; on the opposite case, when a surface is compressed surface concentration increases and surface tension decreases.

2. Background

The Gibbs elasticity modulus relates the variations of surface tension to the surface area when it is expanded or compressed. It comes from the differential equation of Young-Laplace [7–9]. The Gibbs elasticity [10] is defined as

$$\varepsilon = 2 \frac{d\sigma}{d\ln A} \quad (1)$$

where σ is the surface tension and A is the molar surface area. Elasticity is the ratio of the increase in the surface tension resulting from an infinitesimal increase in area [11]. Surface tension can be expressed in terms of surface pressure, defined as ($\pi = \sigma^\circ - \sigma$), where σ° is the surface tension of pure solvent and σ is the surface tension of the solution, so,

$$-d\sigma = d\pi \quad (2)$$

The essence of the Gibbs elasticity concept is determined isothermally from the equilibrium π - A curve [4]. The surface coverage θ is related to the surface concentration Γ defined by ($\theta = \Gamma/\Gamma_s$) and the Gibbsian surface concentration Γ is related to the molar area ($\Gamma = 1/A$); Γ_s is the maximum or saturation surface concentration. Then, the Gibbsian surface concentration or superficial density can be expressed by the surface coverage θ ,

$$d\ln A = -d\ln \Gamma = -d\ln \theta \quad (3)$$

This allows us to express the elasticity through the surface equation of state, and the corresponding adsorption isotherm by the surface concentration or the surface coverage θ leading to

$$\varepsilon = -2 \frac{d\pi}{d\ln A} = 2 \frac{d\pi}{d\ln \Gamma} = 2 \frac{d\pi}{d\ln \theta} \quad (4)$$

Therefore, the two terms in Eq. (4) expressed in relation to bulk concentration, $d\ln x$, allow to introduce the corresponding Langmuir surface equation of state (SEOS) and Langmuir isotherm as explained in the discussion section

$$\varepsilon = 2\theta \frac{d\pi/d\ln x}{d\theta/d\ln x} \quad (5)$$

The studies of surface tension variation with surfactant concentration are the most common methods to calculate the critical micelle concentration. According to Gibbs adsorption equation

$$d\pi = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (6)$$

Where Γ_2 , $d\mu_2$, are the surface concentration and the solute chemical potential, respectively, and Γ_1 , $d\mu_1$, are the surface concentration and solvent chemical potential, respectively.

Boundary conditions on the vicinity of critical micelle concentration [13,14].

$$x \rightarrow x_{cmc} \pi \rightarrow \pi_s \quad (7)$$

$$\Gamma_1 \rightarrow 0 \Gamma_2 \rightarrow \Gamma_s \theta \rightarrow 1 \quad (8)$$

At this saturated region, the Gibbs adsorption Eq. (6) gives

$$d\pi = \Gamma_s d\mu \quad (9)$$

Based on an ideal chemical potential at the bulk phase, and eliminating the subscript "2" of the solute (amphiphile), Eq. (6) is reduced to

$$d\pi = \Gamma_s RT d\ln x \leq x_{cmc} \quad (10)$$

Thus, the derivative finds a maximum before saturation, at the critical micelle concentration:

$$\left(\frac{d\pi}{d\ln x} \right)_T^{max} = \Gamma_s RT \quad (11)$$

In a previous work, it has been reported that based on a thermodynamic model, the adsorption process, and thus, surface saturation, proceeds before micellization [12]. The integral form of Eq. (11) between the intervals ($\pi - \pi_{max}$) and ($x - x_{cmc}$), identified by the linear behavior of π vs $\ln x$ in the vicinity of critical micelle concentration is

$$\pi = \pi_{max} - \Gamma_s RT \ln x_{cmc} + \Gamma_s RT \ln x \quad (12)$$

Eq. (12) provides a linear surface equation of state with $\Gamma_s RT$ as the slope and $\pi_{max} - \Gamma_s RT \ln x_{cmc}$ as the intercept which contains the critical micelle concentration value [13,14].

3. Discussion

In order to understand the methodology followed on this section, it is important to mention that the Gibbs adsorption isotherm allows us to transform an isotherm into a surface equation of state. Surface pressure $i\pi i$ and surface coverage $i\theta i$ can be expressed as a function of composition for a surface equation of state and an isotherm, respectively. Assuming initially that the adsorbed surface film is described by a two-dimensional equation of state, elasticity is determined isothermally by the equilibrium π - A curve [11]. In the following discussion of the theory, equations are first devel-

Download English Version:

<https://daneshyari.com/en/article/591686>

Download Persian Version:

<https://daneshyari.com/article/591686>

[Daneshyari.com](https://daneshyari.com)