Spreading and contraction of a benzene lens on water: A description on the basis of the disjoining pressure

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HIGHLIGHTS

- The equation for liquid-on-liquid contact angle is derived using the disjoining pressure.
- The extent of validity of Antonoff's rule is analyzed.
- Wetting of water by benzene is governed by dissolution of water in a benzene lens.
- The disjoining pressure isotherm is affected by water content in a benzene lens.

GRAPHICAL ABSTRACT
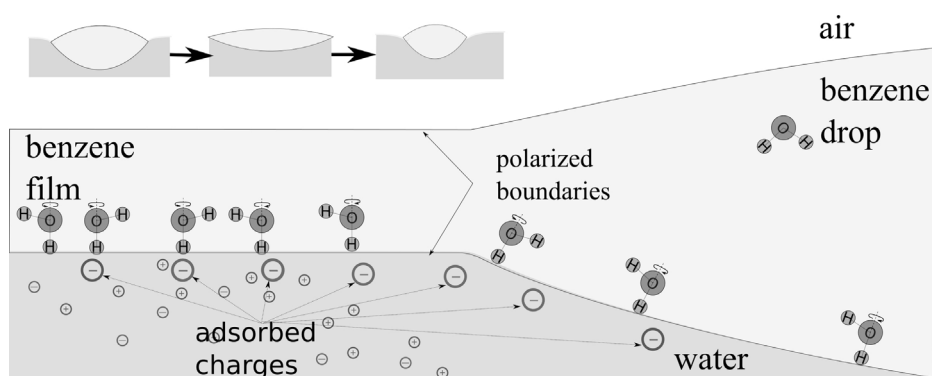
ARTICLE INFO

ABSTRACT

In many cases for the droplet of an organic liquid deposited onto the aqueous phase, initial spreading of a droplet is followed by its contraction into a lens. The equilibrium situation will correspond to the coexistence of a liquid lens with a monomolecular or polymolecular film of organic liquid on the surface of the aqueous medium. Benzene on water represents a typical system showing abovementioned behavior. In this paper, we present the equation for the calculation of benzene lens angle based on the disjoining pressure isotherms. We show that the evolution of water content in a benzene lens is responsible for spreading/contraction of the benzene lens on water due to the interplay of different types of surface forces in the benzene film. The influence of water content on the thickness of a benzene film atop of water and on the instant lens angle is considered.

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1. Introduction

Spreading of one liquid over another is a process that is important for biological systems, as well as for many applications in the fields of pharmaceutics, coating deposition technology, oil spills, the food industry and many others. When a droplet of organic liquid with low surface tension is placed on the surface of an aqueous medium with which it has low mutual solubility, the decrease in Gibbs surface energy of the considered system results in partial or complete spreading of the organic liquid. However, in many cases, the initial spreading of a droplet of top liquid is followed by its contraction into a lens. Thus, the equilibrium situation will correspond to the coexistence of a liquid lens with a monomolecular or polymolecular film of organic liquid on the surface of the aque-
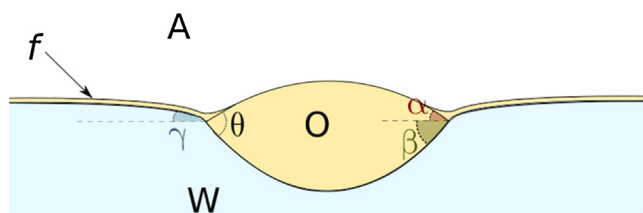
Fig. 1. Lens of organic liquid 1 (O) in equilibrium with thin wetting film (*f*) on the surface of aqueous liquid 2 (W).

ous medium [1]. A typical system showing the complex behavior described above is benzene on water. Since the studies of Miller [2], Harkins [3] and Zisman [4,5], spreading/contracting behavior has been treated in the literature [6,7] in terms of initial and final spreading coefficients. The variation in spreading coefficients is attributed to mutual solubility of the contacting liquids. The initial and final spreading coefficients may be determined experimentally by measuring interfacial tensions. However, correct measurement of the surface tension of water saturated with an organic substance should be done when the vapor pressure is saturated by both liquids, which is a difficult task for volatile organic liquids. Correct estimation of intermediate spreading coefficient values is an even more difficult task due to poorly defined parameters of the system under consideration, such as instant adsorption layer coverage or wetting film thickness, instant water content in oil phase or oil content in water phase, etc. Thus, simple and illustrative consideration based on spreading coefficients does not give a detailed description of spreading and contraction of a benzene lens or any other low surface energy organic liquid on water. We have previously shown that the disjoining pressure concept [1] is useful and powerful for describing the equilibrium coexistence of an oil drop with an oil adsorption/wetting film atop of water or an aqueous medium. It allows one to reproduce the effect of chemical composition of oil and aqueous media on the contact angle formed by the oil lens. The influence of temperature on wetting transitions was also successfully described.

In this paper, based on a theoretical analysis of the disjoining pressure isotherms, we will show that the evolution of water content in a benzene lens is responsible for spreading/contraction of the benzene lens on water. We will give the relation for calculating the benzene lens angle based on the disjoining pressure isotherms and will analyze the influence of water content in the benzene lens on the thickness of a benzene film atop of water and on the instant lens angle. It will be shown that spreading/contraction behavior of a benzene lens on water results from the interplay of different types of surface forces affected by water content.

2. Calculation of lens angle based on the disjoining pressure isotherms

Consider two liquids with low mutual solubility in a system where a droplet of low surface tension liquid 1 is deposited onto the surface of liquid phase 2. If liquid 2 is not completely wetted by liquid 1, the equilibrium configuration of the system (see Fig. 1) is defined by coexistence of a lens of liquid 1 with an adsorption or wetting film of liquid 1 on top of liquid 2. In equilibrium, liquids 1 and 2 are considered to be mutually saturated. Keeping in mind that our objective here is to explain the behavior of benzene on water, liquid 1 is associated with benzene, while liquid 2 corresponds to water. The mechanical equilibrium in the system normal and along the gravity direction may be written as follows:

$$\begin{cases} \sigma_f \, \cos\gamma = \sigma_{1A} \, \cos\alpha + \sigma_{21} \, \cos\beta \\ \sigma_f \, \sin\gamma = \sigma_{21} \, \sin\beta - \sigma_{1A} \, \sin\alpha \end{cases}, \tag{1}$$

where index A denotes air phase, σ_{1A} represents the surface tension of the organic liquid saturated with water and σ_{21} is the interfacial tension on the liquid 1/liquid 2 interface. The parameter σ_f has a more complex and condition-dependent meaning. It is associated with pure liquid 2/air surface tension if a film of liquid 1 is not present on the surface of liquid 2, and is equal to film tension when an adsorption or wetting film of liquid 1 is formed on top of liquid 2 due to surface activity of liquid 1 with respect to the liquid 2/air interface. Angles α, β and γ are shown in Fig. 1. The sum of angles α and β is equal to the lens angle, which is considered as a parameter characterizing the wettability of liquid 2 by liquid 1.

From the system of Eq. (1) it is easy to obtain:

$$\cos(\alpha + \beta) = \cos\theta = \frac{\sigma_f^2 - \sigma_{1A}^2 - \sigma_{21}^2}{2\sigma_{1A}\sigma_{21}}. \tag{2}$$

Eq. (2) makes it possible to estimate the lens angle on the basis of measurement of the corresponding surface and interfacial tensions. It is worth noting that angle γ, which is difficult to measure accurately, is not present in Eq. (2) and thus does not affect the value of the lens angle.

It is physically reasonable to assume that mechanical equilibrium at current mutual concentrations is established much faster than attaining saturated concentration of liquids 1 and 2 in contacting phases. According to the above assumption, Eq. (2) is valid for estimating the lens angle at some transient values of concentration of liquid 2 in liquid 1 and vice versa. Thus, the spreading of droplet 1 along the surface of liquid 2 can be considered as a variation of lens angle during slow mutual dissolution of liquids resulting in variation of surface and interfacial tensions and adsorption/wetting film thickness. The practical use of Eq. (2) for obtaining the variation of lens angle is complicated by poor knowledge of the transient values of σ_f. However, the thermodynamic analysis performed in our earlier study [8] allows us to calculate σ_f, based on the values of σ_{1A}, σ_{21} and the disjoining pressure isotherm. For plane films of liquid 1 on top of liquid 2 or for films with low effective curvature of the film boundaries, the relation for σ_f is as follows [8]:

$$\sigma_f = \sigma_{21} + \sigma_{1A} + \int_{h_f}^{\infty} \Pi(h)dh, \tag{3}$$

where $\Pi(h)$ is the disjoining pressure in the film of liquid 1, equal to the difference between the pressures inside the film and inside the lens, and h_f is the equilibrium film thickness with respect to current concentrations.

Combining Eqs. (2) and (3) for calculation of the lens angle we get:

$$\cos\theta = 1 + \frac{\left(\displaystyle\int_{h_f}^{\infty} \Pi(h)dh\right)^2 + 2(\sigma_{21} + \sigma_{1A})\left(\displaystyle\int_{h_f}^{\infty} \Pi(h)dh\right)}{2\sigma_{1A}\sigma_{21}} \tag{4}$$

For systems like water/oil characterized by low mutual solubility, the interfacial tension is very weakly concentration dependent. As for the oil/air surface tension, due to surface inactivity of water with respect to an oil/air interface, the oil/air surface tension is also nearly insensitive to the transient water in oil concentration. For many systems, the disjoining pressure isotherm can be calculated theoretically with accounting for transient water content both in the lens and inside the film.

Thus, Eq. (4) allows one to calculate the lens angle θ as a function of transient concentration of water in an oil lens, which varies in the course of system equilibration when mutual concentrations tend to saturation. Using Eq. (4), we will show below that it is the variation of lens angle due to continuous dissolution of water in