Current Opinion in Colloid & Interface Science 19 (2014) 9–16

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

journal homepage: www.elsevier.com/locate/cocis

Perpendicular and lateral equations of state in layered systems of amphiphiles

Pierre Bauduin *, Thomas Zemb

Institut de Chimie Séparative de Marcoule ICSM, UMR 5257 (CEA, CNRS, UM2, ENSCM) Centre de Marcoule Bat. 426, BP 17171, 30207 Bagnols-sur-Cèze, France

ARTICLE INFO

Article history:
Received 5 February 2014
Accepted 8 February 2014
Available online 15 February 2014

Keywords:
Equation of state
Lamellar phase
Osmotic pressure
Phase diagram
Surfactant
Metallacoraborane
Hydration

ABSTRACT

For colloidal solutions containing any type of surfactant inducing the formation of locally flat interfaces, we show here that *two* equations of state are required to understand phase behaviour and stability: the perpendicular and the lateral equations of state. This applies to lamellar phases, locally lamellar connected or sponge phases, uni- and multilamellar vesicle phases formed by detergents, lipids, extractants and theta-shaped molecules in all solutions showing optical anisotropy.

1. Introduction

In dilute solutions, surface active agents or surfactants are molecules that tend to accumulate at interfaces, thus lowering surface tension. This is valid for molecules as small as ethanol [1], to more exotic massive (>1 kDA) amphiphilic molecules such as hydrophobically modified cyclodextrins [2]. In the case of ethanol, the shape of the molecule does not allow formation by itself of an interfacial film made by self-assembled molecules located in a 2D continuous surface [3]. In the colloidal approach, used in this short review, the chemical potential of any surfactant system is composed of bulk, surface, curvature and film packing terms. Once formed, the interfacial films interact with each other via long range interactions (LRI) [4]. The total free energy of the chemical system is then the sum of the chemical potential terms and the interaction term between films [5].

In the case where the surfactant film can be approximated as flat, i.e. when the curvature radius of the film is much larger than molecular size, the self-assembled chemical systems show layered structures in large regions of the phase diagram. These layered equilibrium structures are lamellar phases, disordered locally lamellar (sponge) or bicelles, i.e. anisotropic disc micro-structures. The word “bicelle”, designing flat nanodisc made of a central disc made of one bilayer [6], decorated by a rim of segregated surfactant or lipids, has been forged more than twenty years ago to design bilayers with equilibrium size discs by Sanders and Schwonek [7]. It was later understood that these structures were of the same nature as punctuated lamellar “mesh phases” [8], since they both depend on segregation against entropy of mixing [9]. Indeed, nanodiscs and punctuated planes (mesh phases) appear in sequence along isomolar lines in phase diagrams of ternary systems. This occurs when one or the other component is segregated and is enriched in rims or pores, the general route to form mesh phases and bicelles [10].

The “equation of state” is a derivative of the free energy versus length raised to the power D, the dimension of the system, $D = 1$, 2 or 3 for 1D, 2D or 3D systems such as lamellar, planar or bulk systems. This equation expresses osmotic pressure variations via some intensive parameters. The simplest equation of state known for colloids is based on the parallel with van der Waals gas, as demonstrated initially by Jean Perrin in his Nobel price work. The equation of state of van der Waals fluid dates back to the XIXth century, and was extended later for example to charged monodisperse latex spheres in the presence of excess electrolytes by Versmold and co-workers [11–13].

The first equation of state for systems containing lipids dates back to 1977 and is shown in Fig. 1. The figure shows the equation of state in pressure as well as chemical potential ordinate, and in distance between bilayers as well as mole fraction. Osmotic pressure-distance (or pressure-volume or surface pressure-area) is the preferred representation for reporting equations of state in chemical physics, while the colloidal chemical thermodynamics traditionally uses chemical potential versus mole ratios. One should notice that the two plots are equivalent, provided the partial molar volumes and microstructures are known.

---

* Corresponding author.
E-mail address: Pierre.Bauduin@cea.fr (P. Bauduin).

http://dx.doi.org/10.1016/j.cocis.2014.02.002
1359-0294/

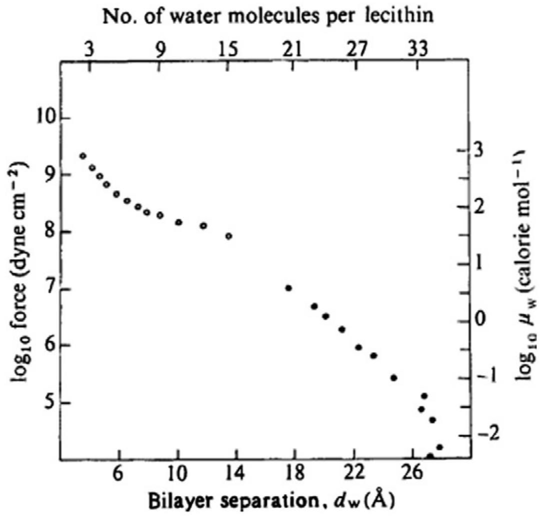

Fig. 1. The first quantitative perpendicular equation of state for neutral bilayers, in pressure versus separation units (left and bottom scales), as well as in chemical potential versus mole ratio (top and right scales). Osmotic pressure measured was nearly the same above and below chain melting temperatures, therefore fluctuation and protrusion mechanisms could be excluded. Establishment of this first "perpendicular" equation of state was the first direct proof of the existence of short range hydration force between uncharged bilayers. Figure reproduced from [29].

The present review concerns the equation of state of complex fluids containing flat bilayers, either as infinite stacks or as disordered locally lamellar phases or as disc-like colloids.

The presence of continuous interfacial films starts to be detectable by neutron and X-ray scattering when the surfactant contains at least octyl chains, and has been investigated in depth in the ternary system sodium octanoate–octanoic acid and water for which the transition of a lamellar (smectic) lyotropic phase to a disordered open connected, "sponge" or anomalous "lamellar phase" was described first. Specific ion effects were apparent in the phase diagram even at high dilution. A general review on this system is available, including the first description of sponge phases known, with their equilibrium with lamellar phases for similar osmotic pressures [14], but without explicit determination of equations of state.

Most experimental studies and theoretical derivations of free energies concern single tailed surfactants (detergents as in the language of biochemists) or lipids, with or without co-surfactants. Inorganic colloidal layered systems have been investigated using the same methodology, for example inorganic covalently bound sheets such as clays [15] or other systems made of inorganic oxide interfaces [16] such as phosphatoantimonate layers [17]. More recently phase diagrams of the so-called "catanionic" systems containing non-stoichiometric anionic and cationic surfactants have been determined with the corresponding osmotic pressure behaviour in the form of a perpendicular equation of state [18]. It is important to notice that equations of state can be very different above and below the chain melting temperature, since the stiffness of the bilayer can vary by orders of magnitude and protrusion force disappears beyond chain melting [19].

All these chemical systems can be diluted with water. The equilibrium phase diagram, when known, indicates the maximum and minimum concentrations of surfactant lipid for which a layered structure minimizes the free energy of the system. In the case of charged bilayers, separation in micro-phases complicates the phase diagram determination, since the phases do not separate at the macroscopic scale even through extensive centrifugation. Clear fluids apparently appearing as single phase can be shown via SAXS or SANS to be made of micro-domains of two phases with low osmotic compressibility. For some of such systems no turbidity can be detected [20]. At "maximum swelling", of a lamellar (smectic) phase, the osmotic pressure is zero and the second phase in equilibrium is nearly pure water. If the equilibrium phase is a diluted micellar phase, equality of osmotic pressure between the two phases present allows determining precisely, with the use of AFM or SFA in the colloidal probe mode, the balance of forces responsible for this maximum swelling [21]. The morphology of seven different microstructures has been reviewed a few years ago for lamellar or locally lamellar phases of anionic, cationic or non-ionic systems determined at maximum swelling and osmotic equilibrium [22].

We come back now to the equation of state for lipids as shown in Fig. 1. This equation relates the osmotic pressure as determined from the "osmotic stress" method relying on dialysis of sample against a reservoir containing a neutral polymer [23] or a polyelectrolyte [24].

However, if one takes into account all terms in the free energy as introduced by Mitchell and Ninham [3], one should consider *two* independent variables in any monolayer or bilayer systems with stacked structure [25]: the one dimensional swelling with a characteristic distance and the area per molecule. Consequently layered molecular systems must be studied on the whole using two different equations of state:

1- an equation of state associated to swelling, i.e. the osmotic pressure as function of spacing between bilayers: this is the "perpendicular" equation of state and this is the one which has been considered first, nearly forty years ago, in the case of lipids. Due to experimental issues, and the low availability of osmometers that are impermeable or even semi-permeable to detergent molecules [26], most of the equations of state for single chain surfactants have been determined only indirectly [27].
2- an equation of state relating the in-plane area per molecule to the free energy: this is the lateral equation of state. The first quantitative theory of the lateral equation of state of a lipid bilayer has been established by S. Marcelja [28].

We now review separately current understanding of the perpendicular and the lateral equations of state for surfactants and lipids that self-assemble in films. The two degrees of freedom, i.e. laterally and transversally to the film plane, must be considered consistently together, even if one of the two derivatives of the free energy is dominant for a given system. The two underlying different transformations associated are shown schematically in Fig. 2: the first one corresponds to the variation of the free energy with respect to the perpendicular equilibrium and the second one to the free energy variation with respect to the contact area per surfactant molecule, A, with the solvent:

$$dG = \left(\frac{\partial G}{\partial D^*}\right).dD^* + \left(\frac{\partial G}{\partial A}\right).dA. \qquad (1)$$

These two derivative terms are associated to osmotic pressure versus spacing and osmotic pressure versus area per molecule in the layer. In the case of systems made of clays, the second term vanishes, since no in-plane elasticity in the clay platelets exists, and only osmotic pressure versus spacing is considered.

2. The classical "perpendicular" equation of state

The perpendicular equation of state of clays is beyond the scope of this review, since clays have no detectable surface activity. It should be noticed that equations of state for clays are simpler in principle, since the area per silicate site does not vary. However, the establishment of an equilibrium state of clays is not always achieved, since clay dispersions can be trapped in nematic or tactoids, "house of card" gels or repulsive glasses, and the most reliable method to reach the equilibrium state relies on long ultra centrifugation in a thin sample holder with on-line analysis [30]. In this later case, partial dissolution of clay particles must be considered [31,32]. For these reasons, the equations of state of clays established are only reliable in the dilute region.