Colloid & Polymer Science Colloid Polym Sci 272:1000–1004 (1994)

Determination of van der Waals forces in monolayer films of lipids & biopolymers. Equation of state for two-dimensional films

K. S. Birdi, F. Madsen, and K. Eberth

Danmarks Farmaceutiske Højskole Department of Chemistry 2-Universitetsparken, Copenhagen, Denmark

Abstract: Amphiphile molecules are characterized by the dual property arising from the interactions between the apolar [alkyl] and the polar part and the surrounding solvent, i.e., water. In assemblies which amphiphiles form in diverse systems, e.g., micelles, soap bubbles, monolayers or bilayers at interfaces, the attractive forces are attributed to the van der Waals forces. It is not easy to estimate the magnitude of van der Waals forces in some of these systems by any direct method.

The magnitude of van der Waals forces in spread monolayers of lipids and biopolymers has been reported to be estimated from experimental data. The magnitude of these forces has been estimated by using an equation of state of a very general form, as delineated herein. In the current literature no such attempt has been reported in the analyses of these monolayers spread on aqueous surfaces. These analyses suggest that the predominant surface forces arise from van der Waals interactions, if the magnitude of electrostatic charge repulsions is weak. The equation-of-state as derived indicates that it is useful in providing information about the molecular interaction in monolayers, for both lipids and biopolymers.

Key words: Monolayer – lipid films – biopolymers – van der Waals

Introduction

Amphiphile molecules (e.g., lipids and biopolymers) adsorb at interfaces (air/water; liquid/liquid; solid/liquid) through various forces, e.g., van der Waals and electrostatic forces. Since van der Waals forces are involved whenever bodies come into close proximity, one can expect to get information on the forces from a variety of phenomena dealing with colloid stability and biophysical systems (monolayers, bilayers, and bilipid membranes).

Monomolecular films of lipids and biopolymers are found to provide much useful information about the forces which stabilize the more complicated systems such as: solid-liquid suspensions, emulsions and the biological membranes. In these structures, we find assemblies of molecules which pack and thus interact through various kinds of forces [8, 7, 4], found to be proportional to various parameters, such as distance between molecules, apolar and polar parts. The estimation of the various forces is possible by using the monolayer method. The main advantage in the monolayer method arises from the fact that the distance between molecules can be estimated very exactly from the area per molecule. This model membrane has been found to provide direct information on the estimation of the van der Waals forces and the electrostatic interactions [7, 4, 5]. The purpose of this study is to report the analyses of amphiphiles, e.g., retinal and various biopolymer monolayers (e.g., proteins (hemoglobin, BSA, ovalbumin), gelatin (bloom 0-30-70-240) and mixtures), by using the equation-of-state which specifically has been found to provide information on the van der Waals forces [4, 5]. This is in continuation with our earlier analyses of lipid monolayers using a similar equation-of-state [4 & 5].

Experimental

The aqueous solutions of various proteins were spread on a clean surface of buffer of pH = 7.4 (Millipore treated water was used) by means of a micrometer syringe. The lipids were spread from their chloroform solutions. Surface pressure (π) vs. area isotherms were obtained by the Wilhelmy plate (platinum) method. The sensitivity of the surface pressure was ± 0.001 mN/m (dyne/cm), as described by us elsewhere [3, 4, 5]. The monolayer was compressed from 600 cm^2 to 100 cm^2. At least three experiments were performed for each temperature, and data used are where isotherms showed minimum differences in reproducibility. The temperature was monitored by thermostat control by circulating water through the trough. The variation in temperature of the subphase was ± 0.1 °C.

Results and discussion

Theory: As described in detail elsewhere, the measured monolayer surface pressure (π) vs. area (per molecule, A) generally exhibits a typical shape as shown in Fig. 1 [1, 4]. The difference between measured isotherm and the ideal film can be described as follows.

In the analyses of the measured surface pressure, π, we will assume it to be composed of various interfacial forces [1, 7, 4], e.g., kinetic, van der Waals, and electrostatic charge repulsion:

$$\pi = \pi_{\mathrm{kinetic}} + \pi_{\mathrm{van\ der\ Waals}} + \pi_{\mathrm{electrostatic}} \cdot \qquad (1)$$

It has been mentioned elsewhere that van der Waals force of attraction gives rise to a lower π values than expected in ideal films. On the other hand, the electrostatic charge repulsion gives rise to an increase in π, thus giving expanded films [1, 4]. It is well known that van der Waals forces are short-range interactions, while electrostatic forces are long-range interactions. In the present study, we will only report systems where the van der Waals forces are predominant, as it will be assumed that either the electrostatic charges are absent (as is the case in neutral films), or that these are negligible in comparison to the van der Waals. These considerations have been previously treated, especially in the case of differences in the magnitudes of van der Waals and electrostatic forces as a function of area/molecule.

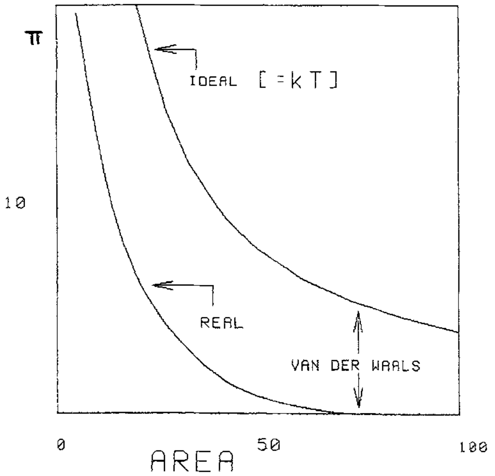

Fig. 1. Typical surface pressure (π) vs. area per molecule (A) isotherm (schematic). The ideal film where $\pi A = kT = 400$ (at $T = 298$ °K) is also shown for comparison.

In ideal films where only kinetic forces are present, $\pi = \pi_{\mathrm{kinetic}}$, we thus get the equation of state for the ideal two-dimensional films:

$$\pi A = kT = \pi_{\mathrm{kinetic}} A \qquad (2)$$

$$= 411 \qquad (\text{when } A = 10^{-16}\ \mathrm{cm}^2 = 100\ \mathrm{nm}^2,\ T = 298/\mathrm{K}),$$

where $k\ [= 1.38 \times 10^{-16}]$ is the Boltzmann constant and T is the temperature. However, if other forces are also present (as given in Eq. (1)), then deviations from Eq. (2) are observed (see Fig. 1). In the case of neutral lipid films, it is reasonable to accept that the term arising from electrostatic interactions will be negligible (π_{el} = ca. 0), and that in real films we will have both kinetic and van der Waals interactions. This difference is seen in Fig. 1, such that the measured π of a film is lower than the ideal π, when the magnitude of A is large. The correction arises from the attraction between the molecules, which gives rise to lower π.

Under these conditions we can re-write the equation of state in the form [7, 4, 5]:

– *for neutral films or with poorly charged films*:

$$[\pi + \pi_{\mathrm{vdw}}]\,[A - A_0] = kT\,, \qquad (3)$$

where π_{vdw} arises from the van der Waals attraction forces, and A_0 is the co-area correction, as determined from the π vs. A isotherms. The magnitude of A_0 was estimated from the inflexion point in the π vs. A isotherm, Fig. 1, the so-called collapse state. The magnitude of π_{vdw} was estimated from the measured data of isotherms (Eq. (3)). The van der Waals forces have been reported to be dependent on the distance, D, [$\pi_{vdw} \sim 1/D^5$] between molecules [10, 9, 2, 4, 5]. Assuming hexagonal packing in the monolayer, we have shown, in the case of lipid films, that the magnitude of π_{vdw} will be dependent on area [$\sim 1/A^{2.5}$]. The values of π_{vdw} were calculated and the dependence on $1/A^{2.5}$ was determined.

In a recent study [11] the relation in Eq. (3) was compared with five other models. This analysis indicated that the present theoretical model was reasonably acceptable in fitting the measured surface pressure vs area isotherms for some 500 data points of 18 different lipids.

In the relationship as given in the Eq. (3), the magnitude of A_0 has been found to have a very significant effect. This is also known from the three-dimensional equation of state in the case of gases. However, in gases the molecules move about in vacuum space, while in monolayers at liquid interfaces these interact with the surrounding medium (water). The magnitude of A_0 has been a subject of much discussion in the literature [1, 7, 4, 5]. We have already reported, in the case of lipid films, that there are two sets of monolayers where A_0 differs as follows when applying Eq. (3) (to both lipid and biopolymer monolayers):

(1) where $A_0 = A_{col}$, and π_{vdw} varies linearly with $1/A^{2.5}$ [for example fatty acids; gelatin]

(2) where $A_0 \neq A_{col}$ (e.g., retinal [5], proteins (hemoglobin, BSA, ovalbumin), and mixed monolayers of proteins + gelatin (gelatin with bloom 0, 30, 70, 240)). We will argue that these are monolayer systems where the water molecules in the subphase are situated in a different configuration, and thus will require a correction for $A_0 = A_{col}\,\phi_h$. Our data suggests that the correction factor, ϕ_h, arising from hydration will be related to some geometrical (fractal) dimension. All the data investigated, however, indicate the value $\phi_h = 2/3$ (or fractal dimension of ≈ 0.6), both for lipids and biopolymers. These data convincingly showed that the assumptions as made in deriving the equation-of-state above are correct. In the case of retinal monolayers [5], it was further found that the magnitude of ϕ_h was independent of temperature.

Typical data for a series of monolayer mixtures (hemoglobin + gelatin) are given in Figs. 2, 3 and 4:

– Fig. 2: Surface pressure (π) vs. area (A) isotherms of mixtures of hemoglobin – gelatin (0 – bloom).

– Fig. 3: Variation of calculated π_{coh} with $1/A^{2.5}$, from Eq. (3), with ϕ_h = ca. 2/3. Similar data were obtained for mixtures of hemoglobin + gelatin (bloom: 0, 30, 70, 240), BSA + gelatin and ovalbumin + gelatin.

– Fig. 4: Variation of a_{vdw} with composition of the (a) hemoglobin + gelatin; similar data was obtained for BSA + gelatin mixtures (for different bloom). The magnitude of a_{vdw} is dependent on the bloom number.

These analyses give the most general equation of state for the two-dimensional neutral films of lipids or biopolymers as:

$$[\pi + (C_1 + a_{vdw}/A^{2.5})]\,[A - A_{col}\phi_h] = kT\,, \tag{4}$$

where $\pi_{vdw} = C_1$ (constant) $+\ a_{vdw}/A^{2.5}$, as found from experiments, and a_{vdw} is the van der Waals constant, and the magnitude of ϕ_h will be equal to 1 or 2/3, depending on the system (i.e., degree of hydration of the polar group in the monolayer). It

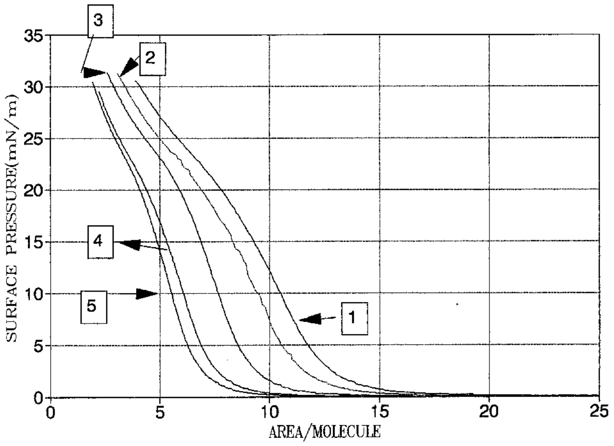

Fig. 2. Surface pressure (π) vs. area per molecule (monomeric amino acid unit = 110 molecular weight) (A) isotherms of different biopolymer films: hemoglobin: gelatin (0 bloom). Hemoglobin: gelatin ratio, 1 = 1:0; 2 = 1:0.25; 3 = 1:0.5; 4 = 1:0.75; 5 = 0:1 (25 °C, pH = 7.4).

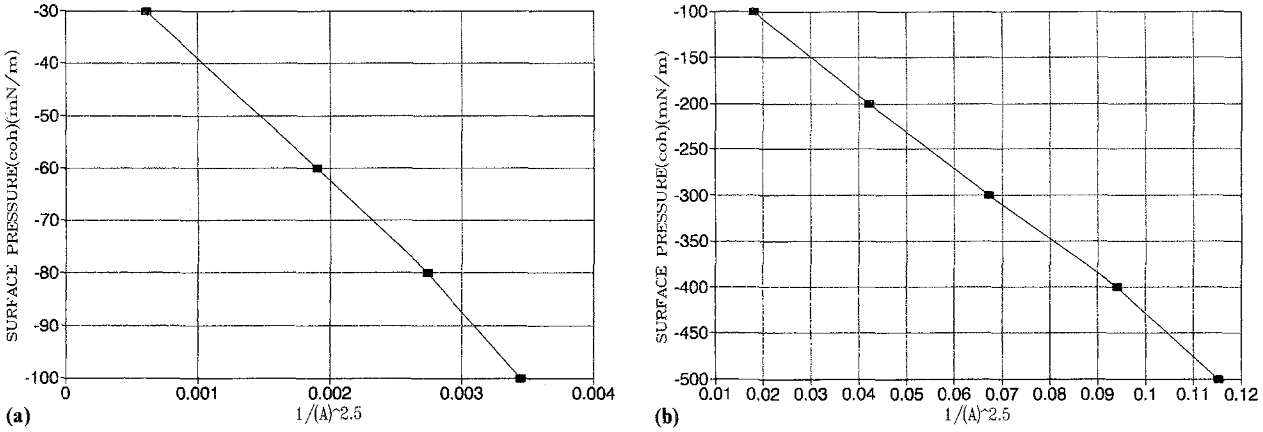

Fig. 3. Variation of surface pressure ($= \pi_{\mathrm{coh}}$) with $1/A^{2.5}$ for mixtures of hemoglobin and gelatin: a) hemoglobin; b) hemoglobin + gelatin-240 (1:1).

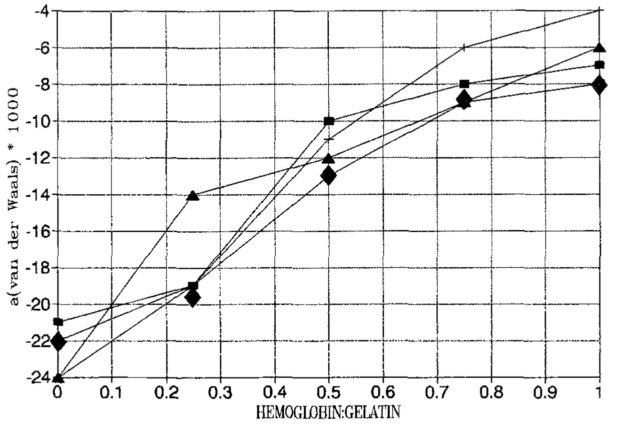

Fig. 4. Variation of a_{vdw} with the composition: hemoglobin + gelatin-0 (◆); − 30 (■); − 70 (▲); − 240 (+).

has been found that both in the case of lipid and biopolymer monolayers, if the plot of π_{vdw} vs. $1/A^{2.5}$ is not linear when $\phi_{\mathrm{h}} = 1$, then by using $\phi_{\mathrm{h}} = 2/3$ one gets a linear dependent, as expected from Eq. (4). The magnitude of a_{vdw} is reported to be related to the number of carbon atoms in the alkyl group and the Hamaker constant [1, 4]. The magnitude of ϕ_{h} is found to be the same in both lipids and biopolymers. This indicates the fractal nature of packing of the solvent (water) molecules surrounding the polar groups. The magnitude 2/3 corresponds to the fractal dimension arising from the hydration water molecules [6].

From the above analysis it is found that the magnitude of a_{vdw} varies as follows:

- Gelatin: a_{vdw} varies with bloom number.
- Hemoglobin + Gelatin: a_{vdw} varies with mixture composition.

Conclusions

The equation-of-state as derived above is found to fit most of the lipid and biopolymer monolayer isotherms. The effect of charges (if present) has been neglected. However, further studies are in progress in order to determine this aspect. The variation of van der Waals coefficient, a_{vdw}, with different parameters is found to correlate with the physical properties of the monolayer molecules, as determined from the area/molecule. A more theoretical treatment of the magnitude of a_{vdw} will be the subject of subsequent reports.

It is thus concluded that by using a very general form of equation-of-state for monolayers, the monolayer compression isotherms can be analyzed, which provides information on the van der Waals forces. These forces are of much importance since monolayers are known to be useful model systems for various complicated systems (e.g., soap bubbles, micelles, emulsions, microemulsions, vesicles, membranes).

Acknowledgements

F. Madsen thanks the Danmarks farmaceutiske højskole for the award of a Ph.D. stipend.

References

1. Adamson AW (1984) Physical Chemistry of Surfaces, J. Wiley, New York.
2. Birdi KS, Sørensen K (1979) Colloid Polym Sci 257:942.
3. Birdi KS, Nikolov I (1979) J Phys Chem 83:365.
4. Birdi KS (1989) Lipid & Biopolymer Monolayers at Liquid Interfaces, Plenum Press, New York.
5. Birdi KS (1991) LANGMUIR, 7:3174.
6. Birdi KS (1993) Fractals-in chemistry, geochemistry & biophysics, Plenum Press, New York.
7. Chattoraj DK, Birdi KS (1984) Adsorption & the Gibbs Surface Excess, Plenum Press, New York.
8. Larsson K (1973) in Surface and Colloid Science, Matijevic, E., editor, John Wiley and sons, New York.
9. Ohki S (1976) J Theor Biol 62:389.
10. Salem L (1960) Molec Phys 3:441.
11. Smaby JM, Brockman HL (1991) LANGMUIR 7:1031.

Received May 27, 1993;
accepted November 5, 1993

Authors' address:

K. S. Birdi
Danmarks Farmaceuticse Højskole
Department of Chemistry
2-Universitetsparken
2100 Copenhagen, Denmark