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Adsorption Study on DDAB Bilayers Using Contrast Variation with SANS

Florence Ricoul (*), Monique Dubois and Thomas Zemb

Service de Chimie Moléculaire, Centre d'Études de Saclay, 91191 Gif-sur-Yvette cedex, France

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Abstract. — Partition coefficients of solutes between bilayers and water are determined with a new method, using contrast variation with SANS. The isotopic composition of the solvent that annuls the contrast is shown to depend on thermodynamical quantities related to the adsorption. Experimental results are given for two organic solute molecules (lactitol and aniline) in the favorable case of the swollen lamellar phase obtained with DDAB double chain surfactant.

One of the basic aspects in the study of biological membranes is to understand what happens at the water-bilayer interface or what interactions are dominant during molecular recognition involved in immunologic processes. It is therefore important to determine directly partition coefficients of solutes between the bulk and the surface of surfactant bilayers.

Consider any guest molecule in a complex fluid. This molecule can exist either as molecularly dissolved in the solvent or associated to the surfactant. The molar fraction ratio of these two situations is the partition coefficient. In the latter situation, the guest molecule can be adsorbed at the interface or embedded in the aggregate. The simplest complex fluid is the spherical micelle. In this case an extended review of the methods used to determine partition coefficients exists for instance in [1]. A number of analytical techniques have been developed: fluorescence probing, NMR self diffusion experiments, differential spectrophotometry, liquid chromatography, conductance, vapor pressure techniques, *etc.* In the case of reverse micelles, a detailed study has been made by Hatton and co-workers [2].

Our aim is to determine the partition coefficient when the complex fluid under study is a swollen lamellar phase at thermodynamical equilibrium.

In this case the host molecule can be dissolved in the interbilayer solvent considered as bulk or attached to the bilayer.

In this paper, we describe a method based on solvent contrast variation with SANS allowing measurement of partition coefficients. The contrast variation technique has been routinely used to determine the internal structure of micelles or of biological objects [3, 4]. It relies on the contrast dependence of the intensity scattered by the sample extrapolated to zero angle:

$$I(q \rightarrow 0) = \Phi V(\rho_1 - \rho_2)^2 \quad (1)$$

(*) Author for correspondence (e-mail: ricoul@nanga.saclay.cea.fr)

where Φ is the volume fraction of the scatterer, V is the molecular volume of the scatterer and ρ_1 and ρ_2 are the scattering densities of the scatterer and the solvent respectively. These densities are given by the following formula:

$$\rho = \frac{b}{V} = \frac{\sum x_i b_i}{\sum x_i v_i} \quad (2)$$

where b_i is the scattering length of the element i and v_i is the specific volume of the element i .

By varying the isotopic constitution of the solvent, for example by adding heavy water to light water, it is possible to annul the contrast and determine the exact scattering length density ρ_1 of the scatterer. The standard procedure to determine ρ_1 is to plot the square root of $I(q \rightarrow 0)$ versus the molar ratio D_2O/H_2O [4].

Since we work with a swollen lamellar phase it is better, to increase the signal/noise ratio, to use the square root of the intensity of the integrated first order Bragg peak. This is possible only if the shape of the form factor $P(q)$ is independent of the contrast. At low angle, if q_0 is the peak position and t the bilayer thickness, then $t \ll \frac{2\pi}{q_0}$ and we can consider in a good approximation that the bilayer is homogeneous and that the form factor has the following expression [5]:

$$P(q) = \Phi \frac{2\pi}{q^2} t (\rho_1 - \rho_2)^2 \left(\frac{\sin(qt/2)}{qt/2} \right)^2 \quad (3)$$

Thus $P(q)$ is linear with the square of $(\rho_1 - \rho_2)$. Since the intensity of the sample is the form factor modulated by a numerical structure factor which is independent from the contrast, we assume the linearity in intensity as for $P(q)$. Typical result obtained with a pure bilayer [6] is shown in Figure 1.

In the following, we show on a complete example how it is possible to extend this contrast variation method to determine the partition coefficient of a solute between the bulk and the interface of a bilayer. The model system chosen is a dilute lamellar phase of DDAB, (didodecyltrimethylammonium bromide), with two different solutes, aniline and lactitol, which is a lactose derivative. The DDAB presents a large domain of stable swollen lamellar phase, so that the bulk water thickness is much larger than the bilayer thickness [6]. Moreover the DDAB lamellar phase is a rigid phase with no fluctuation so that no strong central diffusion can perturb the observation of the Bragg peak. The two solutes chosen are expected to have different behaviors: the lactitol molecule being more hydrophilic with its hydroxy groups than the aniline molecule that contains an aromatic ring.

1. Experimental

We use DDAB from Kodak recrystallized 3 times in ethyl acetate. Lactitol monohydrate ($C_{12}H_{24}O_{11}, H_2O$) is used as received from Aldrich. To increase the contrast between DDAB and aniline molecules and thus to get a better precision on K , the equilibrium constant, we use deuterated aniline ($C_6D_5NH_2$) from Eurisotop.

Numerical constants used for the scattering length and the molecular volumes are given in Table I. The molecular volumes of DDAB and lactitol have been measured using a Density Measurement Apparatus DMA 60 from A. Paar (Graz, Austria). The volume of the bromide is taken from crystallographic data [7]. The volume for aniline and water are calculated from the densities values given in [8]. We assume that these molecular volumes in liquids are independent of the structure and we also neglect the effects of strong interactions that may exist with association [9].

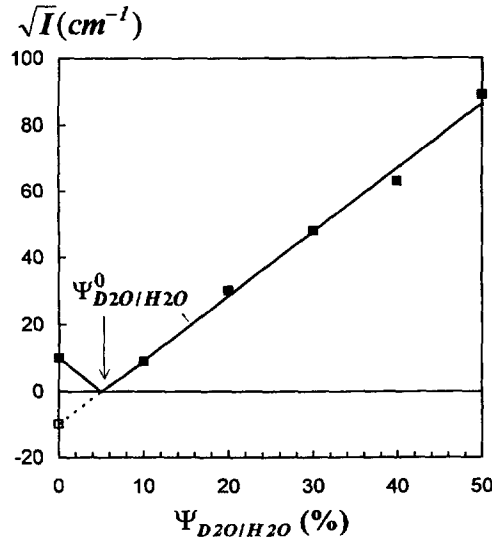


Fig. 1. — Typical contrast variation experiment with DDAB 10 wt% in water (from [6]). Ψ_{D_2O/H_2O} is the volume fraction of heavy water over light water and I is the scattering intensity. The squares are the experimental values and the line gives the best linear fit. Ψ_{D_2O/H_2O}^0 is found equal to 4.3% which is in good agreement with the value of 4.14% calculated according to the model described in the text.

Table I. — Numerical constants used for the calculation of the contrast (details for the molecular volumes determination are given in the experimental part).

	b ($\times 10^{-12}$ cm)	\bar{v} ($\times 10^{-24}$ cm ³)
DDA ⁺	-2.723	751
Br ⁻	0.679	39
H ₂ O	-0.168	30
D ₂ O	1.9152	30
Lactitol (C ₁₂ H ₂₄ O ₁₁)	$-8.7526 + 9 \times [\Psi_{D_2O/H_2O} \times b_D + (1 - \Psi_{D_2O/H_2O}) \times b_H]$	350
Aniline (C ₆ H ₅ NH ₂)	$8.2576 + 2 \times [\Psi_{D_2O/H_2O} \times b_D + (1 - \Psi_{D_2O/H_2O}) \times b_H]$	151

The composition of the samples is defined by the values of the volume fractions of DDAB, Φ_{ddab} , of solute, Φ_s , and of water $\Phi_w = \Phi_{D_2O} + \Phi_{H_2O} = 1 - \Phi_{ddab} - \Phi_s$ as well as the volume ratio of heavy water over light water $\Psi_{D_2O/H_2O} = \Phi_{D_2O} / (\Phi_{D_2O} + \Phi_{H_2O})$.

Φ_{ddab} was fixed to 5% so that the periodicity of the lamellar liquid crystal is 480 Å. At room temperature, the chains are in the liquid state (L_a). 10 samples with different ratios Ψ_{D_2O/H_2O} from pure H₂O to pure D₂O were prepared for each of the 3 experiments we made: $\Phi_{lactitol} = 0.1$, $\Phi_{aniline} = 0.005$ and $\Phi_{aniline} = 0.01$. The scattering experiments have been performed on PAXE spectrometer at the LLB laboratory at Saclay with a wavelength of 7 Å and the detector at 5 m. The samples were placed in 1 mm quartz cells from Thuet-Bichelin (B.P. 7-Blodelsheim-France).

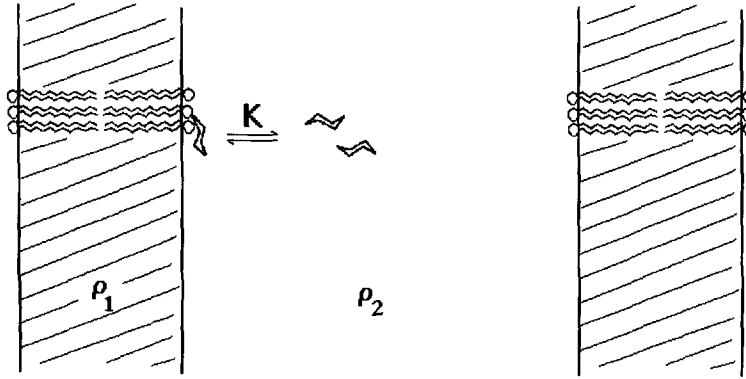


Fig. 2. — Schematic structure of the lamellar phase in presence of the solute: K is the equilibrium constant of the solute between the bulk and the interface, ρ_1 and ρ_2 are the average scattering densities respectively for the bilayer and for the bulk (quantities are defined in the text).

2. Theory

From the measurement of $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$, the volume ratio of heavy water over light water that annuls the contrast between the bulk and the lamella one can deduce the amount of solute that adsorbs at the surface. Indeed, we show now that the binding constant of the solute depends on $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$.

Let us consider our system as schematized in Figure 2. In order to calculate the contrast between the lamella and the bulk, we introduce:

$$\rho_1 - \rho_2 = \frac{b_1}{V_1} - \frac{b_2}{V_2} \quad (4)$$

where b_1 and b_2 are the scattering lengths for respectively the lamella and the bulk; V_1 and V_2 are the volumes of respectively the lamella and the bulk. In the following these quantities are evaluated per DDAB molecule.

We introduce the parameter λ , the interfacial composition, as defined by Leodidis and Hatton [2]: $\lambda = n_s^{\text{ads}}/n_{\text{ddab}}^0$ (where n_s^{ads} is the number of solute molecule adsorbed on the bilayer and n_{ddab}^0 is the number of DDAB molecule in the sample). Thus for the bilayer, per DDAB molecule, we have:

$$v_1 = b_{\text{dda}+} + \beta b_{\text{Br}-} + \lambda b_s \quad (5)$$

β is the ratio of bound bromide counterion per DDAB molecule. We assume $\beta \approx 0.9$ as it was found in DLVO fit of forces measurement in [10]. However we have verified that a variation in the value of β less than 10% is in the range of the experimental error on the determination of $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$. The scattering density of the solute, b_s , depends on $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$ as the solute can exchange labile protons with the solvent (*cf.* Tab. I).

In equation (4), V_1 is derived from:

$$V_1 = \bar{v}_{\text{dda}+} + \beta \bar{v}_{\text{Br}-} + \lambda \bar{v}_s \quad (6)$$

Since we have $\bar{v}_w n_w^0 = \Phi_w V$ and $\bar{v}_{\text{ddab}} n_{\text{ddab}}^0 = \Phi_{\text{ddab}} V$ with \bar{v}_w and \bar{v}_{ddab} the molecular volumes of the water and DDAB respectively and V the total volume of the sample, we can write $n_w^0/n_{\text{ddab}}^0 = \bar{v}_{\text{ddab}}/\bar{v}_w \Phi_w/\Phi_{\text{ddab}}$.

The average scattering length of the bulk solvent b_2 is also depending on λ , because the adsorbed host molecule should not contribute in the bulk scattering:

$$b_2 = (1 - \beta)b_{\text{Br}^-} + \left(\frac{\Phi_s}{\Phi_{\text{ddab}}} \frac{\bar{v}_{\text{ddab}}}{\bar{v}_s} - \lambda \right) b_s + \left(\frac{\Phi_w}{\Phi_{\text{ddab}}} \frac{\bar{v}_{\text{ddab}}}{\bar{v}_w} \right) b_w \quad (7)$$

with $b_w = \Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}} b_{\text{D}_2\text{O}} + (1 - \Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}) b_{\text{H}_2\text{O}}$. The volume of the bulk is given by:

$$V_2 = (1 - \beta)\bar{v}_{\text{Br}^-} + \left(\frac{\Phi_s}{\Phi_{\text{ddab}}} \frac{\bar{v}_{\text{ddab}}}{\bar{v}_s} - \lambda \right) \bar{v}_s + \frac{\Phi_w}{\Phi_{\text{ddab}}} \bar{v}_{\text{ddab}} \quad (8)$$

So finally we obtain an expression for the contrast depending on four physical quantities:

$$\rho_1 - \rho_2 = \frac{b_1}{V_1} - \frac{b_2}{V_2} = f_1(\lambda, \Phi_{\text{ddab}}, \Phi_s, \Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}) \quad (9)$$

This equation gives a linear relation between $\rho_1 - \rho_2$ and $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$ so according to (1) it implies also a linear relation between $\pm\sqrt{I}$ and $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$.

For given Φ_{ddab} and Φ_s it is possible to solve numerically the equation $\rho_1 - \rho_2 = 0$ and get the variation of λ as a function of the value of $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$ that annuls the contrast: $\lambda = f_2(\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^2)$.

Besides from the value of λ , one can calculate $x_s^{\text{ads}} = \lambda/(1 + \lambda)$, the mole fraction of solute at the interface, and $c_s^{\text{free}} = ((n_s^0 - n_s^{\text{ads}})/n_{\text{ddab}}^0)/V_2 = (\Phi_s/\Phi_{\text{ddab}} \bar{v}_{\text{ddab}}/\bar{v}_s - \lambda)/V_2$, the concentration of solute that stays in the bulk. Then we can deduce the equilibrium constant K , as defined in [1]:

$$K = \frac{x_s^{\text{ads}}}{c_s^{\text{free}}} = f_3(\Phi_{\text{ddab}}, \Phi_s, \Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0) \quad (10)$$

or a dimensionless partition coefficient K' , as defined in [2]:

$$K' = \frac{x_s^{\text{ads}}}{x_s^{\text{free}}} \quad (11)$$

In sufficiently dilute solutions one has $x_s^{\text{free}} \cong c_s^{\text{free}}/55.5$ (so that $K' \cong K \times 55.5$). These two quantities, K and K' , make no hypothesis on the bilayer being a continuum since x_s^{ads} represents a mole fraction. Moreover if the solute in the aqueous solution has an ideal behavior in the sense of Henry's law, then K or K' can be converted into thermodynamical quantities. For example, for given Φ_{ddab} and Φ_s , it is possible to plot $-\log(K)$, which is proportional to the free enthalpy of adsorption of the solute on the surface, *versus* $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$, the ratio that annuls the contrast. This is illustrated in Figure 3 with computed values of $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$ *versus* $\log(K')$.

Finally, from the experimental measurement of $\Phi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$ it is possible to deduce the thermodynamical quantities about the adsorption of the solute.

3. Results and Discussion

For the different experiments, the maximum intensity of the first Bragg peak has been determined graphically on each scattering spectrum. The square-root of this intensity is plotted in Figure 4 *versus* $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$. for clarity, only the points with $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}$ below 30% are shown and the points below the match point (open symbols in the figure) have been plotted with an opposite sign so that they can align with the others. The lines in the figure are the best linear

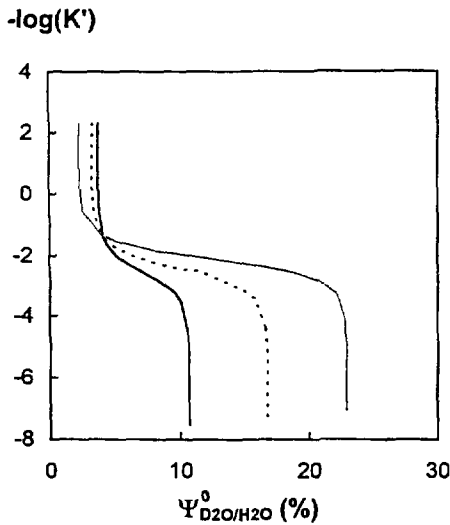


Fig. 3

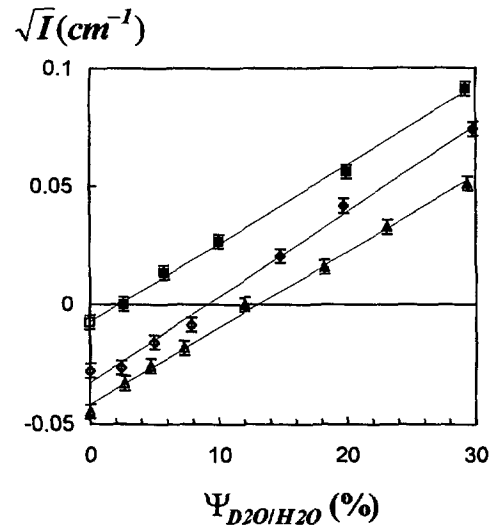


Fig. 4

Fig. 3. — Simulations of the logarithm of K' , the molar fraction based partition coefficient as defined in the text and in [2], as a function of Ψ_{D_2O/H_2O}^0 , the volume ratio of heavy water that annuls the contrast: (—) $\Phi_{aniline} = 0.005$, (---) $\Phi_{aniline} = 0.01$ and (····) $\Phi_{lactitol} = 0.1$ ($\Phi_{ddab} = 0.05$ for the three curves).

Fig. 4. — Square root of the scattering intensity *versus* volume fraction of heavy water in the solvent for 3 experiments: squares $\Phi_{lactitol} = 0.1$, losanges $\Phi_{aniline} = 0.005$ and triangles $\Phi_{aniline} = 0.01$. The open symbols represent the values for which the sign has been changed so that the full lines could give the best linear fits for all the points.

fits which have regression coefficients higher than 0.99 in the three cases. The error on the graphical measurement of the intensity has been reported by the error bars.

In the experiments with aniline, we observe that the points do not align as well. We explain this phenomenon by the fact that the bilayers may not be strictly homogeneous especially if there is some adsorption. Equation (3) for $P(q)$ is modified for heterogeneous bilayers and since we work at finite angle instead of zero angle, $P(q)$ is slightly different when the contrast between the lamellae and the bulk is high compared to the case when the contrast is small. The scattered intensity should be modified by a small factor. However we find that, either using the linear fit of all the points or only several points around the match point, the uncertainty in the determination of Ψ_{D_2O/H_2O}^0 is less than 0.2 units.

From equations (1) and (9) described above, which give a linear relation between $(\rho_1 - \rho_2)$ (or $\pm\sqrt{I}$) and Ψ_{D_2O/H_2O} , it is possible to deduce the value of λ that gives the best fit of the experimental points. The value of the fit is arbitrarily set equal to the intensity of the experimental points at $\Psi_{D_2O/H_2O} = 100\%$ for which the intensity of the Bragg peak is the highest and the error is the smallest. The fit corresponds also to a best linear fit so it should cross the abscissa axis at the same value of Ψ_{D_2O/H_2O}^0 as the experimental points. Thus we deduce the upper and lower possible values for λ by the fits that reproduce the upper and lower experimentally determined limits for Ψ_{D_2O/H_2O}^0 . The results are summarized in Table II.

Figures 5a, b and c show the comparison for $\sqrt{I} = f_4(\Psi_{D_2O/H_2O})$ between computed lines with

Table II. — *Results of the contrast variation experiments for lactitol and aniline.*

	$\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}}^0$	λ	% of solute adsorbed
Lactitol 10%	0.023 ± 0.002	$< 10^{-2}$	$< 1\%$
Aniline 0.5%	0.09 ± 0.002	0.354 ± 0.108	$75\% \pm 2.2$
Aniline 1%	0.13 ± 0.002	0.674 ± 0.101	$71\% \pm 2$

Table III. — *Values of the different partition constants for the adsorption of aniline.*

	K (mol/l)	K'	ΔG (kcal/mol)
Aniline 0.5%	19.5 ± 9.9	1085 ± 553	-4.06 ± 0.24
Aniline 1%	13.0 ± 3.5	725 ± 196	-3.82 ± 0.14

different values of λ and experimental curves. For clarity around the match point, only the points below $\Psi_{\text{D}_2\text{O}/\text{H}_2\text{O}} = 50\%$ are shown.

In the case of the lactitol molecule solubilized in an L_α phase, it is clear that we do not have an adsorption of the sugar at the interface (Fig. 5a). This observation agrees with the observation reported by Katz and Diamond on sucrose and multilayered DMPC liposomes [11]. However in this latter case, the adsorption equilibria were evaluated on liposomes with excess water.

On the contrary, in the case of aniline, we see a strong adsorption, greater than 70% in our experimental conditions (Figs. 5b and 5c). In Table III, we show the values for K and K' calculated using equations (10) and (11). We have also calculated the free enthalpy of transfer of aniline from water to DDAB bilayer using K' . The value we found (~ -4 kcal/mol) is of the order of the value found for the most hydrophobic amino acids in the scale of the transfer from water to AOT interface described by Leodidis and Hatton [2]. This is consistent with the fact that aniline has an aromatic ring and no carboxylic group in comparison with amino acids. It is also possible to correlate these values of the free enthalpies of transfer with the octanol/water scale for partition coefficients, first studied by Collander, [12], who observed that there tend to be systematic relationships among nonelectrolyte partition coefficients measured between water and nonpolar solvents for a family of solutes. Later Hansch and Leo [13], found that biological activity of simple organic compounds correlate with their octanol/water partition coefficients. In [2], Leonidis and Hatton have found that it costs more energy to transfer amino acids from water to the AOT interface than to octanol whereas Katz and Diamond have found that the free energies of transfer for nonelectrolytes are lowered in the case of the DMPC bilayers. In our case, with DDAB bilayers, we have only data for aniline. The octanol/water partition coefficient for aniline is given in [14]: the value 8 is defined as the unitless ratio of the concentrations in the organic phase and in the aqueous phase. Using the same definition we can calculate the partition coefficient DDAB-membrane/water for aniline and we find a ratio of 50, indicating that aniline has more affinity for the bilayers than for octanol.

It is also interesting to define l , a characteristic thickness for the adsorption layer, by $(n_s^{\text{ads}} \times \bar{v}_s)/(n_{\text{ddab}}^0 \times \sigma_{\text{ddab}})$ where σ_{ddab} is the polar headgroup area of DDAB and equals 68 \AA^2 . The calculations with aniline give 0.78 \AA for $c_s^{\text{free}} = 0.013 \text{ mol/l}$ and 1.49 \AA for $c_s^{\text{free}} = 0.031 \text{ mol/l}$. First we observe that l is in the range of 1 \AA , which is less than the aniline molecule size: this means that the surface is not totally covered. Then we observe that l is proportional to c_s^{free} ,

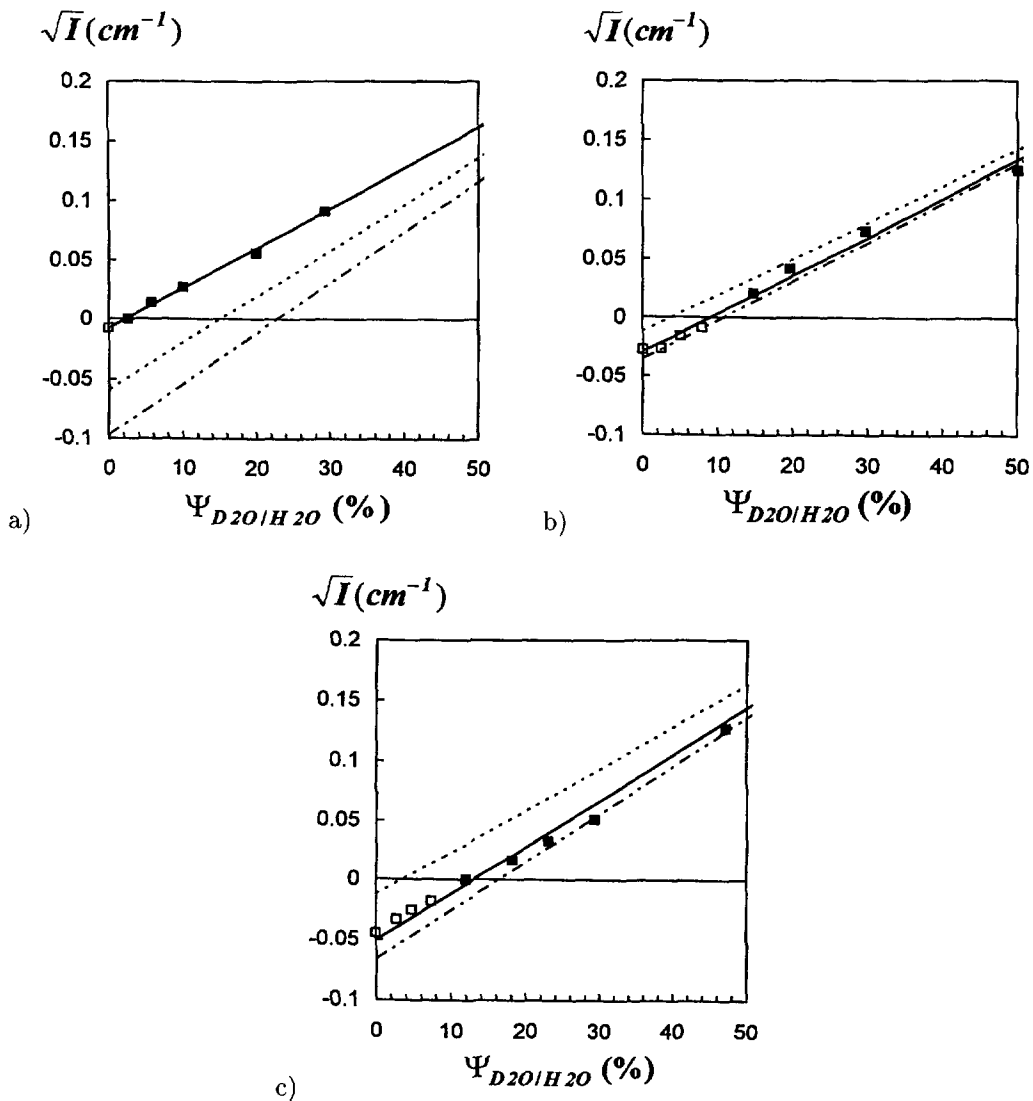


Fig. 5. — Square root of the scattering intensity *versus* volume fraction of heavy water in the solvent. The squares are the experimental results (open squares represent the points that have been plotted negatively) and the lines are predictions calculated with the implicit relation (2) for different adsorption ratios: a) $\Phi_{\text{lactitol}} = 0.1$ and (—) $n_s^{\text{ads}}/n_s^0 = 0\%$; (---) 50%; (- · - ·) 100%; b) $\Phi_{\text{aniline}} = 0.005$ and (- - -) 0%; (—) 75%; (- · - ·) 100%; c) $\Phi_{\text{aniline}} = 0.01$ and (- - -) 0%; (—) 71%; (- · - ·) 100%.

so no saturation seems to happen. If saturation occurs, an extension of this method to higher solute/surface ratio would allow the determination of a full Langmuir isotherm in a lamellar system.

A large number of such a membrane/water partition coefficient study already exist in the literature: a good review of them can be found in [15]. But as the authors explain it, most of the studies are based on the separation of vesicle and aqueous phases like in [11]: this procedure can however lead to errors since the centrifugation may modify the system and the

solute partitioning. Fluorescence spectroscopy or EPR do not require phase separation: for example, in [16], partition coefficients of local anesthetics have been determined in spin labeled membranes. However these methods are indirect measurements of the partition coefficient since they are sensitive to the spectral effects caused by the addition of the solutes to the bilayers; in addition they need probes either on the solute or on the lipids which may give artifacts. Compared to these methods, the SANS technique allows direct determination of partition coefficients in a single phase lamellar liquid crystal. The example given in this paper with DDAB, lactitol and aniline is a first illustration of this method which could also be applied to more classical lipids membranes and other biological solutes. The interbilayer space dimension must allow the penetration of the solute and the presence of solute should also not induce a phase transition which is true at dilute concentration. The main limitation is that the shift of the contrast match point with a possible adsorption of the solute has to be measurable, *i.e.* larger than typical error bars, commonly 1 to 2% on the match point isotopic content. This shift depends on each system but can be calculated as shown in this paper once the molecular volumes are known.

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