Adsorption from binary liquid solutions into mesoporous silica: a capacitance isotherm on 5CB nematogen/cyclohexane mixtures

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ABSTRACT

We present a capacitance method to measure the adsorption of rod-like nematogens (4-cyano-4′-pentylbiphenyl, 5CB) from a binary liquid 5CB/cyclohexane solution into a monolithic mesoporous silica membrane traversed by tubular pores with radii of 5.4 nm at room temperature. The resulting adsorption isotherm is reminiscent of classical type II isotherms of gas adsorption in mesoporous media. Its analysis by a model for adsorption from binary solutions, as inspired by the Brunauer–Emmett–Teller (BET) approach for gas adsorption on solid surfaces, indicates that the first adsorbed monolayer consists of flat-lying (homogeneously anchored) 5CB molecules at the pore walls. An underestimation of the adsorbed 5CB amount by the adsorption model compared to the measured isotherm for high 5CB concentrations hints towards a capillary filling transition in the mesopores similar to capillary condensation, i.e. film-growth at the pore walls is replaced by filling of the pore centres by the liquid crystal. The experimental method and thermodynamic analysis presented here can easily be adapted to other binary liquid solutions and thus allows a controlled filling of mesoporous materials with non-volatile molecular systems.

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1. Introduction

Spatial confinement of liquid crystals can alter their physico-chemical properties substantially. Novel phase behaviour, complete suppression of phase transitions and inhomogeneous structures and dynamics have been reported experimentally and validated both by analytical theory and computer simulation [1–15]. In particular, the advent of porous media with tailororable pore shapes and tuneable pore size from the macro- to the microscale have resulted in an increased number of studies aimed at an understanding of liquid crystalline behaviour in these interface-dominated geometries [1,12,16–18]. Moreover, mesoporous media with pores smaller than 50 nm exhibit structures significantly smaller than the wavelengths of visible light and can thus act as photonic...
metamaterials. Their optical functionality is not determined by the properties of the base materials, but rather by the precise pore shape, geometry, and orientation. Embedding molecular matter, most prominently liquid crystals in pore space provide additional opportunities to control light-matter interactions at the single-pore, meta-atomic scale [19–22]. The resulting hybrid materials get their mechanical stability from the porous solid, whereas the liquid-crystalline pore filling adds an integrated functionality to the system. To exploit and predict the potential of liquid crystal-infused solids as functional nanomaterials, however, a detailed understanding of the physico-chemical changes of the confined compared to the unconfined, bulk liquid crystals is necessary [18].

Another challenge in the study of liquid crystals in porous media compared to other molecular fillings is their often very low vapour pressure under ambient conditions. Therefore, the liquid crystals are typically filled via capillary action (spontaneous imbibition) into the porous solids [3,23,24]. This preparation scheme precludes a partial filling of pore space, e.g. the adsorption of a thin liquid crystalline film at the pore walls. Hence, almost solely completely with LC filled porous solids have been explored so far [12,18].

Here, we present an experimental study, where we fill sequentially a mesoporous monolithic silica membrane with pores 13 nm across by imbibition of binary mixtures of cyclohexane and 5CB, 5CB$_2$CH$_{1-x}$x with distinct concentrations $x$ of 5CB. We try to infer the 5CB adsorption after each imbibition step. The resulting filling-fraction versus concentration isotherm is then analysed with a model for adsorption from binary solutions.

2. Experimental

A monolithic mesoporous silica SiO$_2$ membrane of 280 $\mu$m thickness is prepared by thermal oxidation of mesoporous silicon, pSi, at 1073 K for 12 h. The pSi membranes are synthesised by electrochemical anodic etching of highly p-doped (100)-oriented silicon wafers employing a mixture of concentrated fluoric acid and ethanol (volume ratio 2:3) as electrolyte [25,26]. The resulting pSiO$_2$ membranes consist of an array of parallel-aligned nanochannels of mean diameter $D = 10.8 \pm 0.5$ nm and exhibit a porosity $P = 35 \pm 2\%$, as determined by recording a volumetric nitrogen sorption isotherm at 77 K. The pore diameter is determined from the adsorption branch of the isotherm using the Kelvin method.

The experimental details of the electrical capacitance measurements are presented in Figure 1. Gold electrodes are deposited on the nanoporous membrane of pSiO$_2$. The capacitance $C$ of the sample is measured by a Lock-in amplifier SR830 in internal reference mode at a frequency of 47 kHz, see the electric circuit in Figure 1(c). In such a setup the measured voltage, $U_R$ at the resistor $R$, is given by

$$U_R = \frac{RU}{\sqrt{(\omega C)^{-2} + R^2}} \approx \omega RCU. \quad (1)$$

The simplification of Equation (1) follows from the fact that here $1/(\omega C) \gg R$. The ratio of these values ranges from 20 to 50. Thus the correction to the measured $C$ value due to ignoring of $R$ in the square root denominator is less than 0.001 $C$ at maximum. In this case, the capacitance $C \propto U_R$. Thus, one can refer to the measured $U_R$ for

![Figure 1](image-url)
Figure 2. Adsorption of 5CB from binary mixtures 5CB\(x\)CH\(1-x\) in mesoporous pSiO\(_2\) as explored by electrical capacitance measurements. Marked by different colours are temporal intervals during which the 5CB adsorption into the mesoporous host is monitored by \textit{in-situ} capacitance measurements upon immersion in bulk binary mixtures 5CB\(x\)CH\(1-x\) with 5CB volume fraction \(x\), as indicated in the figure. The gaps between the shaded time intervals indicate the times when the sample cell is empty, see Figure 1(b). The capacitance \(C_e\) is measured immediately after removing the bulk solution, see open circles with distinct colours. After this, the cell is again filled with the bulk binary mixture of 5CB\(x\)CH\(1-x\) with an increased volume fraction \(x\).

lock-in \(U_R\) value as capacitance \(C\) presented in arbitrary units. The absolute capacitance in our measurement is not important, only the relative change is of relevance. Moreover, the phase shift in the whole range of volume fractions \(x\) of the liquid mixture 5CB\(x\)CH\(1-x\) embedded into nanoporous matrix changes roughly between 87 and 89\(^\circ\), i.e. by less than 2\(^\circ\) only. This means that we are evidently far away from any dielectric relaxation frequencies \((\omega \tau \gg 1)\). Otherwise, the analysis of the dielectric measurement would be much more complicated, see Ref. [27].

3. Results and discussion

In Figure 1, a schematics of the experimental cell is shown. It consists of a syringe body. The mesoporous sample is fixed between two spring electrodes. A serious problem in such experiments can be stray (parasitic) capacitances. For this reason, our measurements have been done with and without the binary solution, see panel (a) and (b) of Figure 1, respectively. The adsorption process takes place in the liquid-filled cell and can be monitored \textit{in-situ} by time-dependent capacitance measurements of the membrane \(C(t)\), see Figure 2. This allows one to monitor for each distinct bulk concentration \(x\) the adsorption kinetics and, in particular, the reaching of an adsorption equilibrium in pore space.

Figure 3. Measured equilibrium capacitance, \(C_e\) vs 5CB concentration \(x\) for a mesoporous membrane pSiO\(_2\) immersed into a binary mixture 5CB\(x\)CH\(1-x\).

After equilibration, the liquid cell is emptied and the capacitance \(C_e\) is measured, see open symbols in Figure 3. Thereby we have the same stray capacitance contribution in each measuring point. The resulting equilibrium capacitance, \(C_e\) vs \(x\) for the nanoporous membrane pSiO\(_2\) immersed into binary mixture 5CB\(x\)CH\(1-x\) is shown in Figure 3. After measuring \(C_e\) a new bulk solution 5CB\(x\)CH\(1-x\) was inserted and the procedure repeated as a function of increasing \(x\).
To calculate the adsorption isotherm from the capacitance isotherm certain assumptions have to be made. We anticipate that \( C_e \) in the equilibrium state scales linearly with the fractional volume content \( V^*(x) = V(x)/V_0 \) of 5CB in the pore volume, \( V_0 \). The fractional volume content consists of the molecules located both in the adsorbed 5CB layer at the pore walls plus molecules 5CB located in the binary mixture of the core region of the pore filling. The second assumption is that the volume concentration of the 5CB molecules inside the core region of the pore filling is the same as in the bulk solution surrounding the porous matrix, i.e. it is equal to \( x \). Accordingly, the following equations are valid:

\[
V^*(x) = \frac{C_e(x) - C_e(x = 0)}{C_e(x = 1) - C_e(x = 0)}, \quad (2)
\]

\[
V(x) = fV_0 + (1 - f)V_0x. \quad (3)
\]

Thus for the fractional filling of adsorbed 5CB as a function of \( x, f(x) \) follows:

\[
f(x) = \frac{V^*(x) - x}{1 - x}. \quad (4)
\]

The filling fraction \( f \) versus concentration \( x \) is shown in Figure 4. An unknown parameter in such a calculation is the \( C_e(x = 1) \) value [see Equation (4)], since at \( x = 1 \) the anisotropic nematic LC phase is expected inside the pores at \( T = 296 \) K. Accordingly, our last data point corresponds indeed to \( x = 0.99 \). The hypothetic value \( C_e(x = 1) \), which is quite close to \( C_e(x = 0.99) \) has been obtained (precisely adjusted) assuming that \( f(x) \rightarrow 1 \) at \( x \rightarrow 1 \).

The 5CB adsorption isotherm in Figure 4 is similar to the type II gas adsorption isotherm [28], and thus at low coverage can be described by the Brunauer–Emmett–Teller (BET) equation. For adsorption of a solute in a liquid medium the BET equation was generalised as follows [29]:

\[
q^* = q_m \frac{b_s x}{(1 - b_t x)(1 - b_s x + b_t x)}, \quad (5)
\]

where \( q^* \) is the adsorbed amount, \( q_m \) is the monolayer capacity, \( x \) is the solute concentration, \( b_s \) and \( b_t \) are the equilibrium constants for solute-adsorbent and solute-solute interactions respectively. This equation has been widely used for describing adsorption of various solutes [30], e.g. in a recent work of the Findenegg group it was applied for modelling adsorption of proteins onto silica nanoparticles in aqueous media [31].

We applied Equation (5) to fit the 5CB experimental adsorption isotherm. Note that we expressed the adsorbed amount \( q \) here in units of the complete filling, i.e. \( q = f = 1 \) corresponds to a complete filling of the pores. Unlike the original BET equation, Equation (5) is a three-parametric dependence, thus we used the Trust Region Reflective algorithm, as implemented in SciPy [32] constraining the parameters as non-negative and using various initial guesses. We also varied the interval of concentrations used for the fitting, and found that the solution for the monolayer capacity \( q_m \) changes insignificantly for the range of concentrations between 0.35 and 0.8. The solution for the interval [0, 0.75] gives \( b_1 = 0.560; b_2 = 169.5; q_m = 0.281 \). This solution is plotted as a dashed line in Figure 4 and shows a nice fit within the considered interval.

Beyond this interval, the fit underestimates the amount adsorbed which suggest that a pore-filling beyond film-growth at the pore walls takes place, similar to the capillary condensation in the gas adsorption. Finally, assuming the pore geometry as cylindrical we recalculated the filling fraction for the monolayer \( f_m = q_m/t \) to the thickness of the monolayer \( h_m \) using

\[
f_m = \frac{R^2 - (R - h_m)^2}{R^2}, \quad (6)
\]

where \( R = D/2 \) is the pore radius. Taking \( R = 5.4 \) nm, Equation (6) gives the monolayer thickness \( h_m = 0.8 \) nm. The 5CB molecule has a length of \( 1.9 \) nm and a diameter of \( 0.7 \) nm [33,34]. Thus, presumably the 5CB molecules are lying flat on the silica surfaces, similarly as it has been
inferred for 8CB on planar quartz surfaces by Brewster-
angle reflection ellipsometry and surface optical second
harmonic generation [35].

These conclusions with regard to the adsorption
behaviour are consistent with optical measurements [36]
as well as dielectric spectroscopy studies upon sequential
filling of mesoporous silica with 7CB from binary
7CB/acetone solutions [27,37–39]. In those experiments
also first a regime with monolayer formation at the pore
walls and a subsequent formation of capillary bridges
was inferred from distinct optical signatures (changes in
the optical birefringence and light scattering) as well as
distinct molecular mobilities of these two molecular pop-
ulation in pore space. In particular, it was found that the
first adsorbed layers at the pore walls are significantly slower in their molecular reorientation dynamics. The
study presented here supports these functional differ-
ences by a rather thermodynamic distinction between the
two populations.

4. Conclusions

We presented an experimental study on the adsorption
of 5CB from binary 5CB/cyclohexane solutions in meso-
porous silica by capacitance measurements. The result-
ing adsorption isotherm is reminiscent of classical gas
isotherms of type II indicating multilayer growth on pore
walls with heterogeneous LC-wall interactions and can
be described by a generalised BET-isotherm, adapted
for adsorption from binary solutions. Deviations from
the BET description at higher filling fractions, higher
concentrations, respectively, indicate a transition from
LC-film growth at the pore wall to filling of the pore cen-
tre reminiscent of the capillary condensation transition
of gases in mesoporous media. The monolayer capac-
ity derived from the sorption-isotherm analysis hints
wards the formation of a layer with homogeneous LC
anchoring at the pore walls, i.e. the first 5CB monolayer
is lying flat on the silica surface.

We hope that our study will stimulate complement-
ary experimental and theoretical studies on adsorp-
tion of LC molecules from binary solutions. The tech-
nique presented along with the simple analysis schemes
can also be employed for other molecular systems with
low vapour pressures, like discotic liquid crystals or
chromophores. Its applicability is also not restricted to
nematogens, but rather relies on the electrical polarisabil-
ity of the mesogen along with the existence of a solvent
with an appropriately high vapour pressure. It also could
be extended toward capillarity-driven filling processes,
i.e. the monitoring of spontaneous imbibition phenom-
ena [12,23,40,41]. From a more general perspective, our
techniques allows one to prepare LC-mesoporous hybrid
materials which could be of particular interest for pho-
tonic [18,42,43] and organic electronic applications [10].

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