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DIBUTYL PHOSPHATE/PROPYLAMINE MIXTURES SHOW SUPRA-MOLECULAR SLOW BUILDING UP UNDER MAGNETIC FIELD

MIKOLAJ POCHYLSKI [a], VINCENZO TURCO LIVERI [b]
AND PIETRO CALANDRA [c] *

ABSTRACT. Liquids with anisotropic local nanostructures which are able to be oriented by a magnetic field can give birefringence. Usually magnetically-induced birefringence is low owing to the low magnetic energy of molecules and to the averaging effect due to thermal agitation. At the same time, the response is usually very fast given the typical timescales of molecular orientational dynamics (nanoseconds). However, we show that the dibutyl phosphate/propylamine liquid mixture is characterized by an extremely slow response (hours) to the magnetic field and by an intense overall effect ($\Delta n/\lambda \approx -0.1 m^{-1}$ at 1 Tesla). This surprising behavior has been interpreted as a manifestation of a novel phenomenon of progressive building up of larger and larger internally ordered hetero-associates driven by the magnetic field and involving strongly interacting amphiphiles.

1. Introduction

Induced birefringence is a very peculiar and useful optical effect which can be tuned by an external magnetic or electric field. The origin of the phenomenon in a liquid system is associated with induced orientation of its molecules. Usually simple molecular liquids respond quickly to external stimuli. For example, the time response is of the order of nanoseconds for Kerr effect in fast optical switching cells (Wilhelm *et al.* 2002). This is due to the rapid molecular orientational dynamics taking place at the same timescales. Despite the fast dynamics in simple liquids, in the case of a magnetic external stimulus the orientational order generated by the magnetic field is usually low at room temperature since the magnetic energy of individual molecule is low compared to the thermal energy. For this reasons fast response and low ordering is usually observed. In order to have a significant birefringence, highly optically anisotropic or highly polarizable (parameter which controls the sensitivity to particular external physical field) particles must be exploited. This demand restricts the range of the useful materials to liquid crystals or liquid dispersion of polar particles. In this ambit we wanted to exploit our experience in surfactant-based complex systems (Calandra *et al.* 2015b) to explore the behavior of liquid mixtures of amphiphiles with acidic and basic characters. Such systems, in fact, are truly complex systems: mixing

two neat liquid amphiphiles the resulting mixture can exhibit a lot of unexpected and intriguing emerging properties: local intermolecular self-assembly (Calandra *et al.* 2010, 2013a), enhanced proton conductivity (Calandra *et al.* 2012), 1D anomalous proton diffusion (Calandra *et al.* 2013b), peculiar solubilizing properties towards inorganic salts (Nicotera *et al.* 2014; Calandra *et al.* 2015a; Nicotera *et al.* 2016), anti-Arrhenian behavior of conductivity (Calandra *et al.* 2015c). This happens thanks to the simultaneous presence of both polar and apolar moieties within the molecular architecture of each of the two constituents which gives nanosegregation and peculiar transport properties.

In this ambit, we have recently shown that one of the most interesting properties possessed by such systems is the significant birefringence arising as a response to an external magnetic field (Pochylski *et al.* 2016). This is of particular interest since magnetic field does not induce chemical decomposition of materials thus allowing the possibility to build tunable optical devices with high performance and long time durability overcoming the necessity of electrodes.

The capability of a system (even if created from mixed molecules of low anisotropy and low polarizability) to significantly respond to a magnetic field can be possessed if not only the individual molecules but also their locally assembled structures present in the liquid are able to respond to a magnetic field by opportune reorientation with the resulting formation of anisotropic oriented molecular assemblies. This requirement can be achieved if the amphiphiles are opportunely chosen: if one amphipile is basic (for example a short alkyl chain alkylamine) and the other is acidic (for example protic alkyl phosphate) then the direct acid-base interaction between the two molecule can give the formation of:

- an adduct bridged by a strong H-bond, which is a strongly directional bond

or even

- an ion pair if the proton is definitely transferred from the acid to the base

In any case, in surfactant-based liquid mixtures the overall acid-base intermolecular interaction is expected to be anisotropic and, consequently also their resulting assemblies. The necessary requirement of anisotropic structure presence is therefore fulfilled by definition if directional bonds are formed between the molecules. In this framework constituted by strongly interacting fluids made by two components, the overall dynamics and structure under magnetic field is therefore complex and unexplored. It is dictated by the delicate equlibrium among a lot of interactions (steric hindrance, polar-polar, polar-apolar and van der Waals, magnetic interactions) and dynamic processes (diffusion, orientational and translational order) taking place in nano-heterogeneous fluid where the local composition and viscosity are not even the bulk ones.

We will show that mixing two specifically-interacting short chain amphiphilic molecules, i.e. dibutyl phosphate and propylamine, which themselves have very low intrinsic anisotropy, we can obtain a system with unusual response to external physical field. Despite the generally fast response and low birefringence expected for molecular liquids, we observed an extremely slow response and an induced birefringence significantly higher than that observed for simple molecular liquids.

2. Theoretical Background

Birefringence in a liquid system occurs as a result of preferential orientation of anisotropic molecules. This orientation may be achieved by application of external fields (electric, magnetic, shear ...) (Levy 2002). In the case of magnetically induced birefringence, orientation of molecules appears because of the interaction between the external magnetic field and the molecular magnetic dipole moment (permanent or induced by the field). Here the torque acts on the molecule attempting to minimize the angle between the direction of the field and that of the dipole moment. For any molecule, the magnetic dipole moment can always be induced by the field itself through the tensor magnetic susceptibility of molecules. This is particularly important for those molecules which do not possess permanent magnetic dipole moment as it is for both DBP and PA.

If the magnetic susceptibility is isotropic, then the direction of the induced dipole coincide with the direction of the field. In this case the angle between the dipole and the field is zero, no torque will be acting on such molecule and no induced orientation will be observed.

Non-zero angles will occur if the susceptibility is anisotropic, i.e. if the value of susceptibility in two perpendicular directions are different. In this case the molecule will be forced to orient its direction of highest magnetic susceptibility along the magnetic field.

In order to generate optical anisotropy of the whole sample by the preferential orientation of its molecules it is also mandatory that molecules are further optically (electrically) anisotropic. Just then the optical properties (refractive index) of the system in the direction parallel to the field will be different from that in the perpendicular direction, which is the definition of the birefringence. The sign of the induced birefringence (negative or positive) depends on the relative orientations of magnetic and electric susceptibility (polarizability) ellipsoids. By convention, if the direction of the highest magnetic polarizability coincides with direction of highest electric polarizability, then the induced birefringence is positive.

Borrowing concepts from ferrofluids physics, we can say that the overall magneto-optical effects arises from at least two main phenomena: 1) orientation of prolate/oblate objects with their shape anisotropy axes parallel to the external magnetic field (Skibin *et al.* 1977; Davies and Llewellyn 1980; Hasmonay *et al.* 1998) and 2) spontaneous or magnetic field induced particle agglomeration in chain-like structures that tend to align according to the external magnetic field direction (Taketomi 1991; Socoliuc 1999; Ivanov and Kantorovich 2004) which can be in principle occur at the same time or even concertedly/synergically.

3. Experimental Part

3.1. Materials. Dibutyl phosphate (DBP, Aldrich >99.5%) and n-propylamine (PA, Aldrich 99%) were used as received. DBP/PA mixtures were prepared by weight and stored in sealed vials. Their composition is expressed as amine molar fraction (X)

3.2. Method. The addition of PA to DBP releases a considerable amount of heat so, given the low boiling point of the amine, opportune precautions must be taken (slow addition, gentle mixing, cooling steps, closed vials). This can be taken as a first clue of the occurrence of the exothermic acid-base reaction between DBP and PA. The mixing resulted in the formation of homogeneous and transparent liquid with increased viscosity. Even if the reaction can be considered complete in a short period (stirring + diffusion), due to the

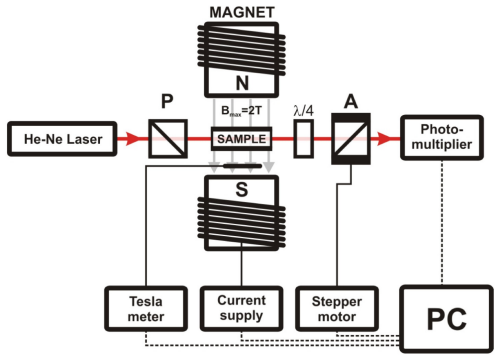

FIGURE 1. Polarimeter for magnetically induced birefringence measurements. P, A and $\pi/4$ stays for Polarizer, Analyser and quarter-waveplate, respectively.

increased viscosity of the mixture, samples were stored in sealed vials and kept overnight prior to the measurements.

Linear birefringence was measured using the laboratory made polarimeter set-up described in details in Koralewski *et al.* (2011a). Briefly, the sample was held in a glass cell between poles of iron-core electromagnet ($B \leq 2T$). The length of the cell was 130 mm. Magnetic field induction was measured by a teslameter place in the middle of the optical path. The magnetic field intensity distribution along the optical path was uniform (within 1.5%) except for the very ends of the poles (5 mm from each side). The light from Zeiss He–Ne laser (λ= 632.8 nm) was used as a probe, passing through a high quality Glan–Thompson polariser (P) whose transmission axis was oriented at 45°C azimuth angle with respect to the electric field direction. After turning the magnetic field on, the sample becomes birefringent. As a result, the linear polarization of incident light beam passing the sample changes into the elliptical one. The quarter-wave plate ($\lambda/4$), whose optical axis is oriented along the azimuth angle of polarizer P, changes polarization from elliptical to linear with simultaneous rotation of the plane of polarization by an angle α. The light is then passed through another linear polarizer, working as analyser (A), and reaches the photomultiplier detector. The angle α is found from the position of analyser for which light intensity is minimum. The instrument allows the precise measurement of the angle of rotation of the light polarization plane, ($\Delta\alpha = \pm 0.001^\circ$) which is proportional to the sample birefringence, Δn:

$$\alpha = \frac{\pi L}{\lambda}\Delta n \tag{1}$$

We found that birefringence signal of the samples studied in this work does not respond immediately when magnetic field is turned on or turned off, but rather a slow and gradual change is observed. For this reason, we followed an experimental protocol, already described in (Pochylski *et al.* 2016), where for each sample the induced birefringence was recorded as a function of time after switching on and switching off the magnetic field of constant induction B=1T.

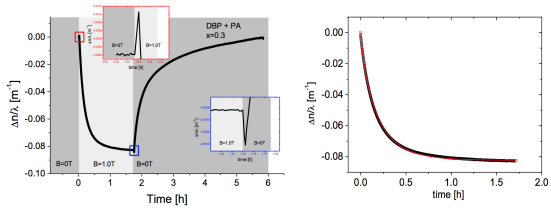

FIGURE 2. (a) time dependences of the induced birefringence recorded for a binary mixture of DBP and PA with X=0.3 for the different intensity of magnetic field applied. Black symbols shows experimental data, red lines are fit with eq.1. (b) Time dependence of the induced birefringence recorded for a binary mixture of DBP and PA with X=0.3 as the magnetic field of induction B=1T was turned on and off again. Right panel shows the fitting with the stretched exponential function (eq.1): black symbols are experimental data and red line is the fitting.

4. Results and Discussion

Figure 1 shows the time evolution of birefringence observed in DBP/PA at amine molar ratio (X) equal to 0.3. The composition of X=0.3 has been chosen as representative of the mixture; however, the study of the effect of composition, certainly deserving further study, will be the subject of a future paper. It can be seen that the system requires some time to reach a constant birefringence value after step change in magnetic field intensity. This is itself striking since response to a magnetic field is typically fast even if the solutions of big molecules like peptides are involved (Kwon *et al.* 2015). Even more interestingly, when the field is switched on and off the system response takes place at different times, and this happens for all the magnetic field values explored. The phenomenon is reversible independently on the history of the sample. In order to quantify these observations we described the time dependence of induced birefringence by a stretched exponential function

$$\Delta n/\lambda(t) = (\Delta n/\lambda)_{max}(1 - e^{-(t/\tau)^{\beta}}) \tag{2}$$

where $(\Delta n/\lambda)_{max}$ is the amplitude (steady-state value) of induced birefringence normalized to wavelength of probing light λ, τ is the characteristic equilibration/relaxation time and β describes stretching of the relaxation time distribution. The choice of this function has been dictated by the observation that a simple exponential function was not adequate to describe the experimental data. On the other hand, the stretched exponential function gave good fitting results (see the red line in the right panel of Figure 1 as compared to the experimental data shown as black points).

From these fittings, the time constant τ, the stretching of the relaxation time distribution $\beta$and the amplitude of induced birefringence normalized to wavelength $(\Delta n/\lambda)_{max}$ can be derived. The values are reported in Table 1 both for switching the magnetic field on and off.

Magnetic birefringence was used before for in situ monitoring of the morphological changes in diamagnetic polymersomes during shape-transformation by dialysis (Rikken *et al.* 2014). This process was also found to proceed over long time.

parameter	Field on	Field off
τ[ks]	0.62	2.21
β	0.84	0.56

TABLE 1. τ and β parameters derived by the fitting by eq. 2 of experimental data when switching the magnetic field on and off.

This behavior of observed birefringence resembles that observed commonly in dispersions of magnetic particles (Socoliuc *et al.* 1999; Ku *et al.* 2008; Gielen *et al.* 2009; Koralewski *et al.* 2011a,b) from which we can borrow the theory. The usual explanation assumes that the system under investigation consists of individual objects (both solid (Wilhelm *et al.* 2002; Ku *et al.* 2008; Koralewski *et al.* 2011a) or soft (Chekanov *et al.* 1985; Levy 2003; Gielen *et al.* 2009; Köber *et al.* 2012; Rikken *et al.* 2014) in the case of ferrofluids but individual molecules, acid-base adducts and ion pairs in our case) dispersed in liquid carrier. In our case, molecules and/or their local assemblies are optically and magnetically anisotropic (anisotropy in optical polarizability and magnetic susceptibility have finite values).

When the system is exposed to external magnetic field the magnetic dipole is induced in these molecular species. Since they are magnetically anisotropic, the dipoles direction does not coincide with the direction of external field. Consequently, the torque on these species is applied (resulting from the interaction between induced magnetic dipole and the external magnetic field) and the assemblies are induced to orient along the magnetic field. Because each of the particles is optically anisotropic, the dispersion as a whole becomes optically anisotropic and so birefringent. This phenomenon can be coupled by an eventual further self-assembly triggered by the magnetic field or by the peculiar orientation that the molecule adopts in presence of magnetic field. The kinetics of this self-assembly can depend on various factors like the local viscosity slowing down the molecular diffusion, the strength of the interactions and the accessibility of the molecular domains involved.

It is to keep in mind the serious differences between currently studied DBP/PA binary mixture and the liquid dispersion for which the model was developed. The model in its simplest form describes the dilute suspension of magnetically interacting molecules in magnetically inert solvent and no inter-particles interactions are included. In our system, however, no solid individual particle exist nor the inert solvent may be indicated. Moreover, because of the high volume fractions of both mixture components (X=0.3) also the assumption of negligible inter-molecular interaction is not fulfilled as separate micellar objects are not expected. Only inter-connected hetero-associated aggregates can be imagined.

Similarly, to the values of relaxation time constants also their distributions depend on whether the magnetic field was turned on or tuned off. After turning the external field on, the orientational process is characterized by narrower distribution (the β value approaches 1) when the magnetic induction increases. On the other hand, return to equilibrium after turning the magnetic field off is characterized by broad distribution.

To comment all the data self-consistently, let's pay deeper attention on Figure 1 and in particular the insets, which expand the regions immediately after the switching on and off of the magnetic field. It can be seen that a fast system reaction is present, after which the

longer-time process takes place. The fast and low-intensity response can be associated with a fast short-range re-orientation of the individual molecules or the acid-base adducts formed by these. The short time is the result of the immediate response expected for simple liquids and, accordingly, the intensity is very weak. This occurs also when the field is switched off after which the individual molecules (or their adducts) immediately return to thermal equilibrium. After the fast molecular re-orientation process, the magnetic birefringence slowly increases resulting from the building up of bigger and bigger structures together with, in principle, their orientation along the magnetic field. Taken into account for the very short timescale in diffusion limited phenomena, the observed timescale must be the consequence of a complex mechanism where both probable and statistically improbable molecular moves are needed at each step for the structure to be built.

The building-up and/or orientation of these structures is pushed by the magnetic field, but their destruction by thermal agitation when the field is switched off turns out to be even less probable as shown by the higher τ value. This can be the consequence of the fact that inter-molecular interactions within the supramolecular aggregate build up by the external magnetic field are quite strong and that exists significant long range correlation between the orientation of all the supramolecular aggregates. These effects are probably assisted by the local viscosity which is particularly high due to the structure.

Of course, deeper investigation are needed. In this ambit, scattering experiments, both X-ray and neutron, have proved to be unique in acquiring detailed structural information in complex systems (Kiselev *et al.* 2013; Lombardo 2014; Kiselev and Lombardo 2017) even in presence of large structures (Lombardo *et al.* 2004) and charged species (Bonaccorsi *et al.* 2009), which sometimes characterize the assemblies of amphiphiles and complex organic molecules. Therefore, scattering experiments and viscosity measurements with magnetic field on and off are planned to shed light on this intriguing phenomenon and to gain more information on the kinetics of the induced formation and destruction of the supramolecular aggregates networks. Despite the theoretical interest, the discovery can be tailored for biological application, where interactions between large molecules/aggregates and bio-structures can give selective cytotoxicity (Bonaccorsi *et al.* 2013a) and bioactivity effects (Bonaccorsi *et al.* 2013b).

5. Conclusions

We showed that distinct birefringence can be generated by a magnetic field in mixtures of dibutyl phosphate/propylamine even if the effect is very small in any of the two neat components. This effect does not come from orientation of individual molecules but, rather, from that of the organized supra-molecular structures enhanced by the action of the external magnetic field and their mutual interactions. Surprisingly, unusually long times (hours) are needed for birefringence to appear and, more surprisingly, even longer time is needed for it to disappear after turning off the field. This proves that structures are very stable since they are hold by stable inter-molecular bonds (mainly H-bonds). At the best of our knowledge, there is no theoretical description of magnetically induced birefringence in self-aggregated inter-penetrable (high concentration) structures, so our findings open new ways for the comprehension of the dynamics in molecular liquids. From a more general prospect, the high sensitivity of the investigated system to the action of a magnetic field suggests to

explore the response of other physico-chemical properties (viscosity, electric conductivity, solubilizing properties towards inorganic salts) suitable for its technological application such as magneto-rheologic actuators, electro-optical devices, novel salt purification methods.

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[a] Adam Mickiewicz University
Faculty of Physics
ul. Umultowska 85, Poznan 62-614, Poland

[b] Università degli Studi di Palermo
Dipartimento STEBICEF
Parco d'Orleans II, Palermo

[c] CNR-ISMN
Consiglio Nazionale delle Ricerche (CNR), Istituto per lo Studio dei Materiali Nanostrutturati (ISMN)
Via Salaria km 29.300, Monterotondo Stazione (RM) - Italy

* To whom correspondence should be addressed | email: pietro.calandra@cnr.it

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