



# Molecular association of small amphiphiles: Origin of ionic liquid properties in dibutyl phosphate/propylamine binary mixtures

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## ABSTRACT

Binary mixtures of liquid surfactants, owing to the amphiphilic nature of the molecules involved, can exhibit nano-segregation and peculiar transport properties. The amphiphilicity, and consequently the resulting self-assembly, can be tuned by changing the length of the alkyl chains and the nature of the polar head group. So, in the present study, the structural and dynamic properties of dibutyl phosphate/propylamine liquid mixtures at various compositions have been investigated by Wide Angle X-ray Scattering (WAXS), FT-IR, rheometry and dielectric spectroscopy in order to study the intermolecular association taking place when alkylphosphates and alkylamines with a small apolar part are mixed together. It was found that a proton transfer from the dibutyl phosphate PO<sub>4</sub>H group to the propylamine NH<sub>2</sub> one takes place, due to the acidic and basic nature of the two molecules involved. This triggers the formation of charged species and an intermolecular association typical of ionic liquid systems and causing an increase in viscosity of two orders of magnitude with respect to the two pure components. Effects due to the different amine isomers have been highlighted since the steric hindrance of the amine alkyl chain can significantly contribute to the molecular slippage thus affecting the overall mixture viscosity. Surprising dielectric properties have also been observed at a specific composition: a strikingly enhanced proton conductivity and a negative value of the dielectric constant in the MHz frequency range, as a result of the local self-assembly and the competition between the mechanism of jump of "free" protons among neighboring polar headgroups and the molecularly-assisted mechanism of charge transport. This work shows new potentialities of such systems as specialized solvent media and proton conducting water-free organic-based liquid systems and, from a more general prospect, the comprehension of the molecular mechanism involved in their transport properties is pivotal for the piloted design of smart materials for specific applications.

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## 1. Introduction

Surfactants are widely used in many fields: detergency, emulsification, lubrication, nanoparticle synthesis and specialized fields of nanotechnology. In the past, a lot of investigations have considered systems where surfactants were dissolved as solute in suitable solvents; however, we have recently set-up an innovative approach involving the use of pure liquid surfactants with appropriately chosen head groups, mixed together with no solvent to form binary mixtures. The absence of any solvent maximizes the surfactant concentration, therefore the merits of the system, deriving from the presence of the two surfactants, are obviously driven to their extreme. With no "solvent" and pushing the choice to surfactants characterized by strongly interacting polar heads, the resulting surfactant-based structures are expected to be

extremely concentrated and somehow percolated/interconnected, leading to the formation of exotic organizations.

The proof for the effectiveness of this strategy is the recent preparation of surfactant-based liquid mixtures with striking properties: enhanced proton conductivity [1,2], anomalous 1D diffusion [3], exotic solubilizing properties towards inorganic salts [4,5,6] anti-Arrhenian behavior of proton conductivity [7]. Even smart materials fully responsive to an external stimulus (magnetic field) have been recently prepared [8].

These features can be tuned by simply changing the concentration ratio of the two surfactants in the mixture, because this allows for a continuous variation of the self-assembled intermolecular local structures and the consequent overall dynamics.

The explanation of these peculiar properties on the molecular basis lies in the uniqueness of the surfactant molecules: the simultaneous presence, within their molecular architecture, of both polar (hydrophilic) and apolar (hydrophobic) moieties. This simple structural

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feature, in fact, triggers the coexistence of interlaced polar and apolar nanodomains hold up by polar-polar, polar-apolar and apolar-apolar interactions (and eventually H-bonds). Consequently, it leads to complex behavior and emerging properties as a result of the delicate equilibrium among all these interactions [9].

Obviously, specific properties can be conferred by the appropriate choice of the mixture components i.e. changing the nature of the hydrophilic head (phosphate, sulfate, carboxylate, hydroxyl, amine) or the hydrophobic tail of the surfactant molecules. The idea inspiring this work comes from the consideration that reducing the apolar parts of the systems would emphasize the properties coming from the polar moieties (self-assembly, conductivity...). Taking into account that alkylphosphates and alkylamines are quite representative classes of acid and basic surfactants, respectively, we have selected a short-chain alkylphosphate (di-butyl phosphate, DBP) and a short alkyl chain alkylamine (propylamine, PA) and studied the structure and dynamics of their mixtures at various amine mole fraction ( $X$ ) by Wide Angle X-ray Scattering (WAXS), FT-IR, rheometry and dielectric spectroscopy. Also, in order to develop an intuition necessary to connect molecular structure with the macroscopic behavior through the molecular association phenomena, we tested the influence of isomeric substitution by studying mixtures of DBP with both  $n$ -propylamine (NPA) and isopropylamine (IPA) isomers.

## 2. Experimental

### 2.1. Materials

Dibutyl phosphate (DBP, Aldrich >99.5%),  $n$ -propylamine (NPA, Aldrich 99%) and isopropylamine (IPA, Aldrich 99%) were used as received. DBP/NPA and DBP/IPA mixtures were prepared by weight and stored in sealed vials. Their composition hereafter is expressed as amine mole fraction ( $X$ ) or, when specifically required,  $n$ -propylamine or isopropylamine molar fraction ( $X_{\text{NPA}}$  or  $X_{\text{IPA}}$ , respectively).

### 2.2. Method

The addition of NPA or IPA 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 NPA or IPA leading to proton transfer from the acid DBP to the basic NPA or IPA. Since the proton transfer is known to be one of the fastest chemical reactions, acid-base reactions are generally diffusion-limited, i.e. their rate is limited by the diffusion of the reacting molecules. So the reaction can be considered complete in a short period (stirring + diffusion). In our case, given the increased viscosity of some mixtures, all samples were stored in sealed vials and kept overnight prior to the measurements. The mixing resulted in the formation of homogeneous and transparent liquid samples of increased viscosity especially in the proximity of  $X = 0.5$ .

FT-IR spectra were acquired at 25 °C with a Spectrum One spectrometer (Perkin Elmer), using a cell equipped with  $\text{CaF}_2$  windows. Each spectrum was the average of eight scans in the 900–4000  $\text{cm}^{-1}$  wavenumber range at a spectral resolution of 0.5  $\text{cm}^{-1}$ . By IR spectroscopy no detectable signal due to water was found in all the studied samples. This assured the absence of residual water.

Wide Angle X-ray Scattering (WAXS) patterns in the scattering vector ( $q$ ) range  $0.00685 < q < 25.6 \text{ nm}^{-1}$  were recorded at beamline BL9 [10] of the synchrotron radiation source DELTA (Dortmund, Germany) using a MAR345 image plate detector. The samples were measured at 25 °C by placing the samples within 0.5 mm diameter and 1/100 mm thickness glass capillaries. The two-dimensional diffraction images were calibrated, integrated and brought to  $q$  scale using the program package Fit2D [11]. All WAXS patterns were carefully corrected for the cell + solvent contributions.

Broadband dielectric measurements were performed using a modular system from Novocontrol Technologies based on an Alpha-A analyzer connected to a ZGS test interface. The liquid samples were placed in invar/sapphire cells which in turn were inserted into a cryostat with a temperature stability of 0.2 K as achieved using a Quatro controller. From the measured complex impedance, both the real and the imaginary part of the complex permittivity ( $\epsilon^*$ ) of the sample were obtained as a function of frequency. From it, the static permittivity ( $\epsilon_R$ ) and direct current (DC) conductivity were extracted from the plateau value of the complex permittivity.

The complex shear modulus was measured using a Modular Compact Rheometer MCR 502 from Anton-Paar. A plate–plate geometry with a disk diameter of 35 mm was used. The distance of the plates was about 0.5 mm, and the strain amplitude was adjusted at each temperature to maintain linearity of response. The shear stress  $\sigma$  was measured as a function of the macroscopic shear rate  $d\gamma/dt$ . These experiments were performed in the shear rate range 0.1–100  $\text{s}^{-1}$ . Zero-shear viscosity was extracted from the low-frequency behavior of the viscosity.

## 3. Results and discussion

### 3.1. FT-IR

The spectra of DBP/NPA and DBP/IPA mixtures at amine molar fraction ( $X$ ) of 0.5 are shown in Fig. 1, where the spectra of pure DBP and NPA or IPA are also reported for comparison. It can be immediately seen that the spectra of the mixtures cannot be rationalized in terms of additive contributions of the components. In particular, it can be noted:

- (i) the disappearance of the characteristic doublet of pure primary amines occurring at 3302 and 3377  $\text{cm}^{-1}$  for NPA and 3283 and 3360  $\text{cm}^{-1}$  for IPA due to symmetric and antisymmetric stretching of  $\text{NH}_2$  group and the appearance of a strong and broad band in the range 2500–3600  $\text{cm}^{-1}$ . This last band is a clear hint of the presence of protonated  $\text{NH}_2$  group and its position and intensity depend on the hydrogen bond distance  $\text{N}-\text{H}^+\cdots\text{Y}^-$  and the nature of the anion  $\text{Y}^-$  of the protonating species (oxygen atoms of the DBP phosphate group, in our case) [12];
- (ii) the disappearance in the 1500–2800  $\text{cm}^{-1}$  spectral region of the three characteristic broad bands of medium intensity occurring at about 1686, 2310 and 2623  $\text{cm}^{-1}$ , observed in the spectrum of pure DBP and due to strongly hydrogen bonded POH group [13–15];
- (iii) the appearance, in DBP/NPA, of new bands occurring at about 2580, 2675 and 2740  $\text{cm}^{-1}$  (2568, 2662 and 2758  $\text{cm}^{-1}$  for IPA), attributable to stretching vibrations due to  $\text{NH}_3^+$  group of protonated primary amines;
- (iv) interestingly, the single absorption at about 1600  $\text{cm}^{-1}$  due to  $\text{NH}_2$  scissoring vibration observed in pure NPA and IPA is replaced by two symmetric and antisymmetric deformation bands occurring at 1543 and 1643  $\text{cm}^{-1}$  in the mixtures, which are considered diagnostic of the  $\text{NH}_3^+$  group [16,17].

For clarity sake, all the band positions are reported in Table 1 together with their attributions.

All these findings suggest a significant proton transfer from the DBP POH group to the NPA or IPA  $\text{NH}_2$  group. This is a robust clue suggesting the formation of a strongly interacting fluid analogous to protic ionic liquids.

Additional hints concerning the interaction between the DBP POH group and the amine  $\text{NH}_2$  one can be achieved by the analysis of the band at 1230  $\text{cm}^{-1}$ . In pure DBP, this band is a combination band ( $\nu$

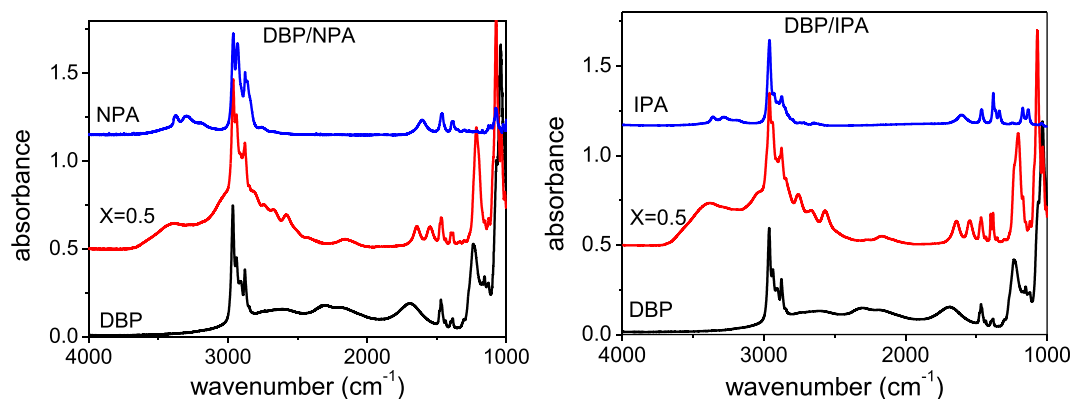


Fig. 1. IR spectra of DBP/NPA (left panel) and DBP/IPA (right panel) mixtures at  $X = 0.5$  and those of the pure components.

(PO) +  $\delta$  (POH)). The band position ( $f_{1230}$ ) for DBP/NPA and DBP/IPA mixtures is reported in Fig. 2.

It can be noted a marked change of the band position above  $X > 0.2$ – $0.3$  and a nearly constant trend above  $X > 0.5$ . This reflects the change from the stretching vibration of the protonated  $\text{PO}_4\text{H}$  group of DBP to the unprotonated one ( $\text{PO}_4^-$ ). Thus, also this observation suggests the occurrence of a proton transfer from DBP POH group to the amine  $\text{NH}_2$  one. In conclusion, our systems can be considered as proper ionic liquids at the DPB-amine equimolar composition ( $X = 0.5$ ) and its solutions in DBP ( $X < 0.5$ ) or propylamine ( $X > 0.5$ ) solvents.

### 3.2. Wide Angle X-ray Scattering

Fig. 3 shows the WAXS patterns of the DBP/NPA (left panel) and DBP/IPA (right panel) mixtures at  $X = 0.5$  chosen as representative as compared to those of the pure components.

It can be noted that both amines show only a broad band which is due to the intermolecular short range distance taking place between first neighboring molecules and due to intermolecular spacing typical of the conventional liquid state [18]: NPA band is centered at  $14.05 \text{ nm}^{-1}$  which corresponds to a distance of  $4.47 \text{ \AA}$ , whereas IPA band is centered at around  $13.55 \text{ nm}^{-1}$  which corresponds to a distance of  $4.64 \text{ \AA}$ . This slight difference is already the first hint of the different structure of the two isomers: isopropylamine has the amino group bound to the secondary carbon of the alkyl chain whereas the *n*-propylamine has its amino group on a primary carbon allowing a more efficient molecular lateral packing thanks to the free linear alkyl

chain. The absence of any defined peak at lower  $q$  values indicates that both NPA and IPA in the pure state do not form associated species.

As for the other pure component (DBP), the broad band occurring in the same  $q$  region is centered at  $14.25 \text{ nm}^{-1}$  corresponding to a distance of  $4.41 \text{ \AA}$ . The slightly lower lateral distance with respect to that in NPA or IPA reveals a slightly more efficient packing probably due to the DBP possibility to establish stronger head-head intermolecular interactions. In addition to this feature, the DBP spectrum is characterized by the presence of another band located at lower  $q$  values and revealing the occurrence of intermolecular association like in *n*-alcohols, [19,20]. The presence of associated molecules causes the arising of a new characteristic repetition distance which may be identified with the longitudinal distance between DBP molecules within the aggregate. In DBP this peak is centered at  $5.46 \text{ nm}^{-1}$  corresponding to a distance of  $11.5 \text{ \AA}$  which is consistent with the fully extended length of the surfactant molecules. Interestingly, X-ray peak below  $10 \text{ nm}^{-1}$ , which is associated to the polar/polar domains typical distance, is usually characteristic of Ionic Liquids [21,22] and can be considered as a signature of mesoscopic order [23]. From this point of view, our systems can be considered structurally analogous to Ionic Liquids and most excitingly characterized by similar peculiar properties and application fields.

In particular, it has been suggested, first by analogy with imidazolium-based ionic liquid [24], and then by alcohols and their mixtures [25] that the low- $q$  contribution in the WAXS spectrum comes from the nanoscale structural heterogeneities in the bulk liquid state caused by the segregation of long enough apolar alkyl chains into domains which are embedded into a three dimensional charged matrix generated by the positively and negatively charged heads [26].

Table 1  
Typical IR band positions in DBP, NPA, IPA and their mixtures.

Pure NPA	Pure IPA	Pure DBP	DBP/NPA ( $X_{\text{NPA}} = 0.5$ )	DBP/IPA ( $X_{\text{IPA}} = 0.5$ )	Assignment
			2400–3600	2400–3600	H-bonded $\text{NH}_3^+$ stretch
3297, 3374	3285, 3358				sy, antisym stretch $\text{NH}_2$
2877, 2931, 2963	2875, 2928, 2960	2878, 2908, 2939, 2965	2879, 2939, 2962	2875, 2937, 2960	C–H stretching
			2582, 2670, 2740	2570, 2663, 2758	$\text{NH}_3^+$ stretching
		1690, 2178, 2297, 2607			POH
			1548, 1642	1549, 1641	$\text{NH}_3^+$ bending
1601	1605				$\text{NH}_2$ bending
1382, 1457	1380, 1463	1386, 1470	1398, 1470	1398, 1466	$\text{CH}_2$ bending
		1236			P=O
			1216	1205	OPO– antisym stretch
		1039	1035, 1073	1030, 1068	P–O–C

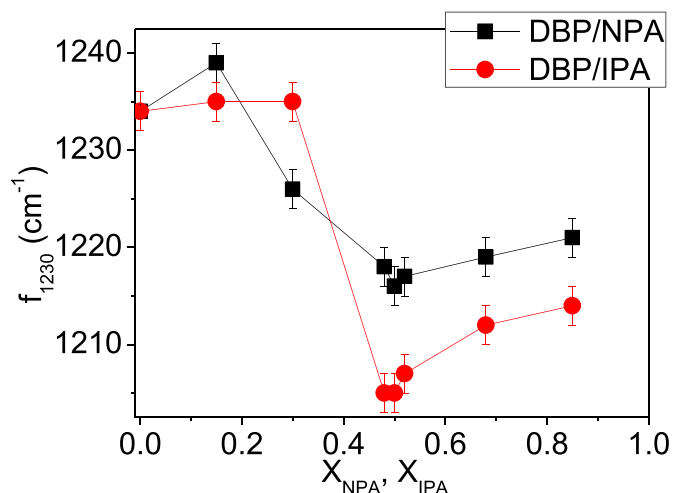


Fig. 2. band position at  $1230\text{ cm}^{-1}$  ( $f_{1230}$ ) for DBP/NPA and DBP/IPA mixtures as a function of amine mole fraction ( $X$ ).

Interestingly, in the mixture the following effects can be observed:

1. the peak at low  $q$  value (hereafter called peak #1) has increased intensity and is located at lower  $q$  values. This is itself a proof for the fact that the mix is more structured than both pure components;
2. the peak at high  $q$  value (hereafter called peak #2) is at slightly higher  $q$  values with respect to both components, indicating a reduction of the intermolecular lateral distance (the effect is more evident for NPA containing mixture, but is still detectable for IPA containing one); this reflects the compaction of the overall system due to an enhancement of intermolecular interactions.

It must be noted that the impact of temperature in such patterns is scarce: for peak #2 the temperature effect is limited and reveals the obvious thermal expansion, whereas for the peak arising from the intermolecular aggregates (peak #1) the temperature effect is almost undetectable, suggesting that such aggregates are made up by strongly interacting associated molecules.

The derived Bragg distances ( $d_1$  and  $d_2$ ), the FWHM and area %, are reported in Fig. 4 as a function of amine mole fraction.

Further comments can be made:

1. the negative deviation of the  $d_2$  values found when DBP is mixed with NPA or IPA indicates the volume contraction caused by stronger intermolecular interactions. Reasonably, a contribution due to the free-volume effect taking place when two differently-sized molecules are mixed, and resulting in a volume shrinkage can also take place, as shown in similar systems [27];

2. the experimental  $d_1$  value in the mixtures suggests that the intermolecular associations are bigger than those of DBP with longer interplanar distance, as a consequence of the mutual DBP/NPA or IPA interactions (steric hindrance, formation of charged species, H-bond formation).

Coherently, the FWHM values decrease in the mix (see Fig. 4 intermediate panel) for the low- $q$  peak due to molecular associations, highlighting the inherent structural ordering.

If the existence of a low- $q$  peak in the WAXS spectrum of neat DBP highlights the occurrence of molecular association triggered by intermolecular H-bond like in  $n$ -alcohols, the marked sharpening of such contribution in the spectra of the mixtures when the composition reaches  $X = 0.5$  value unveils the progressive nanosegregation-induced structural change that we expect as a consequence of the formation of protic ionic liquids. We have seen in FT-IR part, in fact, that the acid-to-base proton transfer triggers the formation of charged species so that a peak that sharp can be rationalized in terms of coexistence of polar/apolar domains typical of ionic liquids [28]. However, due to the liquid nature of the system, rapid molecular and charge association/fission processes take place, so the repetition distance ( $d_1$ ) is to be intended as a time- and space- averaged distance with a characteristic polydispersion. A peak narrowing, therefore, can also indicate a reduction in polydispersion of  $d_1$ . As for the high- $q$  peak (peak #2), the FWHM value is almost constant since this scattering signal is due just to the local molecular packing of the molecules with their first shell.

As regards the area %, which is reported in the bottom panel of Fig. 4, it must be noted that there is not a marked composition effect: the values are almost the same for all mixtures but the peak #1 sudden disappears in the pure amine. This reveals that the structural change can be triggered even by small amount of DBP added to the amine. Similar behavior has been observed by Mariani et al. [29] who, studying transport properties in ionic liquids, detected the possibility of marked and unusual changes in the viscosity when a given solvent (acetonitrile) is added to the ionic liquid ethylammonium nitrate. This was of course a consequence of a local structural change and was reasonably attributed to micelles formation. In our case, the behavior of addition of small amount of PA to DBP (low  $X$  values) or, vice versa, the addition of small amount of DBP to PA (high  $X$  values) do not lead to the same structural effect. The behaviors of our alkylphosphate and propylamine are therefore not symmetrical and this is due to the fact that a structuring effect is present in neat DBP but not in pure propylamines. This is an important clue which will cause, as we will see in the dielectric investigation, the arising of the exotic negative dielectric constant in our PA-rich samples.

It must be noted that a faint bump around  $8\text{ nm}^{-1}$  is present in the samples at  $X = 0.5$ . It is more evident in DBP/IPA mixture but it is present, although at a minor extent, also in DBP/NPA (both at  $X = 0.5$ ). This

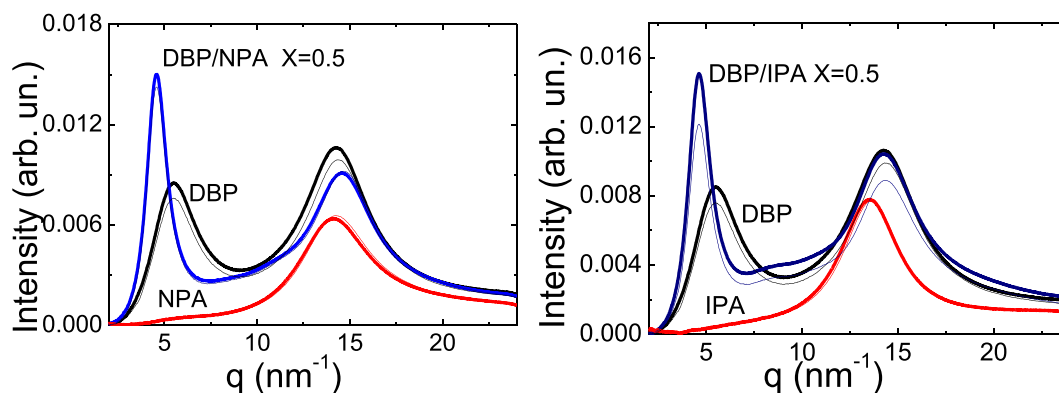
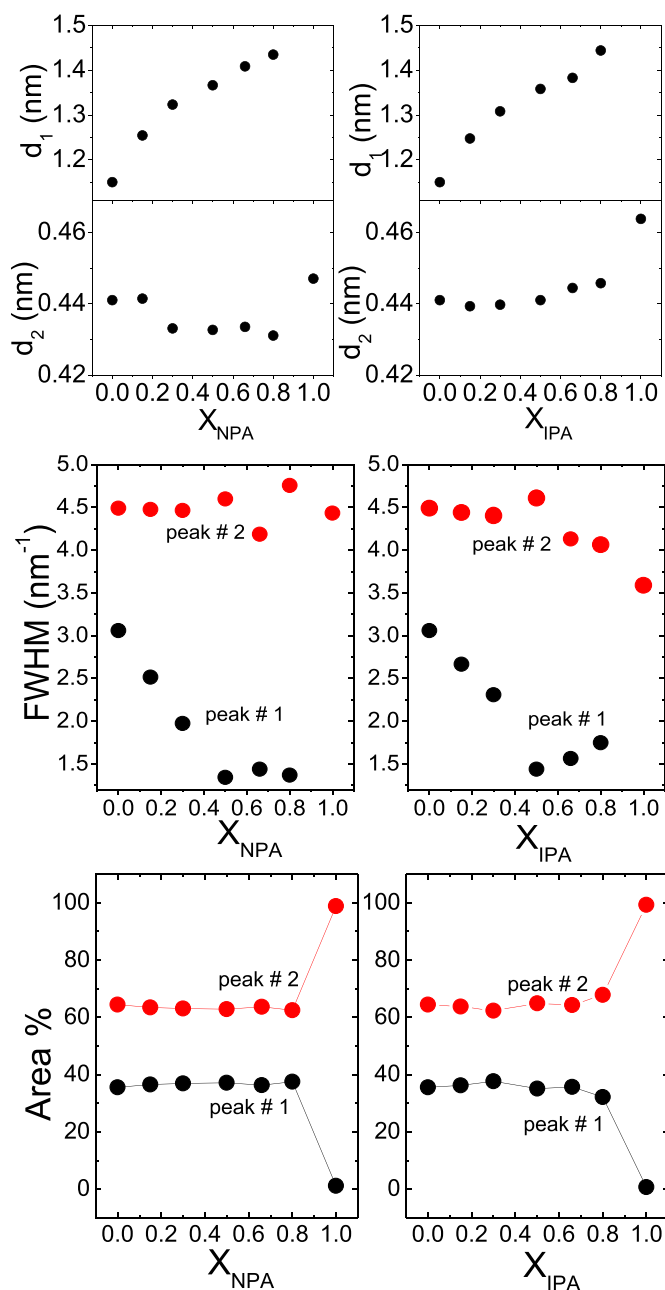


Fig. 3. WAXS spectra of the DBP/NPA (left panel) and DBP/IPA (right panel) mixture at  $X = 0.5$  and of the pure components. Thicker lines refer to samples at  $25\text{ }^\circ\text{C}$  and narrower ones to  $5\text{ }^\circ\text{C}$ .



**Fig. 4.** Bragg distances ( $d_1$  and  $d_2$ , upper panel), Full Width at Half Maximum (FWHM, intermediate panel) and area % of the two peaks of DBP/NPA mixtures (left panels) and DBP/IPA mixtures (right panels). The uncertainty is of the same order of point size.

is usually present in WAXS spectra of ionic liquids and, although several structural features can contribute to this scattering signal, it is generally recognized as coming from charge-charge interactions, i.e. cation-anion characteristic distance repeating in the bulk [30]. This signal is quite weak and the fact that this signal is higher in DBP/IPA mixture than in DBP/NPA reflects the isomeric substitution of the amine. Evidently, the sponge-like structure expected to be made by the charged surfactant headgroups [31] and in which the nanosegregated apolar part are dispersed has a more disordered structure in DBP/NPA mixtures. It can be argued that the linear alkyl chain in NPA will tend, more than in IPA, to arrange in parallel piles; this eventually hinders their accommodation at the ideal curved surface of the sponge-like structure of the charged headgroups. Thus IPA, which has its amino group on a secondary carbon, can better accommodate at such charged surface allowing a better order. This hypothesis is in accordance with the viscosity data

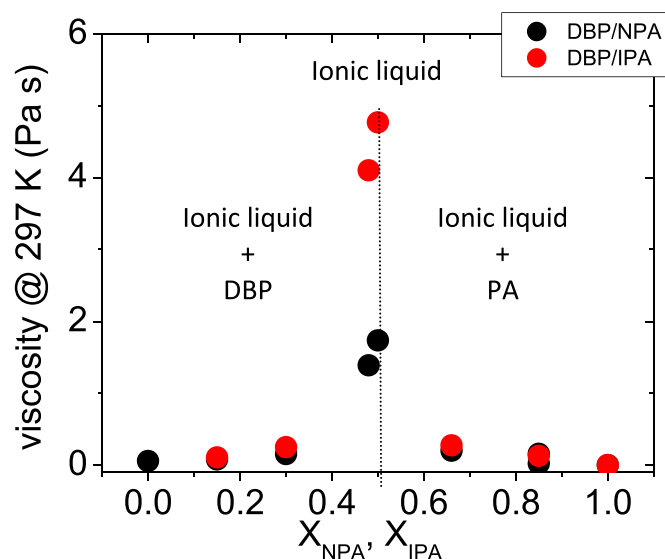
which show a higher viscosity for DBP/IPA mixtures than DBP/NPA ones (see below).

Some other comparisons with literature data are also useful: it must be noted that  $d_2$  values are very similar to the values found for bis(2-ethylhexyl)phosphoric acid (HDEHP)/bis(2-ethylhexyl)amine (BEEA) systems, highlighting the fact that this peak, being due to lateral intermolecular distances, is not influenced by the alkyl part of the molecule and reinforces the hypothesis that the intermolecular association is due to interactions between the polar parts of the molecules. On the other hand,  $d_1$  values are smaller than those found for HDEHP/BEEA systems, due to the fact that this peak probes longitudinal molecular length for which the contribution of the alkyl part has to be taken into account.

However, apart from the specific values which differ due to the fact that DBP is smaller than HDEHP, and NPA and IPA are smaller than BEEA, the three systems behave in the same way, suggesting that the observed behavior can be considered quite universal.

### 3.3. Rheology

The zero-shear viscosity at 25 °C is reported as a function of composition in Fig. 5. It can be seen that when DBP is mixed with NPA or IPA, an increase in viscosity takes place, and the effect is maximum at equimolar phosphate-to-amine ratio. This is clear evidence that intermolecular association takes place and, in accordance with the formation of charged species, they are reasonably due to the coulombic strong interactions. Going deeper into details, the marked viscosity enhancement effect is more evident for the IPA isomer (two orders of magnitude) which itself is less viscous than NPA and has a lower boiling point. This highlights that a significant contribution to the mixture viscosity arises from the more pronounced steric hindrance to molecular slippage due to IPA. It is also interesting to note that the amines are poorly structured (see X-ray data), with low viscosity and actually at room temperature both amines are quite close to their boiling points. Nevertheless, they are able to trigger a marked viscosity increase and this is another signature of the fact that a change in the liquid structure takes place thanks to the acid-base reaction which triggers a proton transfer with ultimate formation of an ionic liquid. The maximum in viscosity takes place therefore at  $X = 0.5$ , i.e. the composition at which the system can be considered as a neat ionic liquid. For all the other compositions, the system is a solution of ionic liquid made by equimolar DBP and PA dissolved in the excess of one or the other solvent (DBP at  $X < 0.5$  and PA at  $X > 0.5$ ). The steep increase in viscosity when approaching the  $X = 0.5$  composition is typical



**Fig. 5.** Viscosity at room temperature for the studied samples.

for ionic liquid solutions in cosolvents as already observed by Seddon et al. [32].

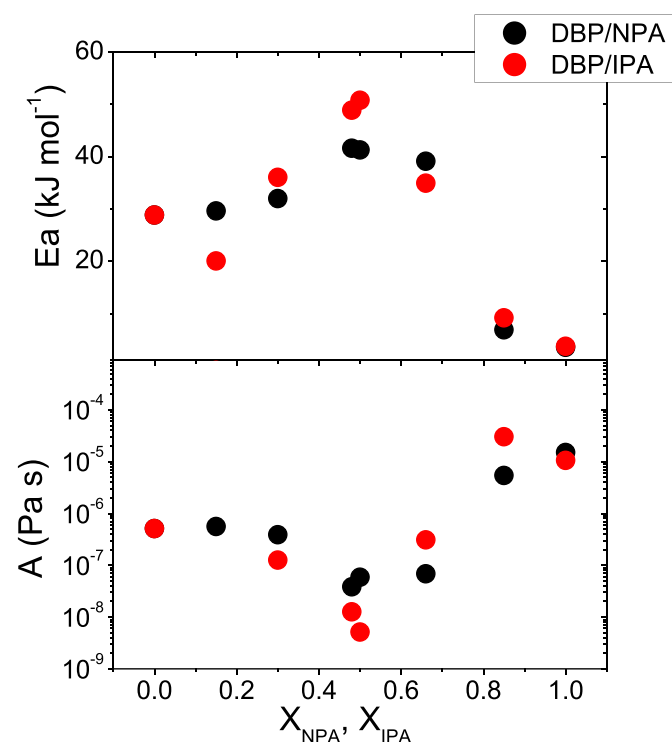
Measurements carried out on each sample at four different temperatures (10, 15, 20, 25 °C) allowed to perform an Arrhenius analysis of the viscosity to estimate its apparent (room temperature) activation energy ( $E_a$ ) and preexponential factor as a function of composition by fitting the data with the well-known Arrhenius equation

$$\text{viscosity} = A \cdot e^{E_a/RT}$$

Given the narrow temperature range Arrhenius analysis is good enough and this is confirmed by the linear trend of the data in the Arrhenius plot of log viscosity vs.  $1/T$  (data not shown). The derived values are reported in Fig. 6.

The activation energy shows a maximum at  $X = 0.5$  in accordance with the dynamics slowing down due to the enhancement of suprastructure formation. It can be noted, indeed, that at this composition the overall coulombic interactions are maximized and therefore a higher energy needs to be overcome for momentum transport to occur. Similar conclusions can be drawn by the specular behavior of the pre-exponential factor. Moreover, especially around  $X = 0.5$ , both  $E_a$  and pre-exponential factor ( $A$ ) values reflect the different steric hindrance offered by the two amine isomers against molecular flow.

It must be pointed out that usually ionic liquids are prepared by a complex synthetic route, basically in two steps, involving the formation of the desired cation and the anion exchange [33]. The easiness of our preparation and the low-cost of the chemicals involved are of added value so we believe to have introduced a new, simple and cheap strategy to prepare ionic liquids deserving to be tailored for up-to-date applications.



**Fig. 6.** Activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) for viscosity in DBP/NPA (black points) and DBP/IPA (red points) mixtures at different  $X$  values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3.4. Dielectric data

The static permittivity, ( $\epsilon_s$ ), and the DC conductivity ( $\sigma_{DC}$ ) at room temperature are reported for every composition in the left panels of Fig. 7. The static permittivity measured for the pure amines is in agreement with literature data [34].

Considering the direct current conductivity data (top left panel of Fig. 7), it must be noted that there is a slight local minimum at  $X = 0.5$  which corresponds to the maximum of the shear viscosity (see Fig. 5 for comparison). Interestingly there is a maximum in  $\sigma_{DC}$  at  $X = 0.85$ , where the viscosity is markedly lower. It is worth to note that small addition of DBP to amine leads to a noticeable increase in the static conductivity.

If we look at the different effect of the amine added to DBP, it must be noted that the conductivity of the mixture with isopropyl amine remains generally lower than the conductivity of the mixture with *n*-propylamine. Correspondingly, the viscosity of the DBP/IPA mixtures is higher than the viscosity of the DBP/NPA mixtures.

It is interesting to note that this behavior is similar to that obtained for HDEHP/BEEA systems [1] and that both in DBP/NPA and DBP/IPA samples the conductivity values are generally slightly higher than those of HDEHP/BEEA systems reasonably due to the higher polar domains volume fraction.

However, since the DC conductivity in the mixtures is generally increased as well as the viscosity, a competition between the molecularly-assisted mechanism of proton transport based on the migration of entire charged molecules and the mechanism of jump of “free” protons among neighboring polar headgroups should be envisaged.

As to the static permittivity of the mixtures, which is shown in the bottom-left panel of Fig. 7, it turns out to be generally about twice that of the pure components, indicating enhanced orientational polarization of the mixtures as a consequence of the ionic liquid formation. Probably the two molecules are associated by parallel alignment of their dipole so that the total dipole in the adduct is enhanced. Further contributions giving such effect may arise from the formation of ion pairs which themselves have high dipole moments. Probably the same kind of nano aggregate characterizes all the mixtures, since the value of the static permittivity does not change dramatically among the mixtures as a function of composition. The increase of the dielectric constant is consistent with the formation of dipolar species ( $\text{DBP}^-/\text{PA}^+$ ) through the acid/base exchange process. So, at the composition where DBP and amine (NPA or IPA) are equimolar, the formation of highly reticulated (percolated) networks whose building blocks are the dipolar species ( $\text{DBP}^-/\text{PA}^+$ ) rather than self-interacting species (DBP-DBP and PA-PA) is more plausible. This would slow down the overall dynamics more and more when the composition of  $X = 0.5$  is approached.

It must be noted a surprising behavior for the samples at  $X = 0.85$  which is shown in the right panel of Fig. 7 reporting the real part of the permittivity ( $\epsilon'$ ) as a function of frequency: for such samples the dielectric constant is strongly dependent on frequencies reaching even negative values. This is a typical behavior when free charges are confined in domains embedded in an insulating matrix, for which a resonance plasma frequency takes place at certain frequencies.

In our samples, at  $X = 0.85$  the amine is in excess, so  $\text{DBP}^-/\text{PA}^+$  ionic liquid with relatively free-to-move protons can be considered as dispersed in the excess of the insulating solvent. This does not happen in the specular side of the DBP-rich compositions, since DBP is not as insulating as PA and is associated. This behavior has already been found for phosphoric acid doped poly(benzimidazole) where the doping of the insulating polymer with phosphoric acid triggers the formation of regions with free protons in certain domains [35], a situation which is conceptually similar to ours. This behavior is the consequence that our systems can be considered at  $X = 0.5$  as ionic liquids and at  $X \neq 0.5$  as an ionic liquid solution into an excess of one or the other solvent (DBP in the case of  $X < 0.5$  and PA for  $X > 0.5$ ). Therefore, the overall

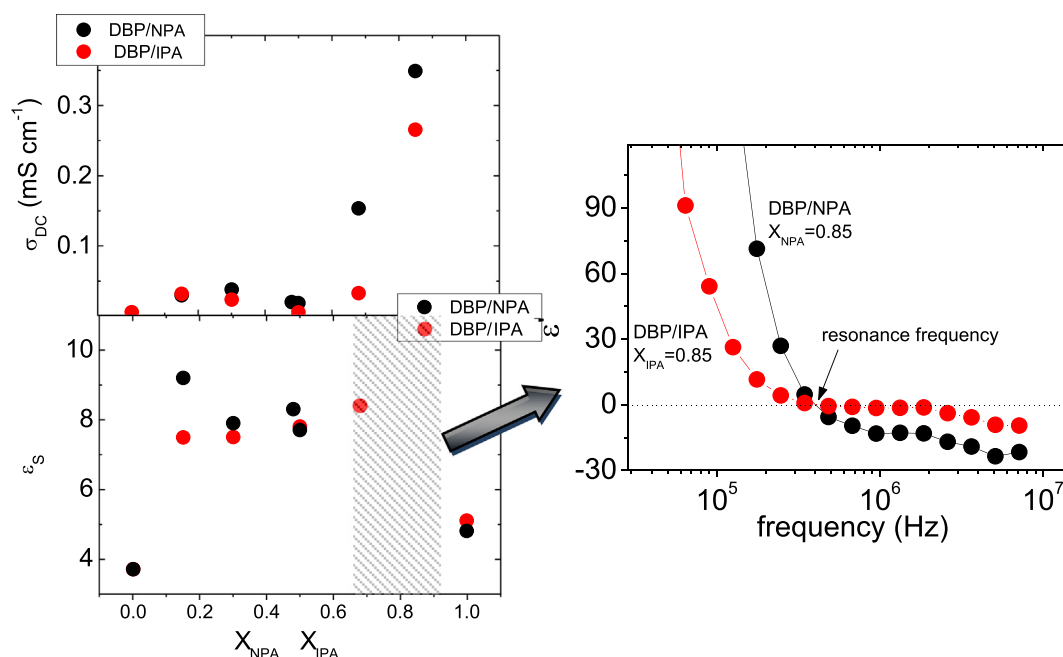


Fig. 7. Concentration dependencies of DC conductivity ( $\sigma_{DC}$ , upper panel) and static permittivity ( $\epsilon_s$ , intermediate panel) at room temperature. The right panel shows the dielectric constant spectrum of the samples at  $X = 0.85$  as a function of frequency.

structure/property is the delicate equilibrium between the intermolecular association due to the H-bond (especially in DBP-rich compositions) and electrostatic ones of the charged molecules (deprotonated DBP and protonated propylamines). This is the reason why the negative dielectric constant is exhibited only in the PA-rich part of the composition range thanks to the fact that PA is more insulating and less structured than DBP. Indeed, as it can be noted from Fig. 7 right panel, at frequencies lower than  $3 \times 10^5$  Hz, the steep rise of dielectric constant is indicative of interfacial polarization, due to the interface between the conductive domains formed by  $\text{DBP}^-/\text{PA}^+$  ionic liquids and the surrounding insulating matrix made by the excess of amine. This effect increases with temperature due to the higher polarization resulting from the higher mobility of charges at higher temperatures. Parallel to this, the dielectric constant “resonance” spectrum appears around the MHz regime, exhibiting a positive to negative transition when the temperature is increased due to the progressive further contribution of sluggish protons to the resonance. Consistently to what shown above, the effect in DBP/NPA is higher than that in DBP/IPA due to the more pronounced structuring effect of NPA with respect to IPA. Systems characterized by a negative dielectric constant could find very interesting applications as metamaterials for optical and microwave applications and in the field of high temperature superconductors [36–38].

It is worth noting that the strategies for preparing negative constant materials are usually based on rather complicated procedures [39,40] so that the systems we propose, being based on the simple mixture of two liquid surfactants, seems to open a new, simpler and cheaper method exploiting the natural intermolecular self-assembly to prepare negative dielectric constant materials, which is worth to tailor. Of course this interesting feature requires a dedicated investigation which is in progress and which will be the topic of a forthcoming paper.

#### 4. Conclusions

The self-assembly in binary mixtures of liquid surfactants can be tuned by changing the length of the alkyl chains and the nature of the polar head group. Shortening the surfactant alkyl tails should enhance the resulting self-assembly triggered by the acid-to-base proton transfer between the surfactant polar parts with ultimate formation of an ionic

liquid-like fluid. We have studied the molecular association taking place when di-butyl phosphate (DBP) is mixed with *n*-propylamine (NPA) or isopropylamine (IPA). As ascertained by IR spectra, this molecular association is driven, in both cases, by proton transfer from DBP to propylamine with the formation of protic ionic liquids. From the structural point of view, as shown by WAXS, a marked nanosegregation of the apolar molecular moieties has been observed in the mixture, with the maximum effect at the amine molar ratio ( $X$ ) of 0.5. Surprisingly, changing NPA with IPA causes no striking effect on the structure but exerts a big effect on the viscosity: even though IPA is less viscous than NPA, the viscosity of the DBP/IPA mixture can be even twice than that of the DBP/NPA due to the larger steric hindrance offered by IPA to molecular slippage. The comparison with other alkylphosphate/alkylamine systems [1,7] has confirmed that the volume fraction of the polar part in these systems contributes to the charge transport, so a conductivity further increased with respect to similar systems can be reached by reducing the size of the apolar moieties i.e. using amphiphiles with small sized apolar part. Interestingly, a negative dielectric constant is shown at a composition  $X = 0.85$  as a consequence of the resonance of relatively free-to-move protons moving within the H-bonded networks dispersed in the excess of insulating amine. From a more general prospect, although it is known [21] that the structure formed by the ionic-liquids are non-birefringent, we have shown [8] that for some compositions the birefringence may be easily induced by an external magnetic field, so our strategy to mix two surfactants allows producing ionic-liquid-like structure which can be further externally altered or shaped. For this reason, this strategy may also allow to finely tune the properties of the fluid increasing the range of possible applications of ionic liquid-like fluids. We believe to have introduced a new strategy to prepare ionic liquids easily and from low-cost materials: this deserves to be tailored for up-to-date applications. In particular, the occurrence of systems characterized by a negative dielectric constant at low frequencies could find very interesting applications as metamaterials for optical and microwave applications and in the field of high temperature superconductors [36–38].

#### Conflicts of interest

There are no conflicts of interest to declare.

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