



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 PO₄H group to the propylamine NH₂ 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_{NPA} or X_{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 CaF₂ windows. Each spectrum was the average of eight scans in the 900–4000 cm⁻¹ wavenumber range at a spectral resolution of 0.5 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 (ϵ^*) of the sample were obtained as a function of frequency. From it, the static permittivity (ϵ_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 σ 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 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 cm⁻¹ for NPA and 3283 and 3360 cm⁻¹ for IPA due to symmetric and antisymmetric stretching of NH₂ group and the appearance of a strong and broad band in the range 2500–3600 cm⁻¹. This last band is a clear hint of the presence of protonated NH₂ 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 Y^- of the protonating species (oxygen atoms of the DBP phosphate group, in our case) [12];
- (ii) the disappearance in the 1500–2800 cm⁻¹ spectral region of the three characteristic broad bands of medium intensity occurring at about 1686, 2310 and 2623 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 cm⁻¹ (2568, 2662 and 2758 cm⁻¹ for IPA), attributable to stretching vibrations due to NH₃⁺ group of protonated primary amines;
- (iv) interestingly, the single absorption at about 1600 cm⁻¹ due to NH₂ scissoring vibration observed in pure NPA and IPA is replaced by two symmetric and antisymmetric deformation bands occurring at 1543 and 1643 cm⁻¹ in the mixtures, which are considered diagnostic of the NH₃⁺ 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 NH₂ 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 NH₂ one can be achieved by the analysis of the band at 1230 cm⁻¹. In pure DBP, this band is a combination band (ν

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