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SHORT COMMUNICATION

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Ionene–surfactant complexes: temperature and humidity sensitive materials

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Abstract Solid stoichiometric complexes of [3,12]-ionene and dodecyl sulfate form upon reaction of the bromide of the ionene and the silver salt of dodecyl sulfate in methanol. IR, DSC, and TG investigations indicated that the solid complexes are stable between 30 and 120 °C. TG and DSC also showed that the complexes easily take up water at ambient conditions. These samples are optically isotropic. When exposed to an increased humidity they exhibit optical anisotropy, i.e., birefringence, which is caused by the formation of a hexagonal mesogenic phase. Mesogenicity is necessarily accompanied by a further uptake of water (4–5 H_2O molecules per ionic unit), which is dependent on the relative humidity. The phase behavior as a function of temperature and controlled relative humidity was studied using birefringence measurements and polarizing microscopy.

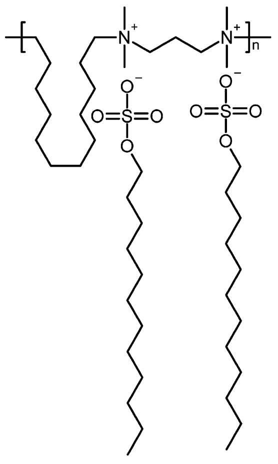
Keywords Humidity · Lyotropy · Mesogenic phases · Phase transition · Polyelectrolyte–surfactant complex

Introduction

Stoichiometric polyelectrolyte–surfactant complexes represent a type of comb-shaped or hairy polymer, in which ionic surfactants constitute electrostatically bound "side chains" attached to every polyelectrolyte chain unit. These complexes are water-insoluble and in the solid state they are reported to assemble spontaneously into mesogenic structures [1, 2, 3]. A variety of mesogenic structures was determined [4, 5], and transitions between them were induced by varying the length of the surfactant chains [6]. In poly(α-L-glutamic) acid complexed by long chain amines thermotropic transitions were also observed [7].

The polyelectrolyte–surfactant complexes are most often prepared by mixing aqueous solutions of surfactant and polyelectrolyte. Complexes obtained by this method inevitably contain adherent low molecular weight salt and have to be purified by re-precipitation. We recently suggested the use of hydroxides of quaternary ammonium salts and polyelectrolyte acids to avoid salt formation [8]. In contrast to previous reports, films of our dry samples exhibited optical isotropy. Upon exposure to ambient humidity, however, the samples became anisotropic.

In this paper we report on ionene–alkyl sulfate complexes (Scheme 1), which turned out to be sensitive to both temperature and humidity, with respect to their optical properties (isotropic–anisotropic phase transition) constituting a new type of stimuli responsive polymers, i.e., smart materials [9, 10]. We chose the ionenes as polyelectrolyte component because their relevant properties can be adjusted by varying the length of the alkyl chains between the quaternized ammonium moieties. We aimed to find a complex exhibiting the isotropic–anisotropic transition at a temperature that was easy to handle. We have investigated the solid stoichiometric complexes by IR-spectroscopy,



structure of 3,12-ionene DS complexes

Scheme 1

differential scanning calorimetry (DSC), thermal gravimetry (TG), polarized optical microscopy, and birefringence measurements under controlled relative humidity.

Experimental

Apparatus

The detection of optical isotropy or anisotropy (phase transition) makes use of the fact that optically anisotropic phases are capable of converting linearly polarized light into circularly polarized light. Therefore, when the sample displays an anisotropic phase, the light of a He-Ne-laser can pass through a thermostatted sample placed between perpendicularly crossed filters for linearly polarized light (Fig. 1). The transmitted light is recorded by the detector as photodiode voltage. Controlled relative humidity was achieved by placing an appropriate aqueous salt solution in the vicinity of the sample in the sealed cell. This assured contact through the gas phase between the sample film and the salt solution. Constant relative humidity at 25 °C was provided by aqueous NaCl solutions with concentrations according to the desired water activity: e.g., for 91.4% relative humidity the salt solution was 2.5 mol kg^{-1} NaCl [11], (100% corresponds to pure water, i.e., $a = 1.0$).

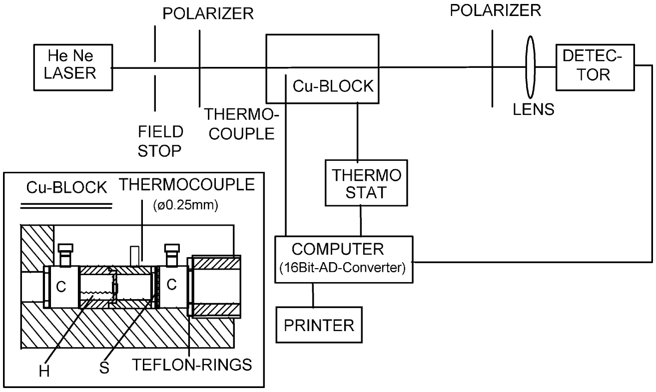


Fig. 1 Schematic representation of the apparatus for the determination of phase transition temperatures. *S* sample, *C* cuvettes filled with water, *H* salt solution for controlled humidity of the gas phase, which is in contact with the sample film *S*

Thermogravimetric analyses were performed using a Netzsch TG/DTA STA 409 instrument, which is capable of controlling the evaporating material via mass spectrometry. Differential scanning calorimetry (DSC) curves were taken on a Setaram DSC 121 instrument. For attenuated total reflection (ATR), an IR-spectra Thermo-Nicolet AVATR instrument, fitted with a model 360 FT-IR detector, was available. Textures of mesogenic samples were obtained via polarized microscopy using a Jenapol polarizing microscope. NMR spectra were taken on Bruker models Drx-500 and Ac-200, respectively.

Preparation of inonenes

The preparation followed published procedures [12, 13] with the exception that for [3,22]-ionene the docosane dicarboxylic acid was prepared and purified as described by Ashikaga et al.[14]. We determined molecular masses for [3,12]-ionene of about 2090 g mol^{-1} and for [3,22]-ionene of about 8370 g mol^{-1}, by light scattering experiments in methanol.

^{1}H-NMR of [3,12]-ionene bromide (δ/ppm at 200 MHz in CD_3OD): 1.42–1.49 (m, 16 H, ($\gamma,\delta,\varepsilon,\zeta$)-$CH_2$), 1.89 (m, 4 H, β-CH_2-dodecano-), 2.43 (m, 2 H, β-CH_2-propano-), 3.29 (s, 12 H, $(CH_3)_2N^+$), 3.66 (s, 8H, α-CH_2); (δ/ppm at 500 MHz in DMSO): 1.27 (br, 16 H, ($\gamma,\delta,\varepsilon,\zeta$)-$CH_2$), 1.68 (br, 4H, β-CH_2 dodecano-), 2.20 (br, 4 H, β-CH_2-propano-), 3.10 (br, 12 H, $(CH_3)_2N^+$), 3.32 (br, α-CH_2 and H_2O).

Preparation of the ionene–dodecyl sulfate complex

$$\mathrm{SDS} + \mathrm{AgNO_3} \xrightarrow{\text{water}} \mathrm{AgDS}\downarrow + \mathrm{NaNO_3}$$

$$\mathrm{n\,AgDS} + [3,\ 12]\text{–ionene bromide} \xrightarrow{\text{methanol}}$$
$$[3,\ 12]\text{–ionene} - \text{DS complex} + \mathrm{n\,AgBr}\downarrow$$

Silver dodecyl sulfate (AgDS) precipitated from an aqueous solution of sodium dodecyl sulfate (SDS, Merck, 0.9 mol L^{-1}) and silver nitrate (Merck, 5.6 mol L^{-1}) at room temperature. AgDS was recrystallized several times from water (< 50 °C) until all the sodium salt was removed. [3,12]-Ionene bromide (0.9645 g in 50 mL dried methanol) was added drop-wise to AgDS (50 mmol L^{-1}) dissolved in 50 mL dried methanol (precipitation–titration). The addition of ionene bromide was stopped, when the voltage of the electrochemical cell $<\mathrm{Ag}|\mathrm{Ag}^+$, DS^-, ionene, AgBr(s), methanol $||$ $\mathrm{HNO_3}$ (30 mmol L^{-1}), H_2O $||$ K^+, Br^- (1 mol L^{-1}), H_2O, $\mathrm{AgBr(s)}|\mathrm{Ag}>$ had passed its steepest slope as a function of added ionene bromide solution. Silver bromide precipitated and was easily filtered off from the solution. After slow evaporation of the solvent, the salt-free complexes formed opaque films on a quartz plate placed at the bottom of the reaction beaker. Finally the films were dried in a desiccator over phosphorous pentoxide for two days at normal pressure and for another three days in vacuo.

The swelling of ionene–DS complexes due to uptake of water from the gas phase as a function of controlled relative humidity was investigated as follows: a film of the complex was cast from methanol on the inner wall of an open polyethylene screw cap bottle and dried over phosphorous pentoxide until constancy of weight. A high complex concentration in methanol assured a high viscosity of the solution so that the film at the wall remained stable during the drying process. Then the bottle with the dry film was weighed, placed in a desiccator at 23 °C together with a cup of aqueous NaCl at the desired water activity for 24 h, and weighed again. The bottle was tightly capped while weighing it in order to rule out uptake or loss of moisture from ambient air.

Results

To prepare water and salt-free complexes according to reference [8], ionene hydroxide as a necessary component would be unstable at room temperature. Therefore stoichiometric complexes of [3,22]- and [3,12]-ionene and dodecyl sulfate (DS) were prepared via the reaction of the bromide of the ionene and the silver salt of dodecyl sulfate in methanol under precipitation of the silver halide. Films produced from [3,22]-ionene turned out to be cloudy and to form undulated surfaces. These complexes were not investigated further. Films produced from [3,12]-ionene complexed with DS, however, were clear, transparent, and optically isotropic and flat; i.e., they showed the desired properties.

The IR spectrum before and after heating the [3,12]-ionene–DS complex to 200 °C was almost constant (Fig. 2). This shows that the functional groups of [3,12]-ionene–DS complexes did not change during heating, i.e., the complex is stable under these conditions. The spectra also reveal that the complexes contain some water (peak at 3200 cm^{-1}), which the sample must have taken up after exposure to air for taking the spectrum.

The DSC curve for a sample equilibrated at 92.2% relative humidity (Fig. 3, curve for $a(H_2O) = 0.922$) exhibits an absorption peak at about 100 °C, which is very weak. Its enthalpy is only 2.661 J g^{-1}. This peak is assigned to the evaporation of weakly adsorbed water. On further inspection of the figure we note that the temperature of the maximum of the absorption peak increases with decreasing water content of the sample (see Fig. 3, curve for $a(H_2O) = 0.881$, enthalpy = 2.919 J g^{-1}). This indicates slightly different lyotropic structures of the various samples (see below). However, no caloric effect was found accompanying the transition isotropic–anisotropic between 45–55 °C described later.

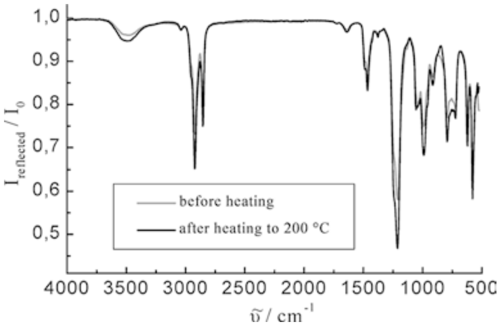


Fig. 2 ATR-IR spectra of [3,12]-ionene stoichometrically complexed with dodecyl sulfate

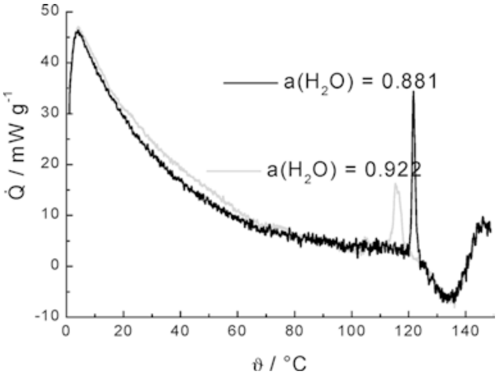


Fig. 3 DSC-curve of [3,12]-ionene stoichometrically complexed with dodecyl sulfate for two samples equlilibrated at constant relative humidities: 88.1% and 92.2%; heating rate 1 K/min

The assignment of the absorption peak to the loss of water is supported by a thermogravimetric analysis (TG). In the TG diagram (Fig. 4) of the sample from Fig. 2 a fragment peak at m = 18 is found at about 100 °C in the mass spectrum of the evaporating material, clearly indicating water as the fragment. The according weight loss of the ionene–DS complex is about 3.78%. From this value we calculate that every ion pair unit of the complex adsorbs at least 0.9 water molecules, when the complex is in equilibrium with ambient air. The samples are optically isotropic when prepared at ambient conditions, so the [3,12]-ionene–DS complex is stable below 120 °C, but it can easily absorb water in air.

From the birefringence measurements at constant temperature (Fig. 5; performed using the apparatus sketched in Fig. 1) we learn that the ionene–DS complexes can absorb more water when they are exposed to increased relative humidity. While the optical properties do not change at relative humidities up to 89.4%, at 91.4% the film changes from optically isotropic to optically anisotropic. We will show below that a mesogenic phase is thereby formed. Note that quite a

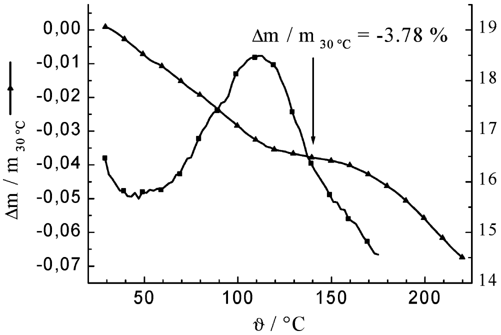


Fig. 4 Thermogravimetric analysis of [3,12]-ionene stoichometrically complexed with dodecyl sulfate illustrating the loss of water

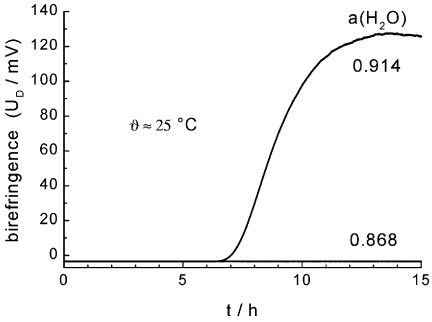


Fig. 5 Birefingence measured as detector voltage U_D in the apparatus sketched in Fig. 1 at 25 °C as a function of time at two activities $a(H_2O)$ of water in aqueous NaCl corresponding to 91.4% and 86.8% relative humidity

long period is needed for equilibration. From Fig. 6 it follows that the take-up of water depends linearly on the fraction of water in the gas phase.

For a sample at 91.4% relative humidity, Fig. 7a depicts changes from the anisotropic to the isotropic phase and vice versa upon periodically sweeping the temperature (5 K h^{-1}) from 30 to 55 °C, i.e., across the transition point (using the apparatus sketched in Fig. 1). Taking the onset of the anisotropy-signal at decreasing θ as the transition temperature, Fig. 7b reveals a transition isotropic–anisotropic (or isotropic–mesogenic) around 47 °C upon cooling the sample and anisotropic–isotropic around 51 °C upon heating the sample (under constant relative humidity), i.e., a hysteresis of ca. 4 °C is found for the transition in the heating and cooling cycles. The material proved stable for the 7 cycles displayed. However, a drift of transition temperatures by 2–3 °C is noted within 70 h (Fig. 7c).

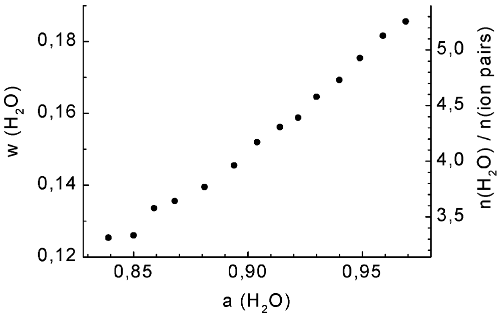


Fig. 6 Swelling mass (fraction w of water) of [3,12]-ionene-DS complexes and number of water molecules per ion pair unit ($n(H_2O)$) as a function of the relative humidity ($a(H_2O)$) applied to the dry sample at room temperature

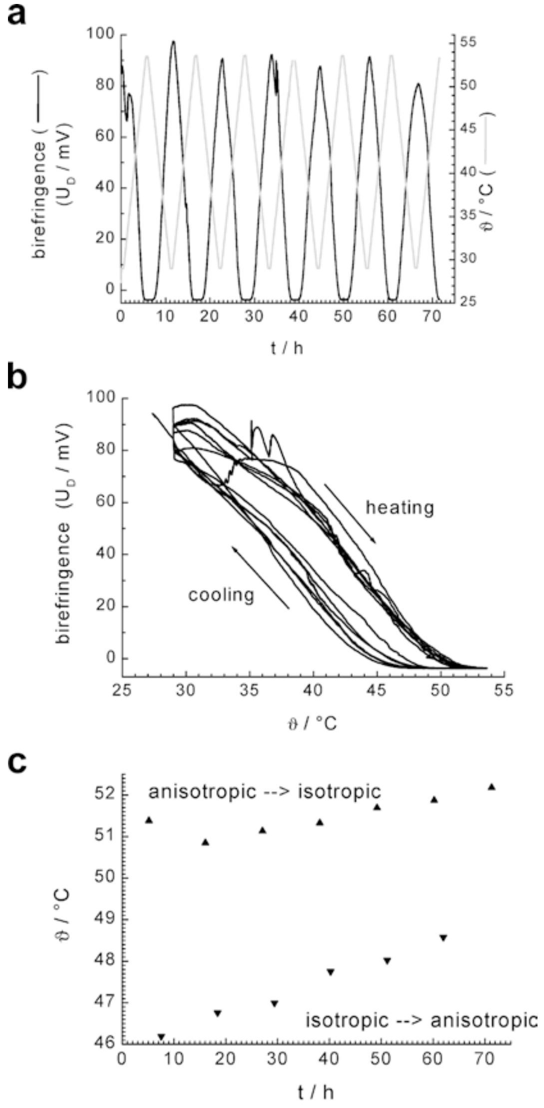


Fig. 7 **a** Birefringence at varying temperature ϑ (5 K h^{-1}) as a function of time measured as detector voltage U_D with the apparatus sketched in Scheme 1. **b** Birefringence as a function of temperature at 91.4% relative humidity for the seven cycles anisotropic–isotropic–anisotropic shown in **a**. **c** Drift of transition temperatures within 70 h

When the relative humidity is raised from 91.4 to 93.0%, the transition temperature increases to ca. 83 °C upon heating and to 68 °C upon subsequent cooling. During the next cycles both transition temperatures dropped. Upon further periodical heating and cooling the sample became liquid and eventually the anisotropy vanished completely.

Figure 8 shows the texture of the mesogenic phase of the stoichiometric complex after cooling from the isotropic phase as it appears on the polarizing microscope. The texture indicates a hexagonal mesogenic structure.

Discussion

Phase transitions in lyotropic liquid crystals of water swollen solid polyelectrolyte–surfactant complexes

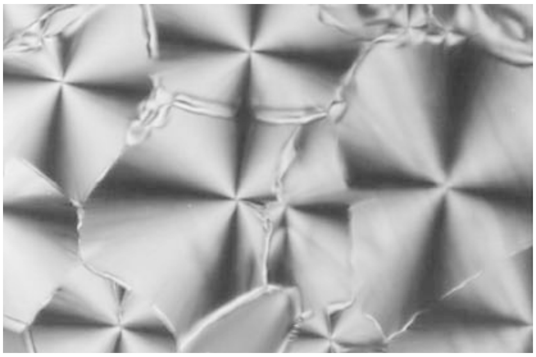


Fig. 8 Texture of the mesogenic phase in [3,12]-ionene-DS complexes obtained from a polarizing microscope

triggered solely by a temperature change are rarely described. In our case, the transition is observed since the use of ionene as a backbone allows balancing electrostatic forces and hydrophobic effects (governing the lyotropic properties), without the addition of inorganic salt, by varying the number of CH_2-groups between the cationic sites. As a consequence, no binding strength of ion pairs has to be sacrificed to allow a phase transition at suitable temperatures.

The apparent discrepancy between the stability of the complex from [3,12]-ionene and DS against temperature at ambient humidity (Fig. 2) and the instability upon periodically heating the hydrated sample to >80 °C has to be rationalized. A likely cause is the instability of DS in the presence of water at high temperature, which leads to hydrolysis yielding dodecyl alcohol and sulfuric acid. Initially, small amounts of dodecyl alcohol may stabilize the anisotropic phase. Further progress of hydrolysis increases the lack of DS resulting in a complete breakdown of the structure of the complex and melting. Formation of dodecyl alcohol was proved by ^{1}H-NMR. Future efforts, therefore, will be directed to the use of more thermally stable anionic surfactants. The exothermic peak at 135 °C in Fig. 3 indicates another chemical process in the system.

The phase transition hexagonal–isotropic observed here can be induced in a thermotropic way (Fig. 7) or in a lyotropic way (Fig. 5), if we accept the take-up of water through the gas phase as a lyotropic process. Obviously, between 4 and 5 molecules of water per ionic unit are necessary for the transition to take place. Only sufficiently hydrated ionic units are flexible enough to allow the molecular motions accompanying the transition.

The hysteresis of transition temperatures observed in heating and cooling cycles (Fig. 7) indicates either a hindered transition or a transition of second order. When the long equilibration time revealed by Fig. 5 is considered, the former explanation is more likely.

Conclusions

The stoichiometric complex of ionene and anionic surfactant investigated here can display lyotropic and thermotropic phase transitions from the hexagonal to the optically isotropic phase. It is, thus, sensitive to both humidity and temperature. Prior to practical application (e.g., as a humidity sensor) the chemical stability of the material, as well as the equilibration times, have to be improved.

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