Monolayer and Bilayer Stability of Ammonium Amphiphiles Carrying an Azobenzene Unit – Effects of Substituents at the Azobenzene Unit

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Novel double-chained ammonium amphiphiles carrying one azobenzene moiety (I) have been synthesized. The bilayer-stabilizing effect of different azobenzenes (ABs) has been investigated by measuring the "gel-to-liquid crystalline" phase transition temperatures of the formed bilayers in water using differential scanning calorimetry. It is found that the stabilizing effect of the azobenzenes strongly depends on the substituents at the aromatic ring. The stabilizing effect increases in the sequence $F < H < NO_2 < CN < OCH_3 < N=N-Ph$, which cannot be correlated with the electron-withdrawing or -donating properties of the substituents. It is concluded that dipole-dipole interactions between the ABs are of minor

importance for the overall stabilization of the bilayer. Instead, other factors determine the strength of the van der Waals interactions between the ABs. In the bilayers the ABs form H-aggregates as is observed by the blue shift of the UV absorption maximum. This blue shift is not affected by the "gel-to-liquid crystalline" phase transition. Bilayers of I-N=N-Ph do not exchange monomers with vesicles of di-dodecyldimethylammonium bromide, whereas all other investigated bilayers do. Compound I-N=N-Ph forms monolayers at the water-air interface, which are much more stable than the monolayers of the other investigated compounds.

Introduction

In recent years much attention has been payed to the development of new organic materials containing azobenzene (AB) units. Being a potential mesogenic unit, the incorporation of AB moieties can induce the formation of thermotropic liquid crystalline phases in both monomeric and polymeric compounds. Another attractive property of ABs is their photoinduced *trans-cis* isomerization^[1-4] so that the physical properties of AB-containing materials can be simply altered by irradiation with UV light.

Kunitake et al.^[5-12] incorporated ABs into the hydrophobic tails of single-chained ammonium amphiphiles. Some of these compounds form bilayer membranes whose permeability can be altered by isomerizing the AB units. The stacking of the ABs in the bilayer results in a shift of the π - π * absorption maximum. This shift is a direct measure for the degree of molecular order in the bilayer.

Substituents at the azobenzene units are important in determining the AB's dipole moment and therefore its selforganizing properties^[13,14]. In this contribution we report the synthesis of a series of novel double-chained ammonium surfactants carrying different ABs at the terminus of one of the hydrophobic chains. The effect of different substituents at the AB moiety on the aggregation behaviour of these compounds in water and at the water-air interface was studied.

The aggregate morphology was investigated by means of optical and electron microscopy. The aggregate stability was judged by differential scanning calorimetry experiments and monomer exchange experiments. The stability of monolayers at the water-air interface was studied by using a Langmuir trough.

Results and Discussion

A series of novel compounds I have been synthesized. The molecular structures are given in Scheme 1. The purity of the compounds was checked by thin-layer chromatography, elemental analyses and 200 MHz ¹H NMR. Of the compounds I, only I-N=N-Ph exhibits an enantiotropic liquid crystalline phase, which is probably smectic A as was determined by polarization microscopy. Upon cooling from the isotropic phase, the liquid crystalline phase appears first as bâtonettes that develop into a fan-shaped focal-conic texture typical of a smectic A phase. Compound I-N=N-Ph also has a considerably higher isotropisation temperature than any of the other compounds I (see Table 1). This shows that this double azobenzene AB-N=N-Ph has stronger mesogenic properties than the other investigated ABs. This is probably due to stronger interactions between these more extended aromatic units.

Lyotropic Properties

The Krafft temperatures of the compounds I are given in Table 1 and lie all above room temperature (The Krafft point is the temperature at which the hydrated crystals are transformed into bilayer structures^[15]). Compounds I–H and I–N=N–Ph have the highest Krafft temperatures (80 and 65 °C). This means that these compounds fit very well

Scheme 1. Molecular structure of compounds I



Table 1. Melting points (T_m) , Krafft temperatures (T_{Krafft}) and phase-transition temperatures (T_c) for compounds I; also the UV absorption maxima of the vesicles in water (λ_{ves}) and the monomers in ethanol (λ_{EtOH}) are given

Compound	$T_{\rm m}$ [°C]	TKrafft [°C]	<i>T</i> _c [°C]	λ_{EtOH} [nm]	$\lambda_{ves} [nm]$
I–H	132	80	24; 28	346	324
I –F	105	29	19	347	326
I–CN	151	52	39	363	334
I-NO ₂	119	48	27	375	341
I-OCH3	135	50	42	357	338
IN=NPh	151-S ^[a] -182	65	_[b]	381	368

^[a] An enantiotropic smeetic liquid crystalline phase is observed. ^[b] Not observed under the employed experimental conditions.

in a crystal lattice and therefore have a poor tendency to get hydrated and to form bilayer structures. The compounds I-CN, $I-NO_2$ and $I-OCH_3$ have Krafft temperatures around 50 °C indicating that hydration of the molecules in the crystal to give bilayer structures occurs more easily. Compound I-F has the lowest Krafft point. Probably, the unfavourable miscibility between fluorocarbon and hydrocarbon segments destabilizes the molecular packing in the crystal lattice.

The double-chained compounds I all form bilayer vesicles upon sonication in water as was observed by electron microscopy (see Figure 1). Giant vesicles, which can be observed by light microscopy, are also formed by allowing the crystalline materials to hydrate above their Krafft temperatures following the procedure described by Menger et al.^[16]. The stability of the vesicle dispersions at room temperature varies from a few hours for I–H to months for I–N=N–Ph and I–F. Although the vesicles are not thermodynamically stable at room temperature, crystallization is kinetically inhibited at room temperature.

The absorption maxima of monomers in ethanol and of vesicles in water at 20 °C are given in Table 1. For the vesicle dispersions, a blue shift of the absorption maximum is observed (see Figure 2) which is attributed to the formation of H-aggregates of the AB units. Previous studies revealed that the ABs from opposite leaflets of the bilayer are inter-digitated^[17]. This interdigitation of mesogenic units is very often observed in thermotropic LC phases^[18,19].

All the investigated bilayer vesicles, except those of I-N=N-Ph, show a "gel-to-liquid crystalline" phase transition (T_c) by DSC. The DSC thermograms are given in Figure 3. The phase transition temperatures as observed upon heating are also given in Table 1. Scan rates of 10°C/min were used for the DSC experiment. Using lower scan

Figure 1. Electron micrograph of vesicles of I-CN, prepared by sonication and stained with uranyl acetate



Figure 2. UV absorption spectra of I-CN as vesicles in water (-) and as monomers in ethanol (...)



rates did not affect the observed phase transition temperatures much. Upon cooling the phase transitions are usually observed at lower temperatures. Under the applied experimental conditions no phase transitions were observed for I-H and I-F upon cooling. The vesicles of I-H exhibit two phase transitions at 24 and 28 °C upon heating. The phase transition temperatures of didodecyldimethylammonium bromide $(C_{12}C_{12}N^+Br^-)$ and dioctadecyldimethylamonium bromide (C18C18N+Br-) bilayers are found at $17 \,^{\circ}C^{[20]}$ and at $45 \,^{\circ}C^{[21]}$, respectively. These compounds are structurally related to the compounds I but lack the azobenzene unit. When the T_c 's of vesicles of compounds I are compared with those of C₁₂C₁₂N⁺ vesicles, it is seen that the introduction of the AB-F moiety ($T_c = 19$ °C) hardly affects the phase transition temperature. All the other ABs cause an increase in T_c with respect to that of $C_{12}C_{12}N^+$. Vesicles of I–OCH₃ ($T_c = 42 \,^{\circ}$ C) have a T_c almost as high as that of $C_{18}C_{18}N^+$ bilayers. This shows that very subtle structural changes in the compounds I cause changes in $T_{\rm c}$ which can only be realized in the dialkyldimethylammonium bromide bilayers by drastic elongation of the alkyl chains.

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Figure 3. DSC thermograms of 1 wt-% vesicle dispersions of compounds I; the solid traces are the heating curves, the deshed traces are the cooling curves; only the regions are displayed where the phase transition peaks are observed



The T_c thus increases in the series $I-F < I-H < I-NO_2 < I-CN < I-OCH_3$. The nature of the terminal group is important in determining the dipole moment of the AB and therefore its self-organizing properties. Because the alkoxy spacer at the 4-position is an electron-donating group, electron-withdrawing substituents at the 4'-position give rise to ABs with high overall dipole moments. For side-chain liquid-crystalline polymers it has been found that apolar substituents on the mesogen tend to induce nematic phases. Polar electron-withdrawing (CN or NO₂) substituents induce the formation of more ordered smectic phases^[13,14]. This has been ascribed to the tendency of mesogens with large dipole moments to assume an antiparallel, interdigitated arrangement.

The observed trend does however not fit with the picture of bilayer stabilization by increased dipole-dipole interactions between the ABs. Also parameters like the polarizability of the ABs and the precise packing mode probably contribute to the stabilization through van der Waals interactions. The various interactions between aromatic units have also been termed π - π stacking interactions. Bilayers of I-F have the lowest $T_{\rm c}$. Possibly, the mesomeric electrondonating property of the F substituent results in reduced dipolar interactions between the AB-Fs. Alternatively, the unfavourable miscibility between fluorocarbon and hydrocarbon segments might destabilize the bilayer. Bilayers of $I-OCH_3$ have a T_c which is relatively high although the methoxy substituent is also an electron-donating substituent. This shows that specific AB-AB interactions, which are not necessarily dependant on the dipole moment of the AB, stabilize lyotropic lamellar mesophases.

Because the blue shift in the absorption spectrum due to the formation of H-aggregates is very sensitive to the AB-AB distance, it was expected that the phase transition would influence this spectral shift. Interestingly, the extent of the blue shift of the UV absorption maxima is not altered by the phase transition. This was tested by measuring the UV absorption spectra of 0.2 mM vesicle dispersions in a 1cm cuvette at different temperatures. This means that although the molecules have increased mobility, the average stacking distance between the ABs remains the same above the phase transition temperature. Sharpening of the NMR signals, however, confirms an increased molecular mobility above the phase transition temperature (data not shown).

When lower concentrations of AB-vesicles are used (0.07 mM), the blue shift disappears at higher temperatures. This is attributed to a dissolution of the bilayers into monomers as a result of the increasing critical bilayer concentration. Ishikawa et al.^[22], who investigated single-chained amphiphiles of the type headgroup-space-AB-tail, observed a decrease in blue shift at increasing temperatures that was attributed to the bilayer phase transition.

The compounds I-H, I-CN, I-F and I-OCH₃ undergo facile trans-cis isomerization in the bilayer state upon irradiation with UV light of 366 nm as could be monitored with UV spectroscopy. The fact that these bilayers are in their gel phase at room temperature does not seem to hamper the isomerization. The thermal isomerization from the cis to the trans form is very slow at room temperature. For $I-NO_2$ and I-N=N-Ph no *cis* isomer is detected upon irradiation at this wavelength. This means that either the cis isomer is not formed or that it isomerizes back to the trans isomer very rapidly. Figure 4 shows the effect of trans-cis isomerization on the "gel-to-liquid crystalline" phase transition of vesicles from I-H. For bilayers in the trans state two phase transitions are observed at 24 and 28 °C. After isomerization the high-temperature transition is lost. This shows that the isomerization affects the bilayer's physical state.

Figure 4. DSC thermograms of a 1 wt-% vesicle dispersion of I-H before (lower trace) and after irradiation (upper trace) with UV light of 366 nm



Monomer Exchange Experiments

When vesicles of I-H, $I-NO_2$, I-CN, $I-OCH_3$ or I-F are mixed with an equimolar amount of vesicles of didodecyldimethylammonium bromide ($C_{12}C_{12}N^+Br^-$), the blue shifted absorbance maximum immediately returns to its monomer value. This is due to the formation of mixed bilayers in which the ABs lose their stacking interaction. This

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process is too fast to be followed with our experimental setup. Previous studies in our group have shown that this mixing occurs by a monomer transfer mechanism^[23]. When vesicles of I-N=N-Ph are mixed with a large excess of vesicles of didodecyldimethylammonium bromide, no spectral changes are observed in the UV absorption maximum at all and a phase-separated state is maintained. Therefore it is concluded that any form of monomer exchange is absent. The penetration of the I-N=N-Ph bilayers by didodecyldimethylammonium bromide monomers is probably hampered by the strong AB-AB interactions in these bilayers. On the other hand, the monomer concentration of I-N=N-Ph must be very low so that the I-N=N-Phmonomers do not escape from their bilayers to migrate towards the didodecyldimethylammonium bromide bilayers.

It can thus be concluded that I-N=N-Ph must have a much lower critical bilayer concentration than any of the other compounds I. When the hydrophobicities of I-N=N-Ph and I-H are calculated using Rekker's hydrophobic fragmental constant^[24], both compounds have approximately the same hydrophobicity. The low critical bilayer concentration of I-N=N-Ph as compared to that of I-H can thus not be caused by the hydrophobic effect. Probably, the larger aromatic system results in stronger AB-AB stacking interactions resulting in a lower critical bilayer concentration.

Monolayer Stability

The monolayer-forming properties of compounds I have also been investigated in order to obtain information about the monolayer-stabilizing effects of the different ABs. The π -A isotherms of the compounds I-H, I-CN and I-N=N-Ph are given in Figure 5. The isotherms of I-Fand I-NO₂ (not shown) are similar to those of I-H and I-CN, respectively. In all the isotherms, an initial rise of the surface pressure is observed around an area of 200 $Å^2/$ molecule. At this molecular area the molecules start to interact. This area corresponds to a situation in which the molecules have their AB-carrying tail flat at the water surface. This orientation would be favoured by a positive interaction between the AB and the water surface. This has also been found before by Heeseman^[25,26]. Upon further compression the surface pressure rises until a plateau value is reached at 33 mN/m. At this pressure the interaction between the AB and the water subphase is broken and the AB-carrying tails are lifted from the surface. The transition to the plateau is sharp for I-CN, I-NO₂ and I-OCH₃ and smooth for I-H and I-F. This is ascribed to a better interaction with the subphase caused by the more polar substituents. This could result in a greater ordering of the molecules in the monolayer of the former three compounds resulting in a more cooperative (sharp) phase transition. Subsequently, the molecules can be compressed until the chains are in a close packed arrangement at about 40 $A^2/$ molecule. Further compression would cause the surface pressure to rise, but the monolayers collapse almost immediately after this point has been reached. Monolayers of $C_{18}C_{18}N^+$ do not collapse below a pressure of 40 mN/m^[27]. Obviously the close-packed arrangement of the molecules I in the monolayer is not a very stable one. Probably the packing mode of the hydrocarbon tails and of the ABs do not match well leading to a destabilization of the monolayer.





The monolayer of I-N=N-Ph shows a quite different π -A isotherm. The plateau value is reached at lower surface pressure. This means that either the interaction of this AB with the subphase is weaker or that the configuration in which the AB-tail is perpendicular to the surface is more favourable than for I-H, I-CN and I-NO₂. Before the plateau is reached an overshoot is observed in the isotherm. This means that the relaxation time of the molecules is slow compared to the rate at which the pressure is exerted on them. Usually, these overshoots decrease when lower compression rates are observed. When the close-packed arrangement is reached at 40 Å²/molecule the surface pressure rises and upon further compression no macroscopic collapse is observed until a surface pressure of 60 mN/m. Upon expansion the isotherm is largely reversible but the overshoot is missing. Upon recompression the initial isotherm is recovered. At 25 mN/m the compressed monolayer is fairly stable in time.

It is obvious that the larger aromatic unit of I-N=N-Ph results in a stabilization of the monolayer, probably due to enhanced AB-AB interactions between these mesogenic units. These interactions are also held responsible for the bilayer-stabilizing effect and good mesogenic properties of this azobenzene unit.

Conclusions

A series of novel double-chained ammonium amphiphiles have been synthesized, which carry an azobenzene unit at the terminus of one of the chains. The effect of different substituents at the AB unit on the aggregate stability has been investigated.

The double-chained amphiphiles I form bilayer vesicles in water and monolayers at the water-air interface. The ABs exert a stabilizing effect on the bilayer due to specific AB-AB interactions. The bilayer "gel-to-liquid crystalline" phase transition temperature increases in the sequence I-F $< I-H < I-NO_2 < I-CN < I-OCH_3 < I-N=N-Ph.$ The strength of the AB-AB interaction does not correlate with the AB dipole moment but depends strongly on the extension of the aromatic system. Possibly, the different substituents contribute to the AB-AB interactions through van der Waals interactions rather than through electrostatic interactions between the permanent dipoles of the AB's. The bilayer vesicles of I-N=N-Ph do not exchange monomers with bilayer vesicles of didodecyldimethylammonium bromide, whereas all the other compounds I give a very rapid monomer exchange. This is caused by extra stabilization of the bilayer by this extended AB system.

All the compounds I, except for I-N=N-Ph, give monolayers at the water-air interface which collapse at surface pressures around 33 mN/m. Only I-N=N-Ph gives more stable monolayers due to stronger AB-AB interactions.

Experimental Section

Syntheses: 4-Hydroxyazobenzene (HO-AB), 4'-fluoro-4hydroxyazobenzene (HO-AB-F), 4'-cyano-4-hydroxyazobenzene (HO-AB-CN), 4-hydroxy-4'-nitroazobenzene (HO-AB-NO₂) and 4-hydroxy-4'-methoxyazobenzene (HO-AB-OCH₃) were prepared by reaction of the diazonium salts of aniline, 4-fluoroaniline, 4-nitroaniline, 4-aminobenzonitrile and 4-methoxyaniline with phenol^[28]. - Benzeneazobenzeneazophenol (HO-AB-N=N-Ph) was prepared by reaction of the diazonium salt of 4-phenylazoaniline with phenol. This compound was purified by column chromatography on silica gel using MeOH/CH₂Cl₂ (5:100; v/v) as eluent.

1-AB-12-bromododecane: A mixture of 25 mmol of the appropriate hydroxyazobenzene and 50 mmol of 1,12-dibromododecane and 50 mmol of K₂CO₃ in 50 ml of 2-butanone was refluxed for 16 h. The salt was removed by filtration and the filtrate was concentrated by evaporation of the solvent. The product was purified by column chromatography on silica gel using petroleum ether (b.p. 40-60 °C)/CH₂Cl₂ (1:1; v/v) as eluent (yield 60%). - ¹H NMR $(CDCl_3, TMS): \delta = 1.40 \text{ (m, } 16\text{ H, } [CH_2]_8), 1.80 \text{ (m, } 4\text{ H, }$ BrCH₂CH₂, AB-OCH₂CH₂), 3.40 (t, 2H, BrCH₂), 4.00 (t, 2H, AB-OCH₂), 7.00-8.40 (m, 8H, AB-H); in case of AB-OCH₃: $\delta = 3.78$ (s, 3 H, AB-OCH₃).

N-(12-AB-dodecyl)-N,N-dimethyl-N-dodecylammonium Bromide (I): A solution of 0.8 mmol of the 1-AB-12-bromododecane and a fourfold excess of N-dodecyl-N,N-dimethylamine in 2-butanone was refluxed for 16 h. The mixture was allowed to cool and the solvent was removed under vacuum. The residue was dissolved in a small amount of dichloromethane and precipitated by addition of diethyl ether. The precipitate was collected and recrystallized from acetone (yield 60%). Melting points are given in Table 1. -¹H NMR (CDCl₃, TMS): $\delta = 0.90$ (t, 3H, CH₃), 1.40 (m, 34H, [CH₂]₈, [CH₂]₉), 1.80 (m, 6H, NCH₂CH₂, AB-OCH₂CH₂), 3.40 [s, 6H, CH₂N(CH₃)₂], 3.50 [m, 4H, CH₂N(CH₃)₂], 4.00 (t, 2H, AB-OCH₂), 7.00-8.40 (m, 8H, AB-H); in case of I-OCH₃: $\delta = 3.78$ (s, 3H, AB-OCH₃).

I-H: C₃₈H₆₄BrN₃O · 0.3 H₂O (664.24): calcd. C 68.71, H 9.80, N 6.33; found C 68.70, H 9.77, N 6.20.

I-F: C₃₈H₆₃BrFN₃O (676.82): calcd. C 67.43, H 9.38, N 6.21; found C 67.67, H 9.51, N 5.92.

I-CN: C₃₉H₆₃BrN₄O · 1.2 H₂O (705.46): calcd. C 66.39, H 9.34, N 7.94; found C 66.34, H 9.16, N 7.88.

 $I-NO_2$: $C_{38}H_{63}BrN_4O_3 + 4.4 H_2O$ (775.90): calcd. C 58.82, H 9.22, N 7.22; found C 58.83, H 9.07, N 6.96.

1-OCH₃: C₃₉H₆₆BrN₃O₂ · 0.2 H₂O (692.46): calcd. C 67.64, H 9.67, N 6.07; found C 67.54, H 9.74, N 5.98.

I-N=N-Ph: C₄₄H₆₈BrN₅O (762.94): calcd. C 69.26, H 8.98, N 9.18; found C 71.77, H 9.31, N 9.02.

Methods: Vesicles were prepared by sonication of the solid compounds in ultrapure water until clear solutions were obtained using a Vibracell sonifier from Sonics and Materials Inc. Giant unilamellar vesicles were prepared by allowing 0.1-0.2 mg of crystals of the compounds to hydrate for several minutes in 200 µl of water at 70-80 °C. – The Krafft temperature was determined by heating an aqueous dispersion of the crystalline material. The temperature at which the formation of bilayer structures was observed by light microscopy was taken as the Krafft point. -- The sample solutions for the Differential Scanning Calorimetry (DSC) measurements (Perkin-Elmer DSC 7) consisted of a 1% (w/w) vesicle dispersion in water prepared by sonication. Scanning rates of 10°C/min were used. Monomer transfer experiments were performed by mixing sonicated vesicle dispersions of the AB compounds I (0.05 mm) with vesicle dispersions of didodecyldimethylammonium bromide in thermostatted cuvettes at 23 °C. The rate of the monomer transfer was monitored by the spectral changes as a function of time. -The monolayer experiments were performed using a Lauda FW2 trough filled with ultrapure water. The monolayers were spread from chloroform solutions (ca. 1 mg/ml) using a Hamilton syringe. After spreading, the monolayer was allowed to equilibrate for 5 min. A compression rate of 1000 cm²/h was used.

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