Intermolecular Electron Transfer in Low-Molecular-Weight Polyaniline Models Associating on Protonation by Amphiphilic Acid in Organic Solvent

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ABSTRACT: Protonation of *N*-(4-aminophenyl)-*N*-{4-[(4-aminophenyl)imino]-2,5-cyclohexadien-1-yliden}-1,4-benzediamine and *N*-[4-(dimethylamino)phenyl]-*N*-(4-{[4-(dimethylamino)phenyl]imino}-2,5-cyclohexadien-1-ylidene)amine as trianiline models of polyaniline emeraldine base (PANI-EB) with dodecylbenzenesulfonic acid (DBSAH), a typical organo-soluble acidic dopant, in chloroform and 1-methyl-2-pyrrolidinone solutions, and also interaction of the resulting products with distearyldimethylammonium chloride (DDAC) as a potential dedoping agent were studied at ambient temperature by UV−vis and ESR spectroscopic methods. It has been shown that protonation is followed by intermolecular proton−electron transfer and results in the formation of monoradical cations apparently paired with the counterions which tend to associate even in rather dilute chloroform solutions and form aggregates characterized by intermolecular electron interchange. These aggregates, however, dissociate on adding an excess of the protonating agent, revealing an ESR signal line with resolved hyperfine structure which corresponds to a monoradical with unpaired electron interacting with two N nuclei. The proposed reaction mechanism probably can be applied to doping higher oligoanilines and PANI-EB. It is also shown that the protonated trimer complexes can be deprotonated ("dedoped") in chloroform solution on adding DDAC. This is in contrast to PANI-EB doped with DBSAH, which could not be deprotonated with cationic amphiphiles.

Introduction

The development of either new conducting polymers or the improvement of known systems such as polyaniline (PANI) is essential to tailor the materials or devices with desired shape, electric, and mechanical properties as well as to understand their structure and conductivity mechanism. Considerable progress has been made in the studies of PANI doping and dedoping regularities.[1−8] Oligomeric PANI analogues have also been synthesized and studied as models.[9−12] In particular, it was shown that phenyl-capped octaaniline could serve as a sufficient PANI model in terms of its spectral characteristics and conductivity.[13] Moreover, low-molecular-weight analogues may be used for designing environmently sensitive composites in particular able to change reversibly their characteristics, e.g., effective conductivity.

This paper presents the results of a study on protonation of the trianiline models of PANI with dodecylbenzenesulfonic acid (DBSAH), a typical amphiphilic acidic dopant in nonpolar and polar aprotic organic solvents, and also interaction of the resulting products with distearyldimethylammonium chloride (DDAC), a cationic amphiphile as a potential dedoping agent.

Experimental Section

Materials. PANI, emeraldine base (EB), $M_w = 15\,000$, was obtained from Aldrich Chemical Co. and used without further purification. All experiments were carried out with its soluble fraction. DBSAH and DDAC were used as purchased from Tokyo Kasei Kogyo Co. Chloroform (permittivity $D = 4.8$) was purchased from "Component" (Russia) and was purified from a trace amount of formic acid by treatment with NaOH fat solution, washing the organic fraction with distilled water until the aqueous fraction gave a neutral pH, drying over desiccant for 24 h, and distillation.[14] 1-Methyl-2-pyrrolidinone (NMP), $D = 30$, was anhydrous grade from Aldrich.

Preparation of the Trimers. *N*-(4-Aminophenyl)-*N*-{4-[(4-aminophenyl)imino]-2,5-cyclohexadien-1-yliden}-1,4-benzediamine (T1), and *N*-[4-(dimethylamino)phenyl]-*N*-(4-{[4-(dimethylamino)phenyl]imino}-2,5-cyclohexadien-1-ylidene)-amine (T2) were prepared by a one-step method using the following procedure. A 0.86 g (8 mmol) sample of *p*-phenylenediamine (**I**) was dissolved in 100 mL of aqueous 1 M HCl and 40 mL of ethanol. The solution was constantly stirred as it was chilled to −5 °C in a salt−ice bath. A 1.8 g (8 mmol) sample of ammonium persulfate was dissolved in 30 mL of distilled water and added to the phenylenediamine solution. After about 5 min, a color change from light yellow to dark brown was observed. At this time 1.5 mL (16 mmol) of distilled aniline (for T1) or 2.0 mL (16 mmol) of *N*,*N*′-dimethylaniline (for T2) (**II**) was quickly added. A blue suspension immediately formed, and the reaction mixture was maintained between −5 and 0 °C. The solid product (**III**) was collected by suction filtration in a Büchner funnel and washed with 40 mL of HCl followed by 80 mL of distilled water. The product was treated with 40 mL of 1 M aqueous solution of ammonium hydroxide for 1.5 h. The mixture was then filtered under a reduced pressure, and the remaining solid was washed with distilled water until the filtrate gave a neutral pH. The precipitate was dried overnight in a vacuum. T1 gave a 28% yield and T2 gave 30% yield (Scheme 1).

Interaction of Trimers and PANI-EB with DBSAH. T1, T2, or PANI-EB solutions were titrated with DBSAH solutions

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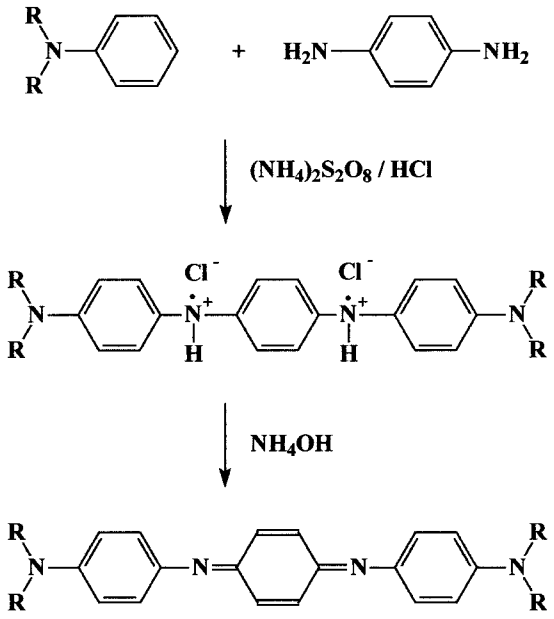
Scheme 1[a,b]



Trimer I, R = H

Trimer II, R = CH_3

[a] Trimer 1: Melting point: no melting under 300 °C. Elemental analysis data: experimental: C, 73.55%; N, 18.73%; H, 5.89%; calculated: C, 74.98%; N, 19.42%; H, 5.59%. FTIR: Table 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.98 (m, 8H, Ar−H ortho to −N=), 6.78 (d, 4H, Ar−H ortho to NH_2), 5.40 (s, 4H, NH_2). [b] Trimer 2: Melting point 165 °C. Elemental analysis data: Experimental: C, 75.60%; N, 16.31%; H, 7.04%; calculated: C, 77.77%; N, 16.26%; H, 7.02%. FTIR: Table 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.03 (m, 8H, Ar−H ortho to −N=), 6.74 (d, 4H, Ar−H ortho to N−$(CH_3)_2$), 3.01 (s, 12H, N−$(CH_3)_2$).

Table 1. Characteristics of the Basic IR Absorption Bands of the Trimers and PANI

compd	absorption max, cm^{-1}				
T1	1600	1500	1280	1170	830
T2	1600	1500	1360	1170	830
PANI-EB	1590	1500	1306	1170, 1163	830

in chloroform or NMP. Different amounts of DBSAH (6×10^{-2} M) stock solution were added to 1.5 mL of T1 or T2 (5.0×10^{-3} M) or PANI (1.0×10^{-3} M) solution at room temperature. The course of the reaction between the components was followed by UV−vis and ESR spectroscopy.

Interaction of Trimer−DBSAH and PANI−DBSAH Complexes with DDAC. A 1.5 mL of trimer−DBSAH (5.0×10^{-3} M) or PANI−DBSAH (1.0×10^{-3} M) solutions in chloroform were titrated by DDAC (4.25×10^{-2} M) chloroform solution at room temperature. The course of the titration was followed by UV−vis spectroscopy.

Measurements. All measurements were carried out at ambient temperature. IR spectra of the trimers and PANI-EB were recorded with a Specord M-80 in KBr pellets. The characteristics of the basic absorption bands (Table 1) correspond to those published earlier.[9,15] UV−vis absorption spectra were recorded with a spectrophotometer Specord M-40 using quartz cells, optical path of 1 cm. Extinction coefficients (ϵ) of PANI-EB, T1, and T2 were determined in chloroform and NMP (Table 2). In the used range of concentrations the solutions obey Buger−Lambert−Beer's law. ESR spectra of the trimer-DBSAH solutions were recorded with an X range RE-1307 spectrometer (Japan) using glass ampules with inner diameter of 2 mm. The reaction mixture was vacuumed to the remaining pressure 5.0×10^{-3} mmHg to remove oxygen. Mn^{2+} in MgO and sugar carbon were used as standards. Radical concentration was calculated by the double integrating method.

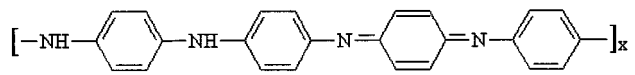
Table 2. Extinction Coefficients (cm^{-1} M^{-1}) of the Investigated Compounds

	PANI-EB[a]	T1[b]	T2[b]
ϵ in $CHCl_3$	1000 (535 nm)	8800 (535 nm)	28800 (592 nm)
ϵ in NMP	3800 (620 nm)	23000 (589 nm)	22000 (602 nm)

[a] Measured in the concentration range [PANI] = 10^{-3}−10^{-4}. [b] Measured in the concentration range [trimer] = 10^{-4}−10^{-5}.

Results and Discussion

In the course of titration of T1 or T2 solution by DBSAH solution in chloroform the color of the mixture changed from blue to green. Figure 1A,B demonstrates evolution of UV−vis spectra of T1 and T2 chloroform solutions with the addition of different amounts of DBSAH. Appearance and increase of the intensity of the absorption bands around 800 nm apparently resulting from protonation of the trimers[16,17] followed by the disappearance of the 534 and 592 nm bands associated with the initial neutral T1 and T2 may suggest by analogy with other oligoanilines[10,13,18] that DBSAH protonates the iminoquinone groups of the trimers. At the same time the new absorption bands around 400 nm appear on protonation. Both of the resulting products form clear solutions. Figure 2A,B shows the dependences of the absorption intensities corresponding to formation and accumulation of the protonation products and consumption of the initial trimer molecules as functions of DBSAH concentration. The intensity of the absorption bands corresponding to the protonated species monotonically increased with increasing the DBSAH concentration up to the molar ratio DBSAH/trimer close to 1 and then remained constant; i.e., the limit protonation level was reached in the equimolar mixtures of the trimers and the DBSAH. Figure 2A,B also shows that at the equimolar DBSAH/trimer molar ratio the absorption bands characteristic of the original trimers practically disappear; i.e., all T1 and T2 molecules are involved in the new complex compound. On the basis of the above stoichiometry, one should conclude that the ultimate degree of protonation of the iminoquinone groups responsible for evolution of the spectra involved only half of the iminoquinone groups. This is in contrast to PANI-EB and its octaaniline model in which all imine groups are available for protonation.[13,19−21] The latter conclusion was confirmed in our experiments on spectrophotometric titration of chloroform soluble PANI-EB fraction with DBSAH (Figure 1C). The absorbance at λ = 821 nm increasing with the addition of DBSAH titrant solution reaches the ultimate value just at DBSAH/PANI-EB molar ratio corresponding to net protonation of the both imino groups in the PANI-EB repeating unit:



i.e., degree of protonation equal to 1 (Figure 2C). In the other words, the composition of the model trianiline complexes ultimately protonated with DBSAH corresponds to the net formula T·DBSAH but not T·$(DBSAH)_2$ as one may expect by analogy with fully doped PANI-EB.

Interestingly, the long-wavelength absorption bands of T1 and T2 protonated complexes reveal a bathochromatic (blue) shifts ($\Delta\lambda$) from their original positions (791

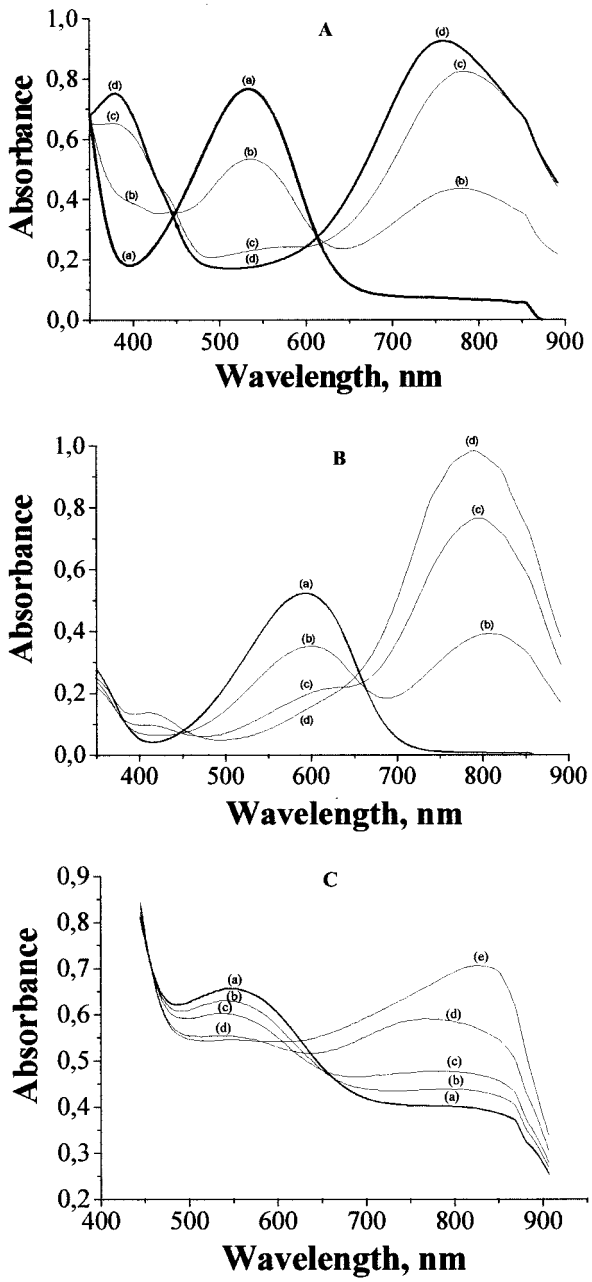


Figure 1. UV−vis spectra in chloroform solution of: (A) T1 (a) and mixtures of T1 with DBSAH at molar ratios DBSAH/T1: 0.4 (b), 0.9 (c), 1.1 (d), $C_{T1} = 7.8 \times 10^{-5}$ M. (B) T2 (a) and mixtures of T2 with DBSAH at molar ratios DBSAH/T2: 0.2 (b), 0.6 (c), 0.9 (d), $C_{T2} = 1.7 \times 10^{-5}$ M. (C) PANI-EB (a) and mixtures of PANI-EB with DBSAH at molar ratios DBSAH/$(PANI)_{ru}$: 0.24 (b), 0.5 (c), 1.5 (d), 2.0 (e), $C_{(PANI)ru} = 2 \times 10^{-4}$ M. Ambient temperature, C_{DBSAH} in titrant solution 2×10^{-3} M.

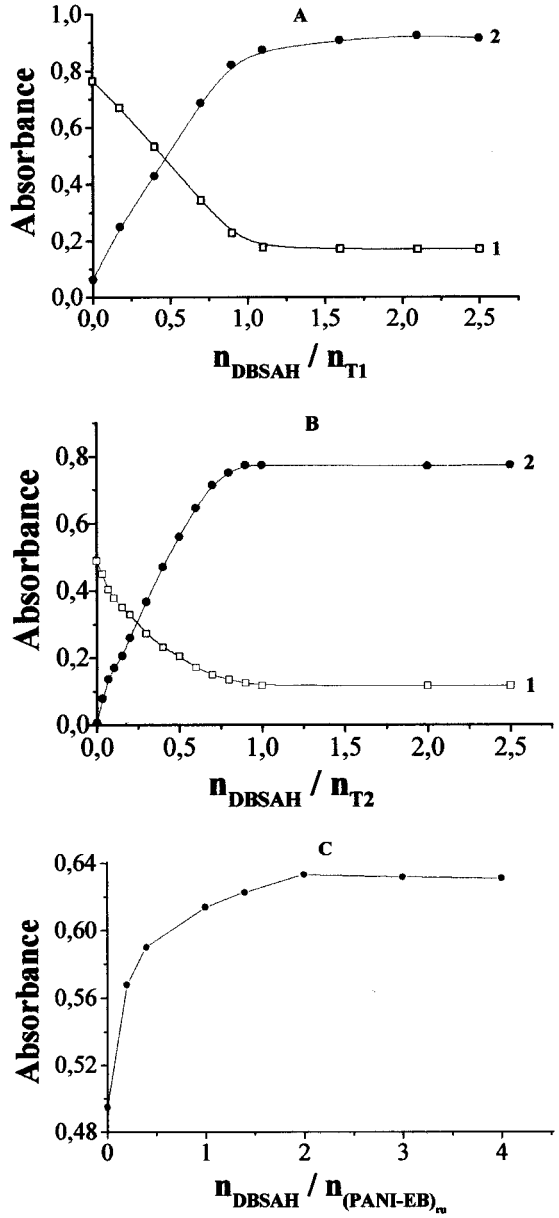


Figure 2. Absorbances of chloroform solutions of: (A) T1 at 535 nm (1) and λ_{max} for the long-wavelength band near 800 nm (2) vs DBSAH/T1 molar ratio, $C_{T1} = 7.8 \times 10^{-5}$ M. (B) T2 at 592 nm (1) and λ_{max} for the long-wavelength band near 800 nm (2) vs DBSAH/T2 molar ratio, $C_{T2} = 1.7 \times 10^{-5}$ M. (C) PANI-EB at λ_{max} for the long-wavelength band near 800 nm vs DBSAH/$(PANI-EB)_{ru}$ molar ratio, $C_{(PANI)ru} = 1.75 \times 10^{-4}$ M. Ambient temperature.

nm for T1 and 813 nm for T2) with the increase of DBSAH content in the reaction mixture (Figure 3). The same is true for the new bands around 400 nm. The blue shifts continue to increase at DBSAH/trimers molar ratios far above 1.

It is known that doping of PANI-EB results in formation of radical cations.[19,20,22−24] To investigate the nature of the species formed on interaction of the trimers with DBSAH, ESR study of their solutions was carried out.

Figure 4 shows ESR spectra of trimer−DBSAH complexes. At higher concentrations both spectra were characterized by singlet signal lines with *g*-factor close to free electron (curves 1 in Figure 4A,B). The integral intensity of the ESR signals, which appeared on adding DBSAH to the solutions of the trimers, drastically increased by 0.2−0.5 spin per a trimer molecule in the range of DBSAH/trimer molar ratio from 0 to 1. It then remained practically unchanged when DBSAH/trimer ratio changed from 1 to 100. In the other words, the number of unpaired electrons responsible for the observed ESR spectra changed in parallel to the intensities of the long-wavelength absorption bands appeared on protonation of the trimers with DBSAH.

Interestingly, for the T1−DBSAH complex the ESR spectral line was rather narrow (1.2 Oe) at higher concentration but slightly broadened on dilution of the complex solution. It indicates a considerable delocalization of unpaired electrons within the complex species

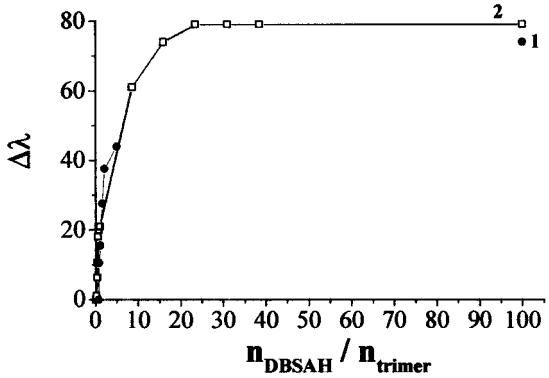


Figure 3. Blue shift of long-wavelength absorption maxima of trimer−DBSAH chloroform solutions vs DBSAH/trimer molar ratio; from 791 nm for T1−DBSAH (1) and 813 nm for T2−DBSAH (2), $C_{T1} = 7.8 \times 10^{-5}$ M, $C_{T2} = 1.7 \times 10^{-5}$ M. Ambient temperature.

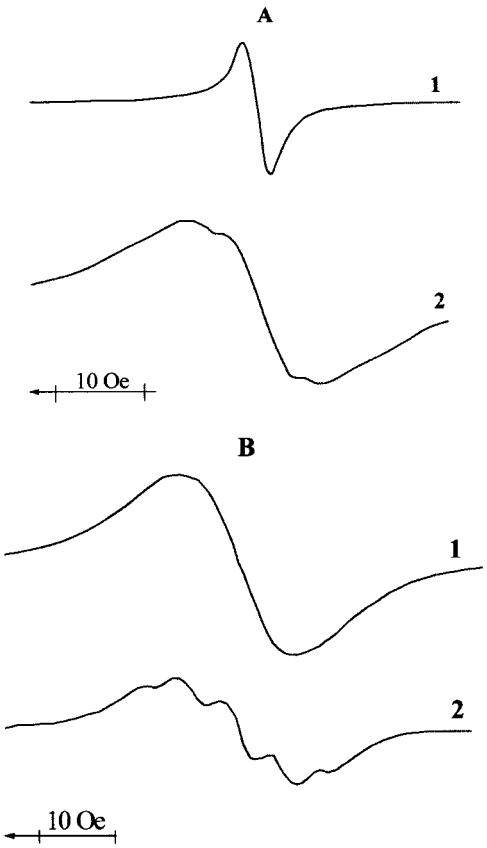


Figure 4. ESR spectra of chloroform solutions of mixtures of the trimers with DBSAH: (A) T1, DBSAH/T1 = 1, $C_{T1-DBSA} = 1.4 \times 10^{-4}$ M (1), DBSAH/T1 = 100, $C_{T1-DBSA} = 2.65 \times 10^{-3}$ M (3). (B) T2, DBSAH/T2 = 1, $C_{T2-DBSA} = 5 \times 10^{-3}$ M (1), DBSAH/T2 = 100, $C_{T2-DBSA} = 2.54 \times 10^{-3}$ M (2). Ambient temperature.

somewhat decreasing at lower T1−DBSAH concentrations. For T2−DBSAH complex the original line was wider (about 14 Oe), and its width remained constant in all studied complex concentration range (Table 3). It is remarkable that at molar ratio DBSAH/T2 = 100 the ESR signal line has resolved to a symmetrical quintet with the resolution constant $a_N = 5.9$ Oe that corresponds to a monoradical with unpaired electron interacting with two N nuclei. At the same time the width of the ESR signal line for T1 at DBSAH/T1 = 100 increased and equalized that of T2 while the shape of the spectral line also transformed into poorly resolved hyperfine structure with a_N value practically equal to that for T2 (curves 2 in Figure 4).

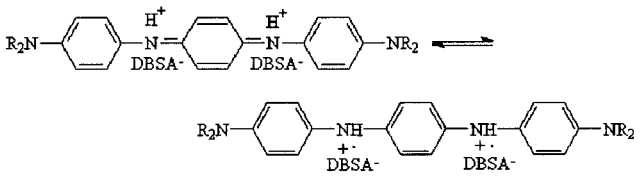
Table 3. Parameters of ESR Lines at Various Concentrations of the Trimers and DBSAH/Trimer Molar Ratios

trimer	*C*, mol/L	[DBSAH[/[trimer]	Δ*H*, Oe	a_N, Oe
T1	5×10^{-4}	1/1	1.2	
T1	1.4×10^{-4}	1/1	2.7	
T1	7×10^{-5}	1/1	3.7	
T1	7×10^{-6}	1/1	6.3	
T1	2.65×10^{-3}	100/1		5.8
T2	5×10^{-3}	1/1	14.3	
T2	5×10^{-4}	1/1	15.2	
T2	1×10^{-4}	1/1	13.4	
T2	2.54×10^{-3}	100/1		5.9

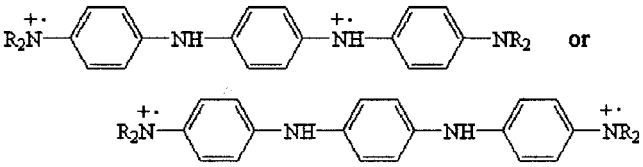
On the basis of the above data, the following net reaction between the trimers and DBSAH can be proposed.

This scheme meets the experimentally observed ultimate degree of protonation of imine groups equal to 0.5 and also that on reaching this degree the number of unpaired electrons detected by ESR becomes commensurable with the number of the trimer molecules in the reaction solution.[25]

The trimer−DBSAH complex structure represented in Scheme 2 can be considered as a product of electron transfer from the original trimer molecule to the double protonated trimer also called a bipolaron:



The bi(radical cation) which may arise from double protonation of the iminoquinone unit obviously cannot reveal the observed ESR spectrum by itself, as well as the two hypothetical radical cations (polarons) localized within a single trimer molecule

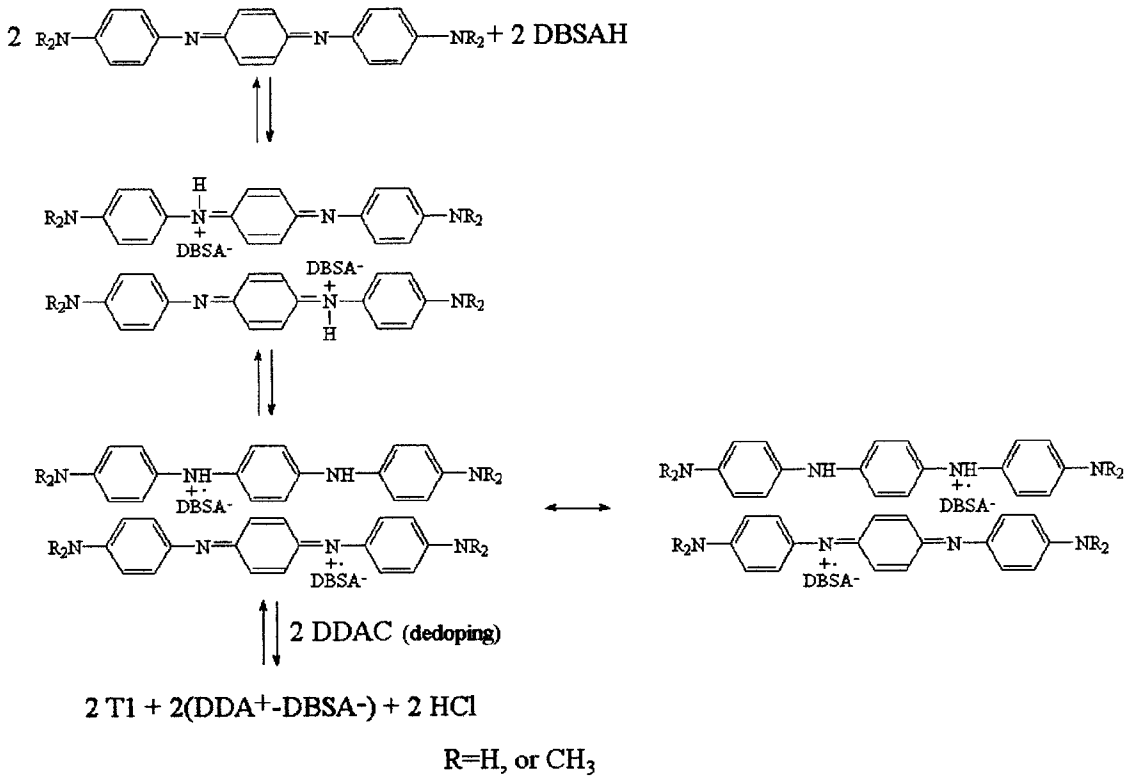


because of an inevitable strong binding of unpaired electrons (summary spin is equal to 1).

Moreover, protonation of one imine group in the iminoquinone unit should result in considerable decrease of basicity of the second one that makes a double protonation quite unlikely. Therefore, bipolarons usually postulated as intermediates on doping of PANI-EB by protic acids[19,20,22−24] hardly form in the studied reaction between the trimers and DBSAH. It is more likely that two monoprotonated trimer molecules reacting to each other disproportionate via proton−electron transfer as shown in Scheme 2. Then absorption bands around 800 and 400 nm whose intensities increased on protonation of the trimers (Figure 1A,B) might be ascribed to $\pi \rightarrow \pi^*$ transitions in iminoquinoid and aminobenzoid radical cations, respectively.

The trimer−DBSAH complex species apparently associate in chloroform solution to form aggregates consisting of trimer radical cations paired with $DBSA^-$ counterions. This conclusion follows immediately from

Scheme 2



the ESR data. Indeed, intermolecular interchange of unpaired electrons within such aggregates probably causes experimentally observed degeneration of hyperfine structure in the ESR spectra of the trimer complexes and narrowing of the singlet line at higher concentration of the T1−DBSAH 1:1 complex, which apparently forms more stable and tightly packed aggregates than the T2−DBSAH complex loaded with dimethylamine end groups. However, at high excess of DBSAH the aggregates dissociate so that hyperfine structure characteristic of the ESR spectrum of the individual radical cations reveals. At the same time addition of the excess DBSAH to the protonated trimers created the above-mentioned bathochromic shift of the UV−vis absorption bands probably caused by decrease of permittivity in the vicinity of the corresponding chromophores.

As mentioned above, the $DBSA^-$ anions and cationic groups in trimer−DBSAH complexes apparently form ion pairs in such low polar solvent as chloroform. At the same time it is known that oppositely charged amphiphilic ions in low polar solvents also form ion-paired associates.[26] Therefore, we could expect that cationic surfactants added to chloroform solution of the trimer−DBSAH complexes may compete with cationic trimer species for binding to $DBSA^-$. In fact, it was confirmed by titration of the trimer−DBSAH complex solutions in chloroform with chloroform solution of DDAC at room temperature.

Addition of DDAC to the trimer−DBSAH complexes results in color change of the mixture solution from green to blue. Figure 5A,B represents the UV−vis spectra of trimer−DBSAH−DDAC mixtures at various DDAC/DBSAH molar ratios. It is seen that the absorption bands intensity corresponding to the protonated trimers decreases in parallel with recovery of the bands characteristic of the original trimers. In other words, DDAC actually deprotonates (dedopes) the trimer−

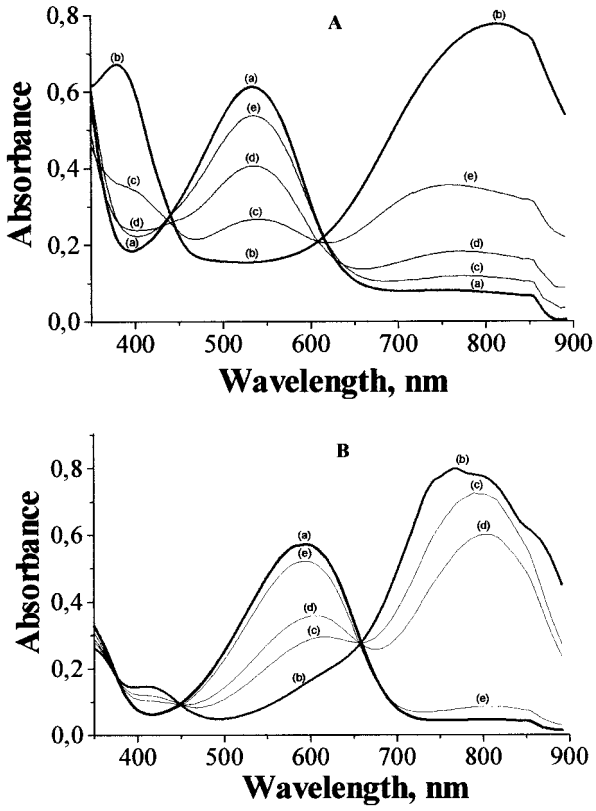


Figure 5. UV−vis spectra in chloroform solutions of: (A**)** T1 (a), DBSAH protonated T1, molar ratio DBSAH/T1 = 1 (b), mixtures of DBSAH protonated T1 with DDAC at DDAC/DBSA molar ratios: 80 (c), 110 (d), 210 (e), $C_{T1-DBSA} = 7.4 \times 10^{-5}$ M. (B**)** T2 (a), DBSAH protonated T2, DBSAH/T2 = 1 (b), mixtures of DBSAH protonated T2 with DDAC at molar ratios DDAC/DBSA: 40 (c), 50 (d), 100 (e), $C_{T2-DBSA} = 1.98 \times 10^{-5}$ M. Ambient temperature, C_{DDAC} in titrant solution 4.25×10^{-3} M.

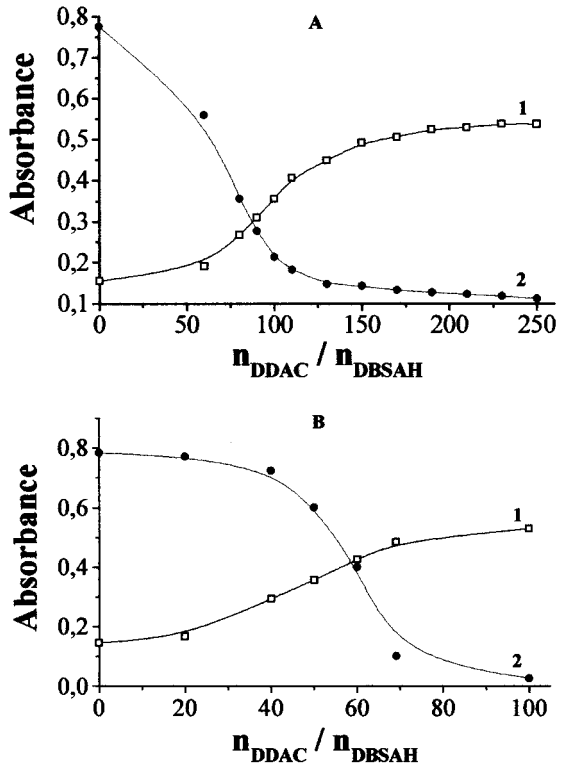


Figure 6. Absorbances of chloroform solutions of: (A**)** DBSAH protonated T1 at 535 nm (1) and λ_{max} for the long-wavelength band near 800 nm (2) vs DDAC/DBSAH molar ratio, $C_{T1-DBSA} = 7.4 \times 10^{-5}$ M. (B**)** DBSAH protonated T2 at 594 nm (1) and λ_{max} for the long-wavelength band near 800 nm (2) vs DDAC/DBSAH molar ratio, $C_{T2-DBSA} = 1.98 \times 10^{-5}$ M. Ambient temperature, C_{DCDA} in titrant solution 4.25×10^{-3} M.

DBSAH complexes, releasing the original trimers (Scheme 2 where DDA^+ is a DDAC cation). Figure 6A,B characterizes the dedoping phenomenon quantitatively. Full deprotonation of T1 requires a higher amount of DBSAH than T2 which probably caused by a lower stability of the T2−DBSAH complex.

Such a deprotonation was not observed on addition of DDAC to the chloroform solution of PANI-EB doped with DBSAH. The UV−vis spectrum of such solution in the region 500−900 nm remained practically unchanged on titration with DDAC solution in chloroform. It means that the complex of PANI-EB with the dopant is significantly more stable that the trimer−DBSAH complexes.

Further studies have shown that both trimers also can be protonated in NMP solution by DBSAH. Figure 7 demonstrates UV−vis spectra for T1 protonation. However, in NMP solutions the maximum protonation levels could be reached only at considerably higher DBSAH/trimer molar ratios (Figure 8). This difference is apparently due to a lower stability of the trimer−DBSAH complexes in the polar solvent. T2 exhibits essentially the same behavior. Unlike the situation in chloroform, no blue shift of the long-wavelength absorption band of the protonated trimers was observed upon spectrophotometric titration in NMP. Protonation of T1 and T2 in NMP also results in formation of radical cation complexes fixed by ESR. Unfortunately, the question of whether the trimer−DBSAH complexes can be deprotonated by a cationic surfactant in NMP solution could not be solved in this instance because of insolubility of DDAC in NMP.

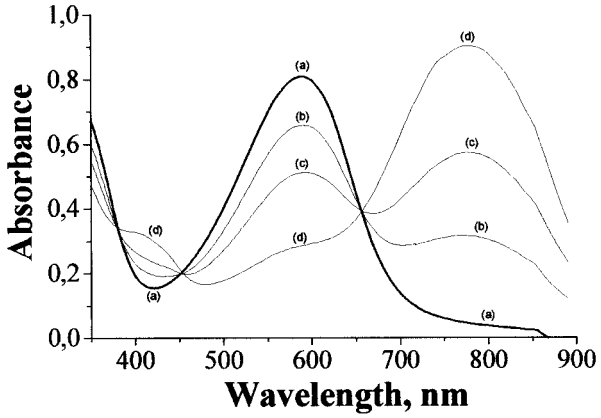


Figure 7. UV−vis spectra of NMP solutions of T1 (a) and mixtures of T1 with DBSAH at molar ratios DBSAH/T1: 2 (b), 3 (c), 5 (d), $C_{T1} = 2.1 \times 10^{-5}$ M. Ambient temperature.

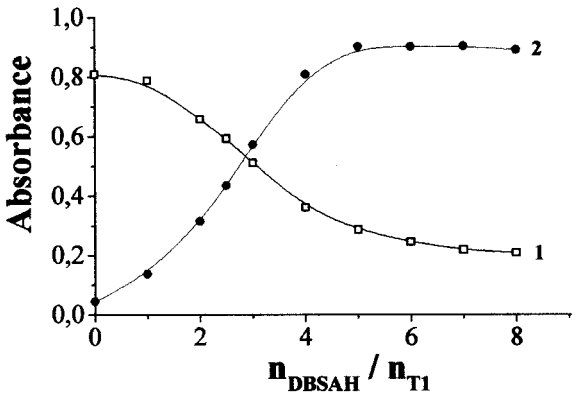


Figure 8. Absorbances of T1 solution in NMP at 591 nm (1) and 780 nm (2) vs DBSAH/T1 molar ratio, $C_{T1} = 2.1 \times 10^{-5}$ M. Ambient temperature, C_{DBSAH} in titrant solution 2×10^{-3} M.

Conclusion

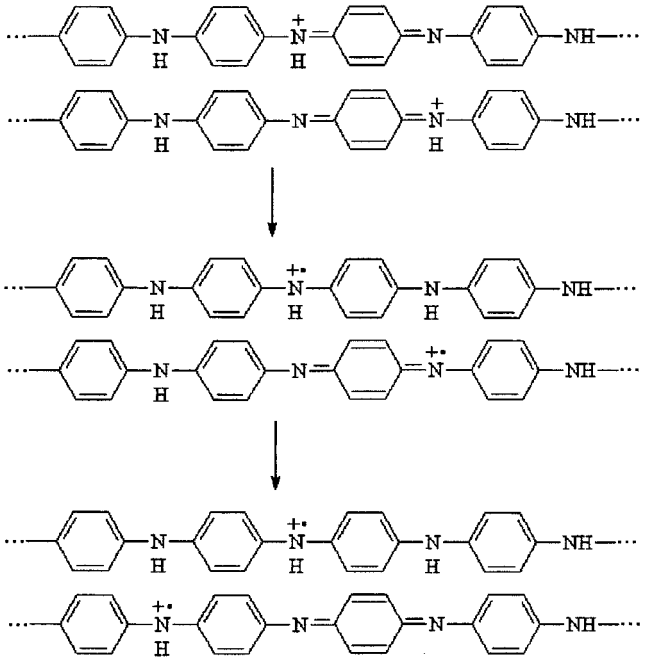
The trimers studied as low molecular models of PANI can be protonated by acidic amphiphile DBSAH in chloroform and NMP solutions at ambient temperature to form radical cation complexes. In contrast to PANI-EB doped with DBSAH, trimer−DBSAH complexes can be deprotonated in chloroform solution at ambient temperature by adding the cationic surfactant (DDAC).

The proposed mechanism for arising the trimer monoradical cations based on the above experimental data definitely excludes formation of bipolaron intermediates in the particular case. Moreover, on the basis of the above considerations one may also suggest the similar mechanism for doping of higher oligoanilines and PANI-EB with protic acids. This alternative mechanism represented by Scheme 3 does not require a step of double protonation of iminoquinoid units, i.e., traditionally accepted for the formation of bipolarons.

In the case of PANI-EB and higher oligoanilines intra- or intermolecular electronic disproportionation of two monoprotonated iminoquinoid units and proton transfer would result in formation of aminobenzoid and iminoquinoid radical cations. The former represents a traditional polaron. The latter can transform into traditional polaron via intramolecular electron transfer, regenerating a neutral iminoquinoid unit which then protonates again, etc. So in contrast to the trimer case here the extent of protonation is not limited by the 0.5 value.

The trimer radical cations paired with the DBSA counterions have been shown by the above ESR mea-

Scheme 3



etc.

surements to associate even at rather low concentration (10^{-3}−10^{-4} M) to form aggregates particularly expressed in the case of T1−DBSAH complex. These aggregates characterized by a considerable intermolecular electron interchange may be considered as a prototype of ordered PANI domains responsible for its "metallic" behavior.[27]

Even more so, such association should be characteristic of doped oligoanilines and PANI in organic solvents. In fact, the important part of intermolecular association phenomena was clearly demonstrated for PANI doped with camphorsulfonic acid in NMP and *m*-cresol.[28]

References and Notes

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(25) According to Scheme 2 (p 5), the number of spins developed in the ESR spectra should be equal to the number of the trimer molecules in solution, i.e. 1 spin per 1 trimer molecule. Nevertheless, the value estimated in our experiments (no less than 0.2−0.5) should be considered as a good correlation, if one takes into account the accuracy of the method and possible decrease of a signal intensity due to the rest aggregation of the trimer/DBSAH complexes in chloroform solution.
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