Kinetics of the *Z-E* isomerization of monosubstituted azobenzenes in polar organic and aqueous micellar solvents

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Dedicated to Prof. Nicolò Vivona on the occasion of his 70th anniversary

Abstract

The rates of *Z-E* isomerization of azobenzene and seven 4-substituted derivatives (CH_3, CF_3, OCH_3, *n*-Butyl, O*t*-Butyl, Br, F) have been investigated at 25 °C in ethanol, in methanol, in methanol/water mixtures and in aqueous solutions of ionic and non-ionic micelles by recording in the dark the spectral changes observed after exposure to UV light of the samples. The competitive contributions of the rotation *vs.* inversion mechanisms by which the isomerization of azobenzenes can occur have emerged from V-shaped Hammett plots. The obtained rate constants can be used as polarity indicators of the different micro-heterogeneous media with two main advantages with respect to other probes. Firstly they are not affected by hydrogen bonding between the substrate and the environment, as in the case of push-pull azobenzenes. Secondly, the derived substrate-independent Hammett ρ values allow to separate the effects of orientation of the probe from the polarity of the supramolecular aggregate.

Keywords: Azobenzene**,** *Z-E* isomerization, polarity indicator**,** micelles, Hammett plot

Introduction

Incorporation of molecular probes into aqueous micelles allows measurement of parameters such as the critical micelle concentration (cmc), the degree of water penetration into the surfactant aggregates and the fluidity of the micellar core. Many studies employ fluorescence intensity values, excitation and emission wavelength maxima and fluorescence lifetimes of molecular fluorescent probes as indicators of the features of the probe's surroundings. Most probes have

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been chosen for their selectivity towards specific micellar domains, such as specific affinity for the hydrocarbon core formed by the surfactant tails (e.g., pyrene, naphthalene and anthracene) or towards the interface composed primarily by the amphiphile head groups (e.g., pyrenesulfonic acid, pyrenebutyric acid, and 1-anilinonaphthalene-8-sulfonate).[1]

Azobenzene and its derivatives are photoreactive molecules that undergo reversible photo-isomerization from the generally more stable trans (*E*) isomer to the less stable cis (*Z*) isomer upon UV irradiation. Vice versa, the thermodynamically favorable cis–trans conversion occurs upon irradiation with visible light or in the dark.[2]

The isomerization of azobenzenes has been recently exploited for the preparation of several molecular machines[3] used as both biological[4] and photonic[5] devices. The strong geometrical difference between the extended trans form and the compact cis form in the gas phase and in solution may provide important details on the distribution and the dynamics of the azobenzene guest into hosts such as cyclodextrins[6] and crown ethers[7] or on the conformational changes of polypeptide chains.[8]

The mechanism by which the *Z–E* isomerization takes place is not unequivocally established since two opposing pathways have been proposed: the reaction may proceed either by rotation about the N=N double bond or by flip-flop inversion of one of the nitrogen atoms.[9] The rotation and inversion pathways are competitive, but one may be favored over the other, depending of the electronic nature of the substituents covalently bonded to one or both the phenyl rings and of the polarity of the reaction medium.[10] It has been shown[9] that a high polarity of the solvent favors the rotation over the inversion mechanism. The main difference between the two mechanisms is in fact that rotation occurs via a dipolar transition state in which the nitrogen-nitrogen π-bond is heterolytically broken, while inversion takes place via a linear transition state in which the double bond is retained.

It has been demonstrated[10,11] that push-pull disubstituted azobenzenes exhibit a changeover in the cis-trans isomerization mechanism on passing from polar to non polar solvents. However, the presence of only one strong electron-donating group, such as the dialkylamino group, bonded to one phenyl ring is sufficient,[11] in polar solvents, to make the isomerization via rotation competitive with the isomerization via inversion. This changeover of the mechanism of *Z-E* isomerization upon changing the substituents on the phenyl ring has been confirmed[12] by non-linear Hammett plots. The conclusion that the rates of isomerization of substituted azobenzenes follow a sharp V-shaped Hammett relation was challenged by Talaty and Fargo[13] who found only a rough correlation for many *meta* and *para* monosubstituted azobenzenes. However the position of the substitutents can influence the mechanism of the transformation[14] and we note that the correlation becomes sharply V-shaped if only *para*-derivatives are considered (with the exclusion of H bond-accepting groups such as NO_2).

Changes both in the fluorescence spectra and in the isomerization rates of push-pull azobenzenes have already been used to study[15] micro-heterogeneous solutions such as micelles, vesicles and inverse micelles. The surprisingly high polarities[15,16,17] for these media were probably the result of a "polar gradient" experienced by the probe in the interfacial region of the

aggregate. In such a situation the amino end of the molecule sits in a relatively non polar environment while the nitro end projects into the highly polar region at the interface with the aqueous solution. This orientation is favored by the capacity of the nitro group to accept specific hydrogen bonds from the water molecules of the medium.[17,18]

In this study we have investigated the *Z-E* isomerization of azobenzene and seven 4-X substituted azobenzenes (where X = CH_3, *n*-Butyl, CF_3, OCH_3, O*t*-Butyl, Br, F), bearing either an electron withdrawing or an electron donating group. We deliberately avoided the push-pull disubstituted azobenzenes, for which the competition of the two independent mechanisms had been previously attributed[17,18] to specific hydrogen bonding interactions with the solvent. We propose to use the thermal isomerization rate constants of the selected monosusbtituted azo dyes to estimate the polarity of micro-heterogeneous media.

The magnitude of the kinetic substituent effects (or of the spectral changes) measured for monosusbtituted should be lower than that observed for push-pull disubstituted azobenzenes, but the advantage of their use is twofold: (1) by avoiding the presence of amino and nitro groups in the azobenzenes, the obtained kinetic data become independent of specific hydrogen bonds with the medium; (2) the use of the V-shaped Hammett plot allows to highlight the changeover of the isomerization mechanism and to distinguish between polar effects which prevail in the case of the rotation mechanism and orientation/steric effects which prevail in the case of the inversion path.[9]

The *Z-E* isomerization has been performed in methanol, ethanol and in micellar solutions of octaethylene glycol monododecyl ether ($C_{12}E_8$), sodium dodecylsulfate (SDS) and dodecyl trimethylammonium bromide (C_{12}TAB). The investigated azobenzenes are poorly soluble in water, as it is apparent from the log $P_{octanol/water}$ (partition coefficient between n-octanol and water) for azobenzene = 3.8.[19] The presence of ionic or non ionic micelles strongly increases the water solubility of all of the investigated azobenzenes allowing a facile measurement of the corresponding rates of *Z-E* isomerization. The isomerization rate of each derivative in pure water has been estimated by extrapolating the rates obtained in methanol-water mixtures.

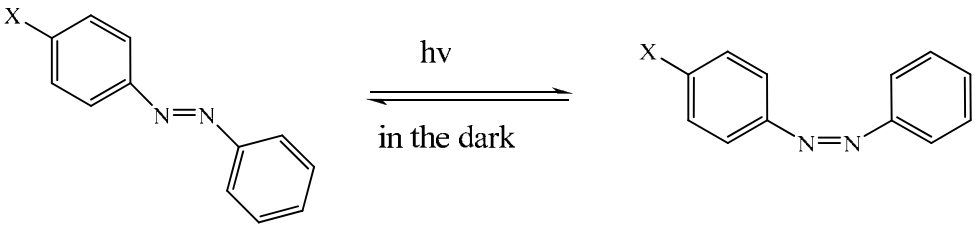
Finally, the kinetics and mechanisms of isomerization have been examined in the light of the dipole moments of the *E* and *Z* isomers, calculated by DFT (B3LYP/6-31G*).[20]

Materials and Methods

Materials

Ethanol and methanol (99% spectroscopy grade), octaethylene glycol monododecyl ether ($C_{l2}E_8$), dodecyl trimethylammonium bromide (C_{12}TAB) and sodium dodecylsulfate (SDS) were purchased from Fluka and used without further purification. Azobenzene and nitrosobenzene were purchased from Aldrich and used without further purification. Substituted azobenzenes were obtained, according to the Mills reaction,[21,22] by heating nitrosobenzene with one

equivalent of the appropriate 4-substituted arylamine in glacial acetic acid. The investigated compounds are reported in Scheme 1.



Scheme 1. *Z*-*E* interconversion of 4-X-azobenzenes (X = H, CH_3, *n*-Butyl, OCH_3, O*t*-Butyl, Br, F, CF_3).

Kinetic measurements

Stock solutions of the 4-X-azobenzenes in ethanol (about 1.05×10^{-2} M) were prepared and kept in the dark at room temperature. A 1.0×10^{-2} M aqueous solution of $C_{12}E_8$ was prepared by dissolving the appropriate amount of the surfactant in ultra-pure water (Milli-Q, Millipore at pH 5.50); the same procedure was followed to obtain a 2.0×10^{-2} M aqueous solution of SDS or C_{12}TAB. These are micellar solutions as, at 25 °C, the corresponding cmc values are 1.1×10^{-4} M,[23] 8.0×10^{-3} M[24] and 1.3×10^{-2} M[25] for $C_{12}E_8$, SDS and C_{12}TAB, respectively. 5 μL of the stock ethanol solution of each 4-X-azobenzene were transferred into a 1-cm light pass quartz cuvette containing 2 mL of the proper solvent (ethanol, methanol, methanol/water mixture or aqueous micellar solution). The final concentration of the sample was about 2.6×10^{-5} M in all cases.

It was assumed, according to previous studies,[26,27] that the *E* isomer, due to its higher stability, was the only isomer present in the solution before irradiation. The molar absorptivities of the substituted (*E*)-azobenzenes in the various investigated environments have been measured according to the Lambert-Beer law (see a typical example in Figure 1).

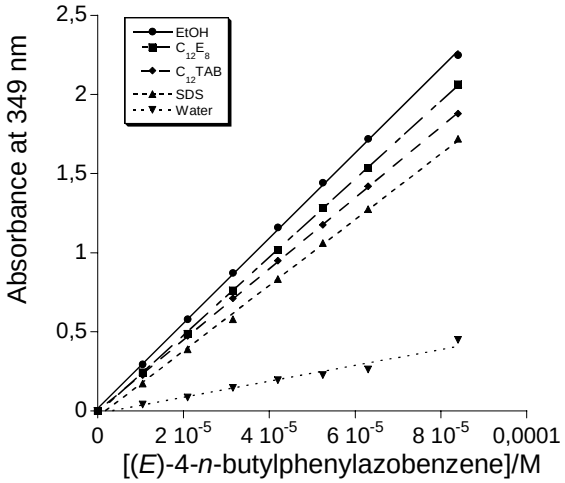


Figure 1. Lambert-Beer plot for (*E*) 4-*n*-Butyl azobenzene in ethanol, pure water, 1×10^{-2} M $C_{12}E_8$, 2×10^{-2} M C_{12}TAB and 2×10^{-2} M SDS solutions.

The solution of the sample was stirred and thermostatted at 25.0±0.1°C. The *Z* isomer was obtained by exposing the sample to a Hg-Xe arc lamp (150 W) for 45 minutes, a time which was demonstrated to be long enough to reach a photostationary state.

The UV-light irradiation induces a decrease of the high-intensity absorption band centered in the wavelength range 315-349 nm (depending of the substituent in the benzene ring and of the solvent) and an increase of the low-intensity band at about 440 nm, due to a $n \rightarrow \pi^*$ transition (an example is reported in Figure 2).

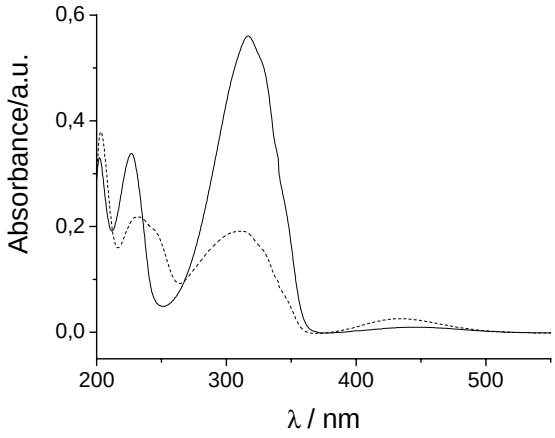


Figure 2. UV-vis spectra of azobenzene before (*E* isomer, solid line) and after (*Z* isomer, dotted line) UV irradiation.

The rate of the *Z-E* isomerization was calculated by monitoring in the dark the absorption change at or near the absorption maximum of the *E* isomer over a period of about 24 hours by using a Jasco V-550 or a Cary 1-E spectrophotometer. The percentage of the *Z* isomer produced upon UV irradiation depends of the substituent, but the isomerization rate constant is independent of the initial concentration, as pointed out by Weiss.[28] Although the isomerization reaction is thermally reversible, the conversion $E \rightarrow Z$ may be kinetically neglected since equilibrium mixtures contain a very low amount of the *Z* isomers at the temperature of our experiments. The kinetic profile of the $Z \rightarrow E$ conversion follows a first-order decay and the corresponding first-order rate constant, k_{obs}, can be calculated according to Equation (1) from the time-dependent absorbance A^t and the absorbance A^∞ a $t = \infty$, which matches the absorbance of the sample before irradiation:

$$\ln(A^\infty - A^t) = k_{obs}\, t \qquad (1)$$

The k_{obs} values measured for the investigated substrates in the various homogeneous and heterogeneous environments are reported in Table 1.

Due to the low solubility of azobenzenes it was not possible to directly measure the rates of the *Z-E* isomerization in water. Nevertheless the rate constants in water, k_0, were estimated by extrapolating to zero percentage of methanol determinations performed in methanol/water mixtures.

Results

A linear correlation of k_{obs} with the (v/v) percentage of methanol was observed for all the investigated compounds (a typical example is reported in Figure 3). An anomalous behaviour was detected only for 4-*n*-butyl-azobenzene (Figure 4) and 4-CF_3-azobenzene (Figure 5).

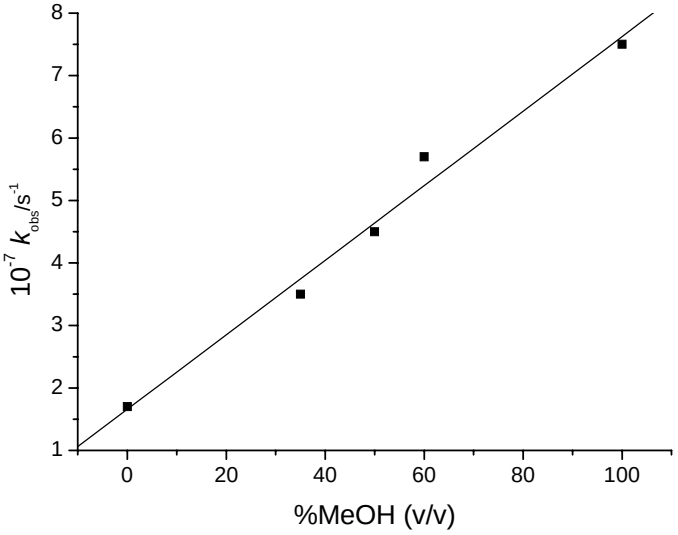


Figure 3. Determination of the first order rate constant in water, k_0, for (*E*)-azobenzene.

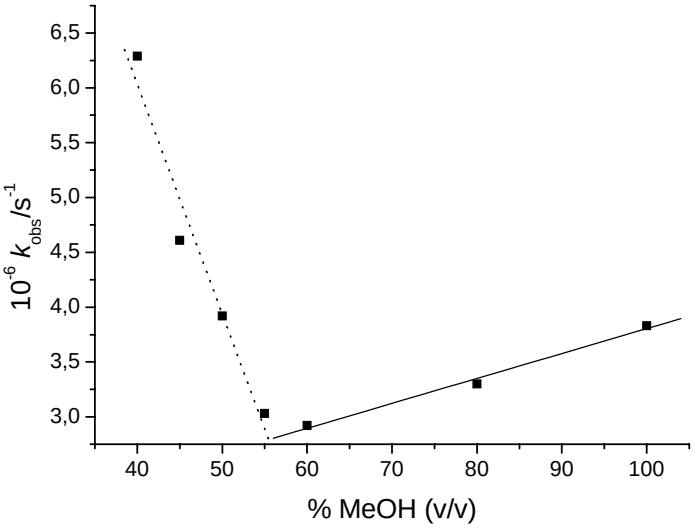


Figure 4. Rate constants for the isomerization of (*E*)-4-*n*-Butyl-azobenzene in aqueous/methanol mixtures of different composition.

For the former compound a V-shaped plot was obtained. Rate constants in more polar water/methanol mixtures fall on the side with a negative slope while rate constants in less polar mixtures fall on the side with a positive slope. The break in the plot corresponds to a 58% (v/v) methanol mixture. The plot of Figure 4 reveals a peculiar sensitivity of the *n*-butyl derivative to the composition of the solvent, probably due to hydrophobic interactions between the bulky alkyl chain and the medium.

In the case of 4-CF_3-azobenzene (see Figure 5), a linear extrapolation to zero percentage of methanol would give a physically meaningless negative value of k_0. However the low solubility of this derivative in water-rich media does not allow measurements in mixtures with less than 50% methanol and a reliable estimate of k_0 by extrapolation appears impossible (see Figure 5).

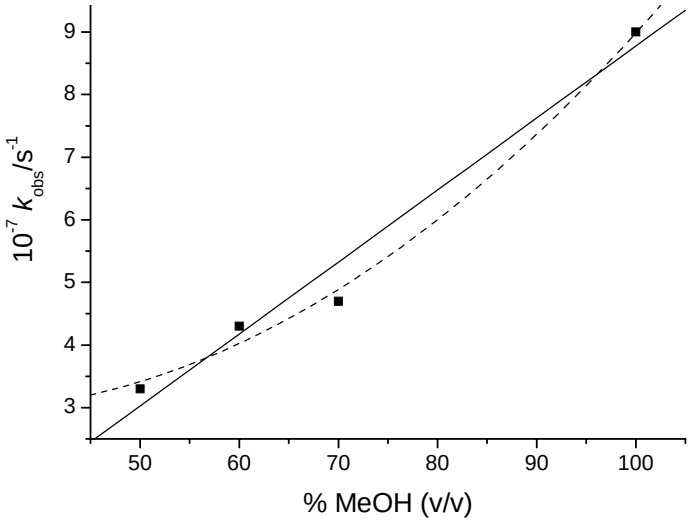


Figure 5. Rate constants for the isomerization of (*E*)- CF_3-azobenzene in aqueous/methanol mixtures of different composition. The two lines are drawn as eye-guides.

The experimental first-order rate constants, k_{obs}, for the *Z*-*E* isomerization of azobenzenes in methanol; ethanol; benzene; $C_{12}E_8$, SDS and C_{12}TAB micellar solutions and the rate constants in water, k_0, extrapolated from methanol-water mixtures, are collected in Table 1.

Recently reported[20] dipole moments for the present 4-X-azobenzenes are collected in Table 2 where it appears that a large change in dipole moment accompanies the $Z \rightarrow E$ interconversion. This fact may give a contribution to the comprehension of the solute-solvent interactions associated with the azobenzenes isomerization.[15] The dipole moment of the *Z* isomer is significantly higher than that of the *E* isomer, the only exception being the CF_3-substituted derivative.

Table 1. First-order rate constants for the *Z*-*E* isomerization of 4-X-azobenzenes in different media.

4-X substituent	$k_0/10^{-6}s^{-1}$	$k_{obs}/10^{-6}s^{-1}$ Methanol	$k_{obs}/10^{-6}s^{-1}$ Ethanol	$k_{obs}/10^{-6}s^{-1}$ Benzene	$k_{obs}/10^{-6}s^{-1}$ $C_{12}E_8$ micelles	$k_{obs}/10^{-6}s^{-1}$ SDS micelles	$k_{obs}/10^{-6}s^{-1}$ C_{12}TAB micelles
H	0.17 ± 0.03	0.75 ± 0.20	0.99 ± 0.04	1.61[a]	0.93 ± 0.04	0.68 ± 0.09	0.61 ± 0.01
OCH_3	2.11 ± 0.05	2.77 ± 0.10	3.66 ± 0.01	4.07;[b]6.44[a]	3.90 ± 0.01	3.42 ± 0.20	3.54 ± 0.09
O*t*-Butyl	1.12 ± 0.12	1.98 ± 0.2	3.02 ± 0.03		3.59 ± 0.05	3.12 ± 0.50	3.66 ± 0.04
CH_3	0.64 ± 0.04	1.32 ± 0. 10	1.56 ± 0.02	3.34;[b]4.42[a]	2.08 ± 0.06	1.46 ± 0.08	1.34 ± 0.02
n-Butyl	(12.5 ± 1.53)[c]	3.83 ± 0.10	4.03 ± 0.02		4.70 ± 0.20	6.32 ± 1.20	5.94 ± 0.20
CF_3	(-0.27 ± 0.10)[c]	0.90 ± 0.10	1.17 ± 0.10	1.74[b]	1.52 ± 0.09	0.67 ± 0.30	0.85 ± 0.01
F	0.36 ± 0.08	0.86 ± 0.10	1.11 ± 0.01		1.08 ± 0.05	0.72 ± 0.04	0.67 ± 0.05
Br	0.12 ± 0.03	1.20 ± 0.10	1.09 ± 0.10	2.81[a]	2.11 ± 0.20	1.29 ± 0.02	2.64 ± 0.10

[a] Calculated from available dielectric-capacity data.[29] [b] Ref. 28. [c] For the significance of this value see the text.

Table 2. Dipole moments μ (Debye) for the 4-X-azobenzenes calculated by DFT (B3LYP/6-31G*)

4-X-substituent	μ *E*	μ *Z*
H	0.00	3.17
OCH_3	1.86	4.54
O*t*-Butyl	1.66	3.26
CH_3	0.81	3.63
n-Butyl	0.76	3.43
CF_3	3.64	2.66
F	1.52	2.34
Br	1.89	2.39

Discussion

A part from the *n*-butyl and CF_3-substituted derivatives, the *Z*-*E* isomerization of azobenzenes at 25°C is from 1.7 to 9.1 times faster in ethanol than in water. Previously reported rate constants[28,29] at 25°C (see Table 1) also show that azobenzenes isomerize faster in benzene than in ethanol. Thus the *Z*-*E* isomerization reaction appears accelerated on decreasing the solvent polarity as it was already suggested by Hartley.[30] This is also in agreement with the dipole moment values as the formation of the less polar *E* isomer appears to be favored in less polar solvents, the only exception being the *n*-Butyl derivative. The reactivity of this derivative increases on going from methanol, to ethanol to water probably due to a higher sensitivity of the rotation mechanism towards additional solvophilic interactions of the *n*-butyl group in ethanol solution and/or towards solvophobic interactions in aqueous solution. It is interesting to note that similarly to our n-butyl derivative, also push-pull disubstituted derivatives exhibit higher rate constants in protic/polar than in apolar solvents due to the formation of hydrogen bonds[17,18] or to the competition of the rotational over the inversion mechanism.[31]

In micellar solutions 4-X-azobenzenes, due to their low solubility in water, prefer to partition into the surfactant aggregates.[15,32] The azobenzene guest will reside in an interfacial region that has some hydrocarbon-like as well as some ionic character. These substrates could therefore be used as probes and their rate of *Z*-*E* isomerization should provide information on the polarity of micro-heterogeneous host systems. The rates of isomerization, k_{obs}, in non-ionic micelles are similar to those in ethanol. In negatively charged SDS and in positively charged C_{12}TAB micellar solutions k_{obs} values are lower than those measured in ethanol and uncharged micelles (again with the exception of the n-Butyl derivative). For charged micelles the site of localization of the azobenzene guest appears to be more polar than bulk ethanol and presumably is characterized by a reduced mobility and enhanced orientational requirements of the guest. Thus the obtained results confirm that the reaction takes place in the interfacial region of the micelles and that, as previously suggested,[33] dyes are solubilized concomitantly with the expulsion of water molecules from the interfacial region. The similar k_{obs} values obtained in SDS and CTAB

micelles show that the charge of the surfactant does not significantly affect the rate of isomerization and this is consistent with spectroscopic[15] and kinetic[18,32] evidence that azobenzenes experience a similar micropolarity in SDS and CTAB micelles.

By plotting the logarithm of k_{obs} for the investigated 4-X-azobenzenes in methanol and ethanol against the corresponding σ substituent constants[34] V-shaped Hammett plots are obtained (Figure 6). The *n*-Butyl derivative has been excluded from the correlations due to the mentioned peculiar solute-solvents interactions in methanol/water mixtures. It is very likely that for this substrate the electronic effects of the substituent are overwhelmed by aspecific interactions with the solvent. Another possible reason of deviation of the *n*-Butyl derivative from the correlation might be the formation of dimers or of small aggregates through solvophobic interactions but no spectroscopic evidence of their formation have been found.

The obtained V-shaped plots can be interpreted in terms of a change in the reaction mechanism. Electron-donating substituents favor the rotation around the N=N bond, while electron-withdrawing substituents favor the inversion path for the *E-Z* isomerization. An analogous change in mechanism had been reported for the isomerization of several N-phenylimines[35] and azomethine dyes.[12]

On the contrary by plotting extrapolated log k_0 values against σ values a linear plot with a highly negative ρ value of ≈ -2 is obtained (Figure 7), suggesting that in water the rotation is the only detectable mechanism for most derivatives.

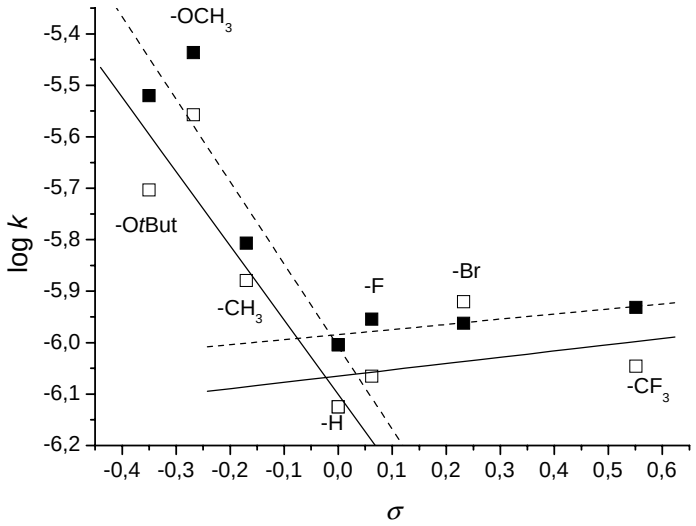


Figure 6. V-shaped Hammett plot for 4-X-azobenzenes in MeOH (solid line, empty square) and in EtOH (dotted line, full square).

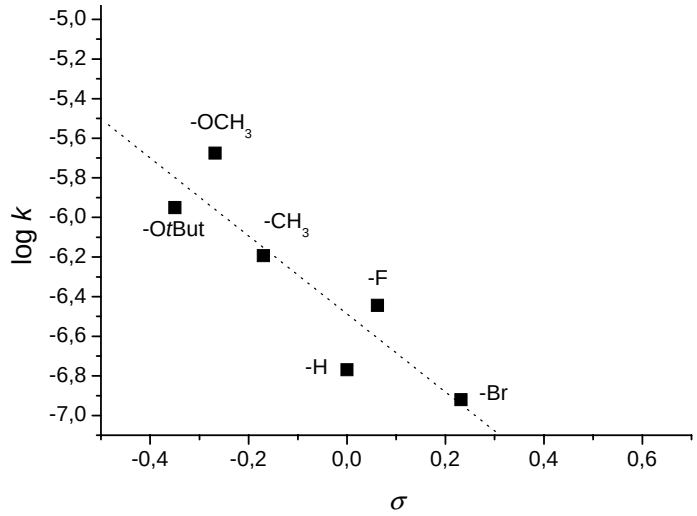


Figure 7. Hammett plot for the *Z*-*E* isomerization of 4-X-azobenzenes in water.

In the presence of micelles V-shaped correlations (Figure 8) were also observed. The CF_3 derivative is probably the deviant compound as its departure can be accounted for by the inversion of the relative dipole moments (Table 2) of the two isomers with respect to the dipole moments of the other substrates. This inversion could favor different interfacial solubilization and orientation which in turn could affect the rate of isomerization of the CF_3 derivative. It is interesting to note that a similar departure was not observed in homogeneous solvents, particularly in ethanol, which do not impose steric and/or orientation constraints to the substrate. The different behavior of the CF_3 derivative in homogeneous and micro-heterogeneous systems points out that interfacial solubilization cannot be easily approximated by measurements in mixtures of homogeneous polar and nonpolar solvents as previously suggested.[15]

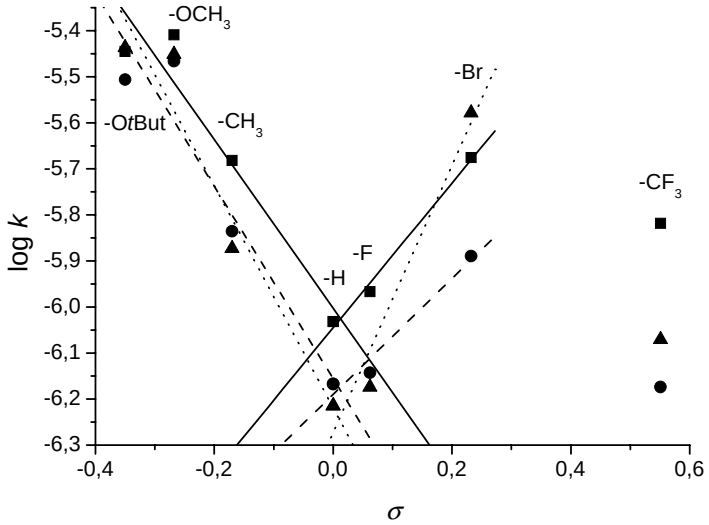


Figure 8. V-shaped Hammett plot for 4-X-azobenzenes in $C_{12}E_8$ (squares, solid line), SDS (circles, dashed line) and C_{12}TAB (triangles, dotted line) micelles.

From the different slopes of the two limbs of V-shaped plots it seems possible to derive a species independent indication of the solvent effect on the inversion (positive ρ) and the rotational (negative ρ) mechanisms (Table 3). By comparing the negative ρ values for the rotation mechanism it appears that the sensitivity of the rates of isomerization to the change of the substituent increases upon increasing the polarity of the solvent in agreement with an increased stability of the dipolar transition state. The oddly low ρ value in benzene ($\rho \approx$ -2.3) calculated from literature data could be due to additional contribution of π–π interactions between the solvent molecules and azobenzenes. The dependence of the rate constants of the polarity of the solvent is consistent with the recently observed correlation[15] of the isomerization rates with the dipole moment of the solvent molecules. On passing from homogeneous to micro-heterogeneous solvents azobenzenes will experience a different environment that depends upon the interfacial structure, the packing of the surfactant in the micelles and the degree of penetration of the probe. The obtained ρ values for electron releasing groups decrease significantly with respect to ethanol ($\rho \approx$ -1.6) for charged micelles (CTAB, $\rho \approx$ -2.4 and SDS, $\rho \approx$ -2.1) while the decrease is small for non-ionic micelles ($\rho \approx$ -1.8).

This fact comes as no surprise and appears to be a good starting point for a comprehensive classification of the polarity of different micro-heterogeneous environments.

What appears quite interesting is the not previously highlighted different behaviour in homogeneous and heterogeneous systems associated to the inversion mechanism. We think that the highly positive ρ values observed in micelles are related to an enhanced orientation and consequently different mobility of the investigated substituted azobenzene in the micellar interfacial region as opposed to the nearly zero ρ values measured in ethanol and methanol (Figure 6).

Table 3. ρ Values obtained from the Hammett plot of log k_{obs} (or log k_0 in the case of water) against σ

Solvent	$\rho_{rotation}$ (correlation coefficient)	$\rho_{inversion}$ (correlation coefficient)
water	-2.0±0.5 (0.9021)	
MeOH	-1.5±0.5 (0.8899)	0.12±0.23 (0.3502)
EtOH	-1.6±0.5 (0.9227)	0.10±0.05 (0.8071)
benzene	-2.3±0.2 (0.9946)[a]	≈1.0[b]
$C_{12}E_8$	-1.8±0.4 (0.9619)	1.6±0.1 (0.9961)
SDS	-2.1±0.4 (0.9606)	1.3±0.2 (0.9838)
CTAB	-2.4±0.4 (0.9725)	2.9±0.6 (0.9793)

[a]ρ value obtained from literature value[29] (i.e. OCH_3, CH_3 and unsubstituted azobenzene). [b]ρ value obtained from only two literature[29] data points (i.e. unsubstituted and Br-substituted azobenzene).

Conclusions

The *E-Z* isomerization of azobenzene and monosubstitued azobenzenes bearing an electron-donating or a withdrawing group in the *para* position has been studied in methanol, ethanol, micellar solution and in methanol/water mixtures. A changeover of the mechanism of isomerization from rotation to inversion has been observed on passing from electron-releasing to electron-withdrawing groups in all the investigated media, the only exception being water, where only rotation, for all the investigated substrates, has been detected. The *E-Z* isomerization in micelles can be hopefully used as a model reaction for probing the polarity of the water-surfactant interface by means of the reaction constants ρ obtained by the corresponding Hammett plot.

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