Preferential solvation and molecular orbital calculation studies of solvatochromic mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives

A. Taha†*[a] and A. Mageed Kiwan[b]

[a] *Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt*
[b] *Department of Chemistry, Faculty of Science, UAE University, Al-Ain, United Arab Emirates*

Received (in Montpellier, France) 12th October 2000, Accepted 23rd November 2000
First published as an Advance Article on the web 13th February 2001

Solvent effects on the electronic spectra of some mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives were investigated in thirteen pure solvents and eight water–organic solvent mixtures. In pure solvents, the solvatochromic shifts of the mesoionic compounds are found to be mainly influenced by the AN, α and π^* solvent parameters. The relative contributions of these parameters depend on the nature of the substituents on the phenyl moieties of the mesoionic derivatives. Thus, electron-donating substituents increase the relative contribution of both AN and α parameters but decrease the relative contribution of the π^* parameter. The behavior of the mesoionic derivatives in water–organic solvent mixtures has been explained in terms of preferential solvation. Different criteria were considered to evaluate the extent of preferential solvation in different solvent mixtures, *viz.* the excess function ($\Delta\nu$), *iso*-solvation point (X^{iso}) and preferential solvation constant (K). Three distinct preferential solvation patterns for the mesoionic derivatives in different water–organic solvent mixtures were elucidated: negative deviation in water–alcohol and water–Py, positive deviation in water–Me_2CO and water–DMF, and a dual behavior in water–MeCN and water–Diox solvent mixtures. Molecular orbital calculations have been carried out for the mesoionic derivatives and the data correlated with the experimental results.

Solvation has always attracted much attention as it plays a major role in all phenomena taking place in the liquid phase. Different solvent parameters have been proposed over the years to express various solvent properties.[1] They have been used to explain the variation of different properties of a given solute with solvent changes.[1,2] In many cases, it has been found that solute properties depend on more than one solvent parameter.[1]

Although various types of solute–solvent interactions have been noted to contribute to the solute solvation in pure solvent,[3] the field of binary solvent mixtures has been much less explored. The non-linear behavior (non-ideality) of some properties of a solute in mixed solvents as a function of solvent mol fraction has been termed preferential solvation[4] and has been used on a number of occasions to make deductions concerning solvation of the solute. The preferential solvation of a solute in a mixed solvent has been one of the most important properties for explaining spectroscopic, equilibrium and kinetic data[5–9] and is also utilized in chemical technology.[10–12] In water–organic solvent mixtures hydrogen bonding, hydrophobic and dipole–dipole interactions lead to the formation of clusters instead of free movement of the solvent.[13–18]

Mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate compounds are known to exhibit solvatochromism.[19–21] This behavior motivated us to use this class of compounds as a good probe to provide insight into the experimental approach to understanding the preferential solvation phenomenon.

One aim of the present work was to discuss the effect of pure solvent on the UV/visible spectral data of some mesoionic derivatives. Another aim was to study the role of preferential solvation on their UV/visible spectra in water–organic solvent mixtures. Finally, molecular orbital calculations were carried out for the mesoionic derivatives and the data correlated with the experimental results.

Experimental

Chemicals and measurements

The reagents used were Merck and Aldrich chemicals and the solvents were purified using standard methods.[22,23]

The UV/visible absorption spectra of 2.5×10^{-5} M solutions of the mesoionic compounds in thirteen pure solvents and eight water–organic solvent mixtures were measured with a Jasco V-550 spectrophotometer equipped with a thermoelectric cell holder. These mixtures were formed by combining water with acetonitrile (MeCN), 1,4-dioxane (Diox), acetone (Me_2CO), *N*,*N*-dimethylformamide (DMF), ethanol (EtOH), 2-propanol (2-PrOH), methanol (MeOH) or pyridine (Py), and the temperature was kept at $25 \pm 0.02\,^{\circ}C$.

Preparation of mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolates

The mesoionic derivatives investigated here were prepared according to the method used by Ogilvie and Crowin,[24] and the synthesis of 2,3-diphenyl-2*H*-tetrazolium-5-thiolate (2-H), as reported elsewhere,[21] is given as an example. Dithizone (1,5-diphenyl-3-mercaptoformazan; 1 g, 4.0 mmol) was dissolved in chloroform (300 mL) and the solution was mixed with an aqueous ammonia solution (200 mL of 1 : 100 v/v). The mixture was stirred mechanically while an equimolar amount (relative to dithizone) of a 6% solution of hydrogen peroxide was added dropwise over 10 min. After the mixture had been stirred for an additional 1 h the organic layer was separated off and allowed to evaporate at room temperature.

---

† Present address: Chemistry Department, Faculty of Science, UAE University, P.O. Box 17551, Al-Ain, United Arab Emirates. E-mail: A.Taha@uaeu.ac.ae.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2001

The orange residue was crystallized from hot ethanol and had an mp of 174 °C (decomp.). Anal. found: C 61.53, H 3.84, N 22.13, S 12.58; calc. for $C_{13}H_{10}N_4S$: C 61.40, H 3.96, N 22.03, S 12.61%.

Results and discussion

Spectroscopic studies

Pure solvents. A procedure was used for the treatment of the experimental results in which the shift of the ν_{max} values of a series of mesoionic derivatives measured in thirteen pure solvents was first correlated individually with each one of the solvent parameters (π^*, α, β, AN, DN, *etc.*) to assess them for their ability to provide a reasonable explanation (the solvents used and their parameters are given in Table 1). Then, to provide an independent interpretation of the ν_{max} results in different pure solvents, the linear solvation energy relationship (LSER) multi-parameter method, based on that of Kamlet *et al.*,[25] was performed using two, three or four solvent parameters for a given solvent. Finally, a conclusion was reached by taking into account only those parameters that gave satisfactory linear regressions. A binary correlation for the solvents studied in this work was previously performed where one solvent parameter was used against another of the same kind and showed that the pairs α, AN and β, DN are essentially orthogonal to each other.[1] Good multi-parametric correlations were obtained when two solvent parameters were considered. The general relationship can be expressed by eqn. (1):

$$\nu_{max} = \nu^0_{max} + aX_1 + bX_2 + cX_3 + \ldots \qquad (1)$$

where ν^0_{max} is the value of ν_{max} in a solvent for which the properties X_i are zero for all i,[26a] X_1, X_2 and X_3 are different

Table 1 Summary of solvent parameters,[a] static dielectric permittivity ε_g, donor (DN) and acceptor (AN) numbers, solvatochromic parameters (π^*, β and α) and polarity $E_T(30)$[a] of the pure solvents at 25 °C

Solvent	ε_g	DN	AN	π^*	β	α	$E_T(30)$
$MeCO_2Et$	6.0	17.1	9.3	0.55	0.45	0.00	38.1
Py	12.3	33.1	14.2	0.87	0.64	0.00	40.5
Me_2CO	20.5	17.0	12.5	0.71	0.43	0.08	42.2
$CHCl_3$	4.7	4.0	23.1	0.58	0.10	0.20	39.1
MeCN	36.0	14.1	18.9	0.75	0.40	0.19	45.6
$MeNO_2$	36.7	2.70	20.5	0.85	0.06	0.22	46.3
Diox	2.2	14.3	10.3	0.55	0.37	0.00	36.0
Formanide	109.5	24.0	39.8	0.97	0.48	0.71	56.6
DMF	36.7	26.6	16.0	0.88	0.69	0.00	43.8
2-PrOH	18.3	36.0	33.5	0.48	0.84	0.76	49.2
EtOH	24.3	32.0	37.1	0.54	0.75	0.86	51.9
MeOH	32.6	30.0	41.3	0.60	0.66	0.98	55.4
Water	78.5	18.0	54.8	1.09	0.47	1.17	63.1

[a] All solvent parameters were taken from ref. 1, except ε_s and E_T, which were taken from ref. 9.

Table 2 Parametric solvent coefficients of mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives[a] obtained from the multi-parametric equation: $\nu_{max} = \nu^0_{max} + a\pi^* + b\alpha$

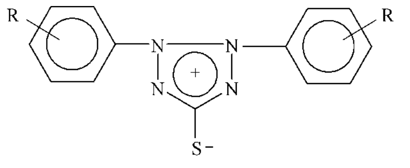
					Relative contribution (%)	
Compound	$\nu^0_{max}/10^3\ cm^{-1}$	a	b	r	π^*	α
2-H	19.81(0.35)[b]	2.07(0.47)	4.53(0.22)	0.98	31.4	68.6
2-Cl	20.06(0.29)	1.90(0.39)	4.52(0.18)	0.99	29.6	70.4
2-F	19.64(0.23)	2.17(0.28)	3.52(0.13)	0.98	38.1	61.9
4-F	19.89(0.28)	2.21(0.35)	3.35(0.16)	0.98	40.0	60.0
2-Me	20.16(0.22)	2.01(0.29)	4.28(0.14)	0.99	31.9	68.1
4-Me	20.41(0.24)	1.86(0.32)	4.58(0.15)	0.99	28.9	71.1
2-OMe	20.92(0.39)	1.83(0.51)	3.86(0.22)	0.98	32.2	67.8

[a] 3-Derivatives give very similar data to the 2-derivatives. [b] Values in parentheses are standard deviations.

Table 3 Parametric solvent coefficients of mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives obtained from the multi-parametric equation: $\nu_{max} = \nu^0_{max} + a\pi^* + b\mathrm{AN}$

					Relative contribution (%)	
Compound	$\nu^0_{max}/10^3\ cm^{-1}$	a	b	r	π^*	AN
2-H	19.55(0.14)[a]	0.98(0.30)	5.81(0.27)	0.99	14.6	85.5
2-Cl	19.82(0.38)	0.74(0.40)	5.86(0.3)	0.98	11.2	88.8
2-F	19.30(0.28)	1.09(0.33)	4.90(0.25)	0.99	18.2	81.8
4-F	19.23(0.39)	1.49(0.47)	4.77(0.36)	0.97	23.8	76.2
2-Me	19.80(0.29)	0.74(0.40)	5.86(0.27)	0.99	11.2	88.8
4-Me	20.05(0.27)	0.66(0.37)	6.08(0.27)	0.99	9.8	90.2
2-OMe	20.76(0.35)	0.53(0.52)	5.22(0.37)	0.98	9.2	90.8

[a] Values in parentheses are standard deviations.



R = 2-H, 2-Cl, 2-F, 4-F, 2-Me, 4-Me, 2-OMe, 3-Me or 3-Cl

Scheme 1 The mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives used in this work.

solvent parameters, and *a*, *b* and *c* are the coefficients of X_1, X_2 and X_3, which can be obtained by multiple linear regression analysis.

The shift of the ν_{max} values was correlated at first with polarity-polarizability (π^*). The correlations were found to be unsatisfactory (correlation coefficients $r \approx 0.12$). On the other hand, when the acidity scale (α) or the acceptor number (AN) parameters of Mayer *et al.*[26b] were correlated individually with the ν_{max} values, relatively good correlations ($r \approx 0.90$) were obtained. However, multi-parameter correlations gave further improvement ($r \approx 0.98$). Correlations of ν_{max} with the π^* and α solvatochromic parameters of Kamlet *et al.*[25] are given in Table 2 with multiple correlation coefficients *r* in the range 0.975–0.99. The relative percentage influences of π^* and α on the ν_{max} values were calculated directly from the coefficients of π^* and α and found to be in the ranges 29–40 and 60–71%, respectively. Another multi-parametric correlation was applied by involving the β parameter[1] as an independent variable. However, the multiple correlation coefficient did not significantly differ from that obtained with the two parameters π^* and α. The relative influence of each one of the solvatochromic parameters on the ν_{max} values of the mesoionic derivatives was found to be 57–67, 21–37 and 6–11% for the α, π^* and β parameters, respectively. These results suggest that the

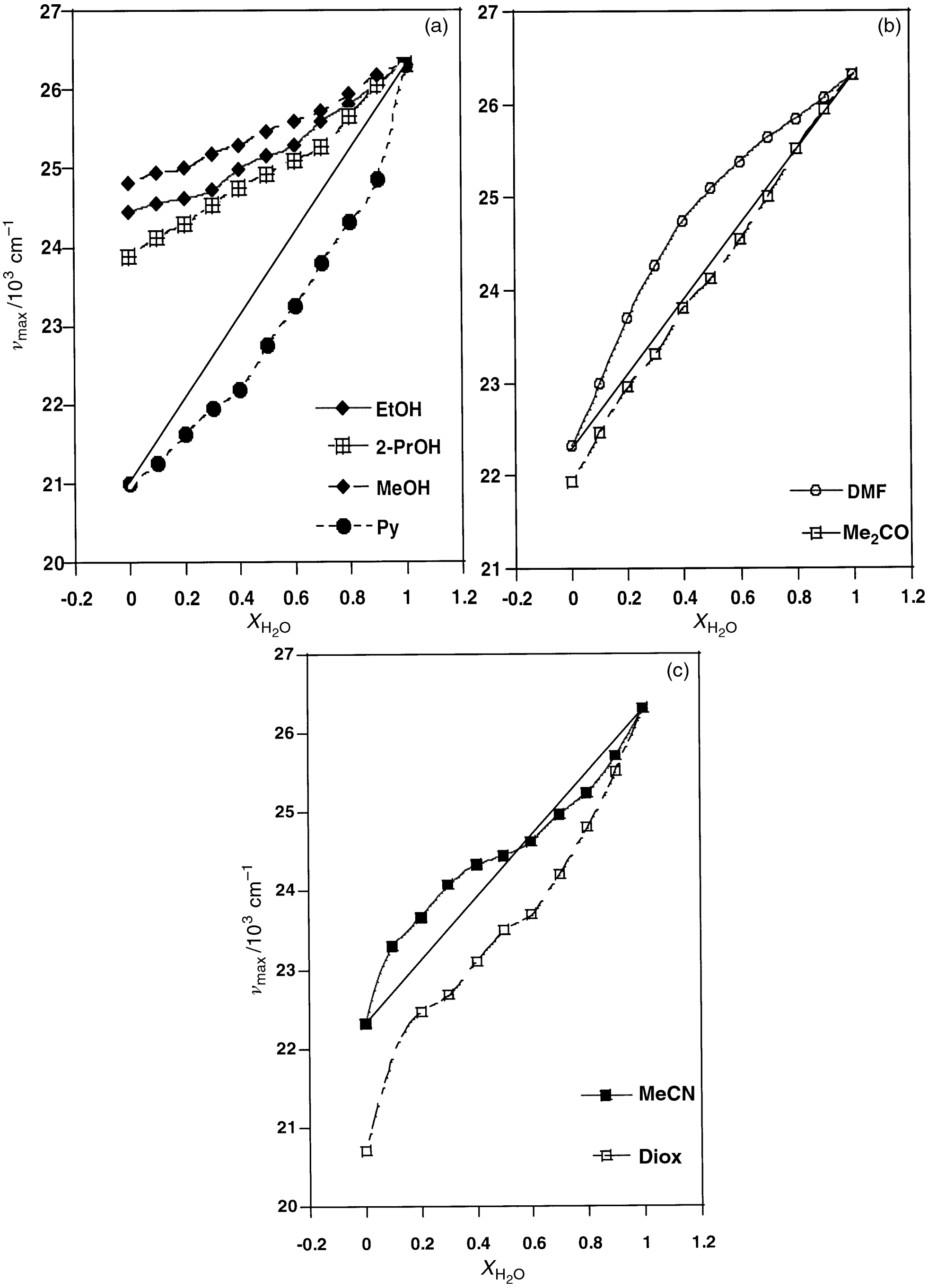


Fig. 1 Dependence of the ν_{max} values of the 2-H mesoionic derivative on the bulk solution mol fraction of water (X_A) in (a) water–alcohol and water–Py solvent mixtures, which show a negative deviation, (b) water–DMF and water–Me$_2$CO mixtures, which show a positive deviation, and (c) water–MeCN and water–Diox mixtures, which show dual behaviour.

Table 4 Excess function $\Delta\nu$ of the mesoionic 2,3-diphenyl-2*H*-tetrazolium-5-thiolate (2-H) in water–organic solvent mixtures at different mol fractions (X_A) of water calculated from the equation $\Delta\nu = \nu_{Exp} - \nu_{linear}$

	$\Delta\nu/10^3$ cm^{-1}							
X_A	MeCN	Diox	DMF	Me_2CO	EtOH	2-PrOH	MeOH	Py
0.1	0.57	—	0.27	0.10	−0.09	0.006	−0.02	−0.36
0.2	0.54	0.65	0.58	0.15	−0.20	−0.07	−0.11	−0.52
0.3	0.55	0.30	0.75	0.06	−0.29	−0.08	−0.07	−0.71
0.4	0.41	0.15	0.83	0.13	−0.21	−0.10	−0.11	−0.72
0.5	0.13	−0.01	0.77	0.01	−0.23	−0.17	−0.09	−0.38
0.6	−0.09	−0.37	0.66	−0.02	−0.28	−0.24	−0.11	−0.69
0.7	−0.15	−0.42	0.52	0.00	−0.17	−0.32	−0.14	−0.75
0.8	−0.27	−0.38	0.32	0.07	−0.13	−0.18	−0.09	−0.96
0.9	−0.21	−0.24	0.15	0.06	−0.06	−0.03	−0.01	−0.94
$\Sigma\Delta\nu$	2.20	1.10	4.87	1.42				
	−0.72	−1.43			−1.66	−1.18	−0.74	−5.32

influence of the β term on the ν_{max} values may be considered negligible. From the data in Table 2, it can be deduced that the capability of mesoionic derivatives to form hydrogen bonds with proton donor solvents (as measured by the α term) plays an important role in determining the shift of the ν_{max} values. The positive sign of the α coefficients (Table 2) indicates that the hydrogen bond formed by the mesoionic derivatives in protic solvents may stabilize the ground state rather than the excited state, resulting in a hypsochromic shift.

Another good correlation was also found when π^* and AN parameters were used as independent variables; the results obtained are collected in Table 3. These results demonstrate that both solvent Lewis acidity (measured by AN) and π^* parameters are important to explain the observed variation in the shift of the ν_{max} values of the mesoionic derivatives with the solvent nature, with relative contributions of 76–91 and 9–24% for AN (using the normalized AN^N, the coefficient of AN was multiplied by 54.8)[1] and π^*, respectively. When the donor number (DN) of Gutmann, which measures the electron-donor ability of the solvent[27,28] was included in the correlation, the multiple correlation coefficients did not significantly differ from those obtained when only π^* and AN were considered. When the three independent variables were taken into account the relative contributions for AN, π^* and DN were in the range 70–88, 8–19 and 4–11%, respectively. These results suggest negligible influence by the DN term on the shift of the ν_{max} values. The positive sign of the π^* coefficient as shown in Table 3 suggests that the ground state is more polar than the excited state. This correlates well with the spectral data of the mesoionic compounds, if one assumes that the C–S group of the mesoionic compound plays an important role in the electronic transition responsible for the long-wavelength absorption band and therefore its solvatochromic behavior. This seems an entirely reasonable assumption since the transition involved is likely to be an intermolecular charge-transfer transition involving the $C^{\delta+}–S^{\delta-}$ group and the delocalized π-electron system of the tetrazolium ring of the mesoionic derivative (see Scheme 1).[20] The longest wavelength band was assigned as an n–π^* transition,[3,12] therefore, as the polarity-polarizability (π^*) of the solvent increases, the ground state is more stabilized than the excited state. This produces a hypsochromic shift of the absorption band (positive π^* coefficient). Furthermore, the positive AN coefficients indicate that the mesoionic compounds are able to donate an electron pair (or a negative charge) to a solvent that has a high Lewis acidity.[29] Therefore, Lewis acid–base interactions of the mesoionic compound with the solvent molecules would also stabilize the ground state more than the excited state, resulting again in a hypsochromic shift of the absorption band.

The quality of the fits obtained with the presented multiparametric correlations for all mesoionic derivatives in the current study is similar. On the basis of these results, it could be concluded that both the solvent electron-accepting character (AN), or capability to donate a proton in a solute–solvent hydrogen bond (α), as well as the solvent polarity-polarizablity (π^*) properties are the most important factors necessary to explain the dependence of the shift of ν_{max} values on the nature of the solvent. The relative contributions of these correlations (Tables 2 and 3) suggest that the shifts of ν_{max} depend mainly on the AN and α parameters rather than the π^* parameter. Moreover, the relative contributions of the AN, α and π^* parameters on the shifts of ν_{max} were affected by the nature of the substituents on the phenyl moieties of the mesoionic derivatives (Scheme 1). Thus, the mesoionic derivatives that have electron-withdrawing substituents (2-F, 3-F, 2-Cl and 2-OCH_3), except 2-OMe and 2-Cl, which have a higher mesomeric effect that might lead to the opposite trend, show, in general, lower relative contributions for the AN and α parameters than those containing electron-donating substituents (2-Me, 3-Me and 4-Me); relative contributions for the π^* parameter show the opposite trend. Furthermore, linear correlations of ν^0_{max} values from Tables 2 and 3 are obtained with the Hammett σ constant ($\nu^0_{max}/10^3$ cm$^{-1} = 19.53 - 0.40\sigma$, $r = 0.998$ and $\nu^0_{max}/10^3$ cm$^{-1} = 19.6 - 0.80\sigma$, $r = 0.97$, for Tables 2 and 3, respectively). Supporting this, the electronic transitions of the mesoionic derivatives are highly influenced by the substituents on the phenyl moieties. The negative slopes reflect the observation that the electron-withdrawing substituents lead to hypsochromic shifts.

Binary solvent mixtures. Fig. 1 shows a representative example for the shift of the ν_{max} values of the parent mesoionic derivative (2-H) in eight water–organic solvent mixtures *vs.* the mol fractions of water (X_A). The non-linear dependence of the ν_{max} values on X_A in the bulk solution mixtures indicates preferential solvation.[4] The deviation from ideality was ascribed to the specific interactions between, and of the mesoionic compound with, the components of the solvent mixture.[30] The extent and type of the preferential solvation can be obtained from the magnitudes and signs of the departure of the experimental shift of ν_{max} values from the ideal linear variation. Fig. 1 shows three distinct patterns of preferential solvation for the mesoionic compound 2-H in water–organic solvent mixtures: (a) a negative deviation in water–alcohol (EtOH, 2-PrOH and MeOH) and water–Py, (b) a positive deviation in water–Me_2CO and water–DMF, and (c) dual behavior, with both positive and negative deviations, in water–MeCN and water–Diox solvent mixtures.

Different criteria were used to evaluate the preferential solvation of the mesoionic compounds in different water–organic solvent mixtures, *viz.* the excess function ($\Delta\nu$), *iso*-solvation point (X^{iso}) and preferential solvation constant (K).

Table 5 Preferential solvation parameters of the mesoionic 2,3-diphenyl-2*H*-tetrazolium-5-thiolate (2-H) in different water–organic solvent (A–B) mixtures at 25 °C

Solvent mixture	Deviation	X_A^{iso}	$K_{A/B}$	$\Sigma\Delta\nu/10^3$ cm^{-1}
H_2O–MeCN	d[a]	0.82, 0.13	1.18, 0.56	2.20, −0.72
H_2O–Diox	d	0.78, 0.18	1.23, 0.56	1.10, −1.43
H_2O–DMF	+	0.70	1.75	4.87
H_2O–Me_2CO	+	0.59	1.51	1.42
H_2O–EtOH	−	0.34	0.81	−1.66
H_2O–2-PrOH	−	0.40	0.77	−1.18
H_2O–MeOH	−	0.41	0.75	−0.74
H_2O–Py	−	0.40	0.61	−5.32

[a] d indicates dual behavior (+, −).

The excess function ($\Delta\nu$) values were calculated according to the following equation:

$$\nu_{\mathrm{Exp}} = X_A \nu_A^0 + X_B \nu_B^0 + \Delta\nu \tag{2}$$

where X_A and X_B are the mol fractions of the solvents A (water) and **B** (organic); ν_A^0 and ν_B^0 are the $\nu_{\max}$ in pure solvents A and **B**. The calculated results are given in Table 4; these data illustrate the negative deviations ($-\Delta\nu$) for the mesoionic compound 2-H in water–alcohol and water–Py solvent mixtures (Fig. 1a), designating preferential solvation by the organic component. Positive deviations ($+\Delta\nu$) have been observed for the mesoionic compound in water–DMF and water–Me_2CO solvent mixtures (Fig. 1b), indicating preferential solvation by water. Dual behavior has been observed for the mesoionic compound in water–MeCN and water–Diox solvent mixtures (Fig. 1c), that is positive $\Delta\nu$ values at low mol fractions of water and negative ones at higher mol fractions of water, suggesting that the mesoionic compounds are preferentially solvated by water first (at low mol fractions of water) then by the organic component at high mol fractions of water.

The extent of preferential solvation can be evaluated from the $\Sigma\Delta\nu$ values, which gives the following results. (a) The extent of preferential solvation by the alcoholic component increases in the order: EtOH > 2-PrOH > MeOH. This trend was ascribed to the increase of the hydrophobicity with increasing size of the hydrophobic alcohol group[31] methyl < ethyl < *iso*-propyl (although *iso*-propyl has a steric effect that might decrease its interaction with the mesoionic compound). (b) The preferential solvation of the mesoionic compound 2-H produced by water is greater in the presence of DMF than Me_2CO as co-solvent. (c) The extent of preferential solvation by water is higher in the presence of MeCN than Diox, at low mol fractions of water. In contrast, at high mol fractions of water the extent of preferential solvation by the organic component is higher with Diox than with MeCN. This might be attributed to the greater ability of MeCN, compared to Diox, to form a hydrogen bond with water as indicated from their α values (see Table 1). Moreover, the transition point found at $X_A \approx 0.5$ and 0.6 for Diox and MeCN, respectively, indicates that the behavior of water as a preferential solvent for the mesoionic compound extends to higher mol fractions in MeCN than in Diox.

The *iso*-solvation point X^{iso}), refers to the solvent composition at which $\nu_{\max}$ of the mesoionic derivatives in different water–organic solvent mixture lies midway between those of $\nu_{\max}$ in pure solvent components.[32] The calculated X_A^{iso} values are given in Table 5; X_A^{iso} values are found to be less than 0.5 in water–alcohol and water–Py solvent mixtures, indicating that the mesoionic compound is preferentially solvated by the organic component,[33] Fig. 1a. However, preferential solvation occurs by water in water–Me_2CO and water–DMF solvent mixtures, since $X_A^{iso} > 0.5$, Fig. 1b. The magnitude of the solvation by water in the presence of DMF is higher than in Me_2CO co-solvent.

The preferential solvation constant ($K_{A/B}$) values for the mesoionic derivatives in different water–organic solvent mixtures by one solvent over the other were calculated on the basis of the thermodynamic model of Frankel *et al.*,[4] according to the following equation:

$$K_{A/B} = \frac{(X'_A/X'_B)_{\mathrm{solvation}}}{(x_A/x_B)_{\mathrm{bulk}}} \tag{3}$$

Here, x_A and x_B represent the mol fractions of components A and **B** in the solvation shell and X_A and X_B refer to the same quantity in the bulk solvent mixture. According to this equation, the plot of x_A/x_B *vs.* X_A/X_B will give a straight line of slope *K*, which represents the preferential solvation constant. Considering that the spectra of the mesoionic derivatives reflects the solvation shell instead of the bulk solvent composition, it is possible to estimate x_A/x_B directly from the plots of Fig. 1. For a given solvent composition, X_A, the measured spectrum corresponds to an effective composition x_A to be determined at the intercept of a horizontal line, extending from the *y*-axis and parallel to the *x*-axis with a diagonal straight line from $X_A = 0$ to $X_A = 1$, as in a typical phase diagram procedure.[4] Preferential solvation constant ($K_{A/B}$) values are given in Table 5, showing $K_{A/B} < 1$ in water–alcohol, water–Py and at high mol fractions of water in water–MeCN and water–Diox solvent mixtures, indicating

Table 6 Preferential solvation parameters of 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives in Me_2CO and EtOH at 25 °C

	X_A^{iso}		$K_{A/B}$		$\Sigma\Delta\nu/10^3$ cm^{-1}	
Compound	Me_2CO	EtOH	Me_2CO	EtOH	Me_2CO	EtOH
2-H	0.59	0.34	1.51	0.66	1.42	−1.66
2-Cl	0.66	0.26	1.73	0.45	1.85	−2.43
2-F	0.52	0.25	1.88	0.38	2.18	−2.52
4-F	0.72	0.21	1.74	0.33	2.51	−3.14
2-Me	0.66	0.28	1.66	0.30	1.41	−2.62
4-Me	0.66	0.24	1.47	0.46	2.24	−3.38
2-OMe	0.69	0.28	2.40	2.62	2.74	−2.02

that the mesoionic derivatives are preferentially solvated by solvent **B** (organic component).[34] On the other hand, $K_{A/B} >$ 1 in water–DMF and water–Me_2CO over the whole range of mol fractions as well as at low mol fractions of water in water–MeCN and water–Diox solvent mixtures, indicating preferential solvation by component A (water).

The data in Table 6 suggest that the extent of preferential solvation depends upon the nature of the substituents on the phenyl moieties of the mesoionic compound. Therefore, the electron-withdrawing substituents decrease the extent of preferential solvation by the organic component (B), as indicated from the higher $K_{A/B}$ values, compared with the effect of electron-donating substituents on the phenyl moieties. This might be attributed to the fact that the electron-withdrawing substituents decrease the charge separation in the mesoionic compound, in contrast to the electron-donating substituents (see below). This trend is more pronounced in water–Me_2CO than in water–EtOH solvent mixtures, as a result of the water–organic solvent interaction, which is higher with EtOH than Me_2CO co-solvent, as indicated by their α and β values (Table 1). Hence, the observed shift of the ν_{max} value is a weighted average of the interactions between the mesoionic compound and the components of the solvent mixture, in addition to the solvent–solvent interactions.[30]

The negative deviation of ν_{max} in water–alcohol solvent mixtures might be attributed to the strengthening of water clusters through the substitutional interaction of alcohols with such clusters.[32] Correspondingly, the OH group of the alcohol works as both a hydrogen-bond donor and acceptor as implied from the higher α and β values for alcohols (Table 1). Accordingly, mixing of alcohol with water is an exothermic process,[35] consequently the opportunity of water molecules to solvate the mesoionic compound will be decreased and the number of hydrogen bonds increased. In contrast, the positive deviation observed in water–Me_2CO and water–DMF as well as in low mol fractions of water with Diox and MeCN solvent mixtures, means preferential solvation of the mesoionic compound by water. This could be ascribed to the additional mixing of these solvents with water, since all these organic molecules work only as hydrogen-bond acceptors. These organic molecules cannot incorporate the hydrogen-bonding network of water, as suggested by their lower α values (Table 1), which means that the organic solvent molecules exist in the space between the water clusters. Hence the water clusters become weaker with these organic solvents, observed as an endothermic mixing.[36] So the chance of the water molecules solvating the mesoionic compound will be enhanced as the mol fraction of the organic component of these solvents increases. While the water clusters are still strong at low mol fractions of MeCN or Diox, so the mesoionic derivatives are preferentially solvated by the organic component. Contrary to what was expected, the mesoionic derivatives in water–Py solvent mixtures show a negative deviation rather than positive (like Me_2CO and DMF) because it is a hydrogen-bond acceptor ($\alpha = 0$). Such behavior cannot be explained and requires further investigation.

Molecular orbital calculations

The experimental results were compared with theoretical data, which were obtained from molecular mechanical calculations, on the basis of the semi-empirical PM3 methods of the Alchemy 2000 computer program. The calculated data are given in Table 7. The partial negative charges (Q_S) on the exocyclic sulfur atom of the mesoionic derivatives are found to be linearly correlated with the reported pK_{BH^+},[37] ($Q_S = -0.435 - 0.10pK_{BH^+}$, $r = 0.962$). The negative slope refers to the increase of Q_S values as the basicity of the mesoionic derivative increases. Furthermore, Q_S values are linearly correlated with the Hammett σ constant ($Q_S = -0.26 + 0.03\sigma$, $r = 0.97$). This finding indicates that the partial negative charge (Q_S) on the exocyclic S atom of the mesoionic derivative increases as the electron-donating properties on the phenyl moieties increase. Furthermore, the dipole moment μ values listed in Table 7 are found to be linearly correlated with the Hammett σ constant ($\mu = 6.59 - 5.18\sigma$, $r = 0.98$; Fig. 2). The negative slope refers again to the fact that the charge separation increases as the electron-donating properties of the phenyl moieties of the mesoionic compound increase. In contrast, the calculated HOMO and LUMO energies of the mesoionic derivatives are found to decrease as the electron-donating properties increase ($E_{HOMO} = -7.873 - 0.20\sigma$, $r = 0.943$ and $E_{LUMO} = -2.09 - 0.67\sigma$, $r = 0.985$). This indicates that the factors that increase the charge separation through the mesoionic compound will stabilize the ground state and increase the basicity at the exocyclic S atom; consequently, the sensi-

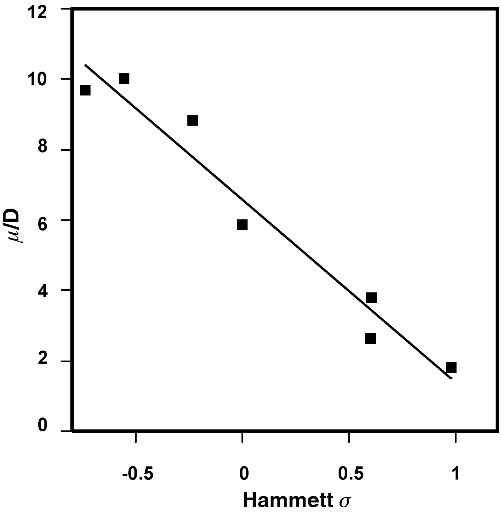


Fig. 2 Dependence of the calculated dipole moment μ of the mesoionic derivatives on the Hammett σ constant.

Table 7 Atomic charges Q, HOMO and LUMO energies and total energy, volume of the molecule V and dipole moment μ calculated by the PM3 method for the mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives

Compound	Q_s/e	E_{HOMO}/eV	E_{LUMO}/eV	E_{tot}/eV	pK_{BH^+} [a]	V/Å^3	μ/D
2-H	−0.26	−7.92	−2.07	−2523	−1.73	217.13	5.89
2-Cl	−0.23	−8.02	−2.16	−3125	−2.05	246.9	1.84
2-F	0.03	−9.11	−1.96	−3374	−1.85	229.07	3.83
4-F	0.02	−9.21	−2.18	−3374	−1.51	228.62	2.67
2-Me	−0.29	−7.75	−1.66	−2822	−1.55	249.00	10.03
4-Me	−0.26	−7.86	−1.98	−2822	−1.13	249.72	11.65
2-OMe	−0.29	−7.65	−1.63	−3409	−1.43	267.34	9.55
3-Me	−0.26	−7.87	−1.99	−2823	−1.76	249.27	10.43
3-Cl	−0.24	−8.04	−2.22	−3126	−1.83	244.12	10.96

[a] Taken from ref. 37.

tivity of the mesoionic compound towards the Lewis acidity of the solvent will increase.

References

1 Y. Marcus, *Chem. Soc. Rev.*, 1993, 409.
2 W. R. Fawcett, *J. Phys. Chem.*, 1993, **97**, 9540.
3 K. Morinaga and K. Miyaji, *Denki Kagakuogubi Kogyo Butsuri Kagaku*, 1982, **50**, 736.
4 L. S. Frankel, C. H. Langford and T. R. Stangle, *J. Phys. Chem.*, 1970, **74**, 1376.
5 J. G. Dawber, J. Ward and R. A. Williams, *J. Chem. Soc., Faraday Trans.*, 1988, **84**, 713.
6 P. Chatteejee, A. K. Laha and S. Bagchi, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1675.
7 N. Papafopoulus and A. Avranas, *J. Solution Chem.*, 1991, **20**, 293.
8 H. Kovacs and A. Laaksonen, *J. Am. Chem. Soc.*, 1991, **113**, 5596.
9 J. G. Dawber, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 287.
10 H. Schneider, in *Solute–Solvent Interactions*, ed. J. Cotes and C. D. Rich, Marcel Decker, New York, 1976, vol. 2, ch. 11.
11 A. K. Covington and K. E. Newman, *Pure Appl. Chem.*, 1979, **51**, 2041.
12 F. Tanaka, Y. Kawasaki and S. Yamashita, *J. Chem. Soc., Faraday Trans.*, 1988, **84**, 1083.
13 N. Nishi, *Z. Phys. D*, 1990, **15**, 239.
14 S. Okazaki, H. Touhara and K. Nakanishi, *J. Chem. Phys.*, 1984, **81**, 890.
15 A. Wakisaka, Shimizu, N. Nishi, K. Tokumaru and H. Sakuragi, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1129.
16 A. Wakisaka, Y. Yamamoto, Y. Akyiyama, H. Takeo, F. Mizukami and K. Sakaguchi, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3339.
17 A. Wakisaka, Y. Akyiyama, Y. Yamamoto, T. Engst, H. Takeo, F. Mizukami, K. Sakaguchi and H. Jones, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3539.
18 A. Wakisaka, *J. Org. Syn. Chem. Jpn.*, 1994, **52**, 478.
19 A. M. Kiwan and H. M. N. Irving, *J. Chem. Soc., B*, 1971, 898.
20 A. M. Kiwan and H. M. Marafie, *J. Heterocycl. Chem.*, 1976, **13**, 1273.
21 A. M. Kiwan and A. Y. Kassim, *J. Heterocycl. Chem.*, 1978, **15**, 133.
22 G. Porter and V. Hanten, *J. Inorg. Nucl. Chem.*, 1979, **18**, 2053.
23 *Autorenkollektiv*, *Organikum*, 16th edn., VEB Deutscher Verlag der Wissenschaften, Berlin, 1986.
24 J. W. Ogilvie and A. H. Crowin, *J. Am. Chem. Soc.*, 1961, **83**, 5023.
25 J. A. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **43**, 2877.
26 (*a*) J. L. M. Abboud and R. Notario, *Pure Appl. Chem.*, 1999, **71**, 645; (*b*) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235.
27 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum Press, New York, London, 1978.
28 V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Lett.*, 1966, **2**, 257.
29 M. B. Moressi, M. A. Zon and H. Fernandez, *Electrochim. Acta*, 1997, **42**, 303.
30 C. Rafols, M. Roses and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1997, 243 and 1341.
31 A. Wakisaka, H. A. Carime, Y. Yamamoto and Y. Akyiyama, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 369.
32 L. S. Frankel, T. R. Stangle and C. H. Langford, *J. Chem. Soc., Chem. Commun.*, 1965, 393.
33 B. F. Shraydeh, M. Abu-Eid and N. Abu-Ghulwah, *Monatsh. Chem.*, 1995, **126**, 631.
34 H. E. Toma and M. S. Takasugi, *J. Solution Chem.*, 1983, **12**, 547.
35 L. Benjamin and G. C. Benzon, *J. Phys. Chem.*, 1963, **67**, 858.
36 K. W. Morcom and R. W. Smith, *J. Chem. Thermodyn.*, 1969, **1**, 503.
37 A. M. Kiwan and G. A. Wanas, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1534.