Preferential solvation studies using the solvatochromic dicyanobis(1,10-phenanthroline)iron(II) complex†

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Solvent effects on the electronic spectra of dicyanobis(1,10-phenanthroline)iron(II) have been investigated in thirteen pure solvents and twenty binary solvent mixtures. In pure solvents, the shifts of the ν_{max} values are found to depend on more than one of the known solvent parameters (AN, α, β, DN and π^*). AN, α and π^* are found to be the most important solvent parameters, exerting a considerable effect on the solvatochromic shifts of the title complex. The preferential solvation of dicyanobis(1,10-phenanthroline)iron(II) in binary solvent mixtures has been investigated by monitoring the metal–ligand charge transfer band of the indicator complex. Organic solvents are preferred near the indicator complex in aqueous binary solvent mixtures (negative deviation), except in regions rich in MeCN, Me_2CO and 1,4-dioxane, where water molecules are preferred over the organic component (dual behavior). However, the indicator complex is preferentially solvated by the component which has the higher acceptor number in non-aqueous binary solvent mixtures. Negative deviation was observed in binary mixtures of $CHCl_3$ and Me_2CO with alcohols and positive deviation in mixtures of $CHCl_3$ with THF, DMSO and Me_2CO. Different criteria were considered to evaluate the extent of preferential solvation in different solvent mixtures, *viz*., the local molar fraction (X_A^L), the excess function (ΔX), the iso-solvation point (X_B^{iso}) and the preferential solvation constant ($K_{A/B}$). The preferential solvation data have been linearly correlated with the different solvent parameters.

Introduction

The study of solute–solvent and solvent–solvent interactions, and how they affect the intimate structure of the solute, has attracted much attention as they play a major role in all phenomena occurring in the liquid phase. In many cases, it has been found that solute properties depend upon more than one solvent parameter.[1,2] Solvent mixtures have become an important subject of research because of their frequent use and the wide field of application they offer.[3–10] The most important feature of these mixed solvents is the gradual variation of properties they show when their composition is gradually modified. Therefore, there is currently considerable interest in the study of physicochemical phenomena in mixed solvent systems and their interpretation in terms of preferential solvation of solutes by one of the component solvents in the mixture.[1,2,11] In connection with this, we have previously studied the preferential solvation of solvatochromic mesoionic 2,3-diaryl-2*H*-tetrazolium-5-thiolate derivatives.[12]

Studying the strong solvatochromicity of the metal-to-ligand charge transfer (MLCT) band of $Fe^{II}(LL)(CN)_2$ complexes,[13–18] where LL = diimine, 1,10-phenanthroline (phen) or 2,2′-bipyridine, enables one to measure the extent of preferential solvation. Although the solvation of $Fe(phen)_2(CN)_2$ in pure solvents has been extensively studied,[19–21] only limited attention has been paid to its behavior in binary solvent mixtures.[22] This is surprising since this compound can be used as a color indicator for providing an insight into the microscopic characteristics of the cybotactic zone of solutes in pure and mixed solvents.

The goal of this study was to monitor the effect of solute–solvent and solvent–solvent interactions on the preferential solvation characteristics. For this purpose, the MLCT bands of $Fe(phen)_2(CN)_2$ in pure and binary solvent mixtures have been used as an indicator solute.

Experimental

Chemicals

The reagents used were Merck and Aldrich chemicals. The water used in all experiments was distilled twice. All organic solvents were of the highest grade available and were purified using standard methods.[23,24]

Synthesis

Dicyanobis(1,10-phenanthroline)iron(II) complex was synthesized according to the reported method,[13] by heating a mixture of 6.0 g of phenanthroline monohydrate (0.03 mol) and 3.90 g of ammonium iron(II) sulfate hexahydrate (0.01 mol) in 400 cm^3 of water, followed by addition of 9.80 g of KCN (0.15 mol) with continuous stirring for 2 h. The obtained product was filtered, then dissolved in 30 cm^3 of concentrated sulfuric acid followed by the addition of 1 dm^3 of bidistilled water. The resulting dark violet crystals were dried *in vacuo* for several hours at 35 °C. The composition of the prepared indicator complex, $Fe(phen)_2(CN)_2 \cdot 2H_2O$ was characterized by elemental analysis, found: C 66.60, H 3.40, N 18.0; calc. for $C_{26}H_{20}N_6O_2Fe$: C 66.69, H 3.44, N 17.95%. Furthermore, IR and magnetic susceptibility measurements were used to

† Electronic supplementary information (ESI) available: tables listing various solvent parameters (Table S1), ν_{max} values (Table S2) and local molar fractions (Table S3). See http://www.rsc.org/suppdata/nj/b1/b104093f/

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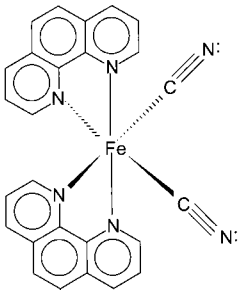


Scheme 1 The structure of the dicyanobis(1,10-phenanthroline)-iron(II) indicator complex.

confirm the proposed structure of the complex. The IR spectrum of a KBr disc of the complex shows the following stretching frequencies: 3430, 2071 and 1628 cm^{-1}, corresponding to ν_{OH}, $\nu_{C\equiv N}$ and $\nu_{C=N}$, respectively.[25] Magnetic susceptibility measurements show that the complex is diamagnetic, which suggests that the indicator complex is low spin octahedral (Scheme 1).

Measurements

The electronic absorption spectra of 2.5×10^{-5} M solutions of the indicator complex in thirteen pure solvents and their binary solvent mixtures were recorded on a Jasco V-550 spectrophotometer equipped with a thermostatted cell compartment and using a cell of path length 1 cm. The solvent mixtures included both aqueous and non-aqueous mixtures. The aqueous binary solvent mixtures were formed by mixing water with acetonitrile (MeCN), 1,4-dioxane (Diox), acetone (Me_2CO), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), ethanol (EtOH), 2-propanol (2-PrOH) and methanol (MeOH). The non-aqueous binary solvent mixtures were obtained by mixing chloroform with EtOH, 2-PrOH, MeOH, DMSO, Me_2CO and tetrahydrofuran (THF), and acetone with EtOH, 2-PrOH, MeOH and DMSO solvents and the temperature was kept at 25 °C. The infrared spectrum in KBr (400–4000 cm^{-1}) was recorded using a Shimadzu FTIR 8101 spectrometer. The magnetic moment was measured using the Gouy method and a Johnson Matthey Alfa Products MSB-MK I magnetic balance.

Results and discussion

Pure solvents

When, the shift of the lowest energy metal-to-ligand charge transfer band (MLCT) of the indicator complex, corresponding to the $t_{2g} \rightarrow \pi^*$ transition, was correlated *vs.* the acceptor number (AN) or Reichard's E_T solvent parameter, two separate lines were obtained for dipolar aprotic solvents and for alcohols. Points for water and carboxylic acids don't fit with any one of these lines. This finding is similar to that of Al-Alousy and Burgess.[19] For that reason, it was of interest to re-examine the present data for the indicator complex solution in thirteen pure solvents using multi-parametric correlations, based on the linear solvation energy relationship (LSER) proposed by Kamlet *et al.*[26] Good multi-parametric correlations were obtained using different combinations of two or three variables. These variables include: π^* (polarity–polarizability), α (hydrogen bond donor ability), β (hydrogen bond acceptor ability), DN (donor number) and AN (acceptor number).[2] The general relationship can be expressed by eqn. (1):

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

where, ν^0_{max} is the value of ν_{max} in a solvent for which the properties X_i are zero for all i,[27] X_1, X_2 and X_3 are different solvent parameters, and a, b and c are coefficients of X_1, X_2 and X_3, which can be obtained by multiple linear regression analysis.

Correlation of ν_{max} values with the π^* and α solvatochromic parameters of Kamlet *et al.*,[26] yields $\nu_{max} = 15.10 + 2.32\alpha + 1.44\pi^*$, $r = 0.99$. The relative percentage influences of α and π^* on the ν_{max} values were calculated as described in previous work[12] and found to be 61.7 and 38.3%, respectively. This correlation demonstrates that the capability of the indicator complex 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 in different solvents. The positive sign of the α coefficient indicates that the hydrogen bonds formed with the indicator complex in protic solvents may stabilize the ground state rather than the excited state, resulting in an hypsochromic shift.

Another good correlation was also found when the π^* and AN parameters were used as independent variables, $\nu_{max} = 15.00 + 3.84AN + 0.385\pi^*$, $r = 0.98$. This result demonstrates the importance of both the solvent Lewis acidity (measured by AN) and π^* parameters to explain the observed variation in the shift of ν_{max} values of the indicator complex, with relative contributions of 91 and 9% for AN and π^*, respectively. The positive sign of the AN coefficient suggests that as the solvent acceptor number increases, the ground state of the indicator complex is preferentially stabilized. This might be attributed to the removal of electron density from the cyanide ligand and increasing π back bonding with the metal ion, leading to hypsochromic shifts in the MLCT bands as a function of AN. This seems an entirely reasonable assumption since the transition involved is likely to be metal-to-ligand charge transfer from the iron coordination center to the π^* orbitals of the phenanthroline ligands.[17] Electron withdrawal due to interaction with Lewis acids thus leads to changes in the σ bonding molecular orbitals (including the e_g levels of the iron), which in turn leads to a deformation of $Fe(phen)_2(CN)_2$ complex and the concomitant p orbitals (including the split t_{2g} levels of the coordination center), thus influencing the energies of the antibonding π^* ligand orbitals.[21] Therefore, as the polarity–polarizability (π^*) of the solvent increases, the ground state is more stabilized than the excited state. This produces an hypsochromic shift of the absorption band (positive π^* coefficient).

The quality fit obtained with the presented multiparametric correlations for the indicator complex is similar to that reported for mesoionic compounds.[12] According to these results, it can be concluded that both the solvent AN and α parameters, as well as the π^* parameter, are the most important factors necessary to explain the dependence of the ν_{max} shift on the solvent nature. The relative percentage contributions of these correlations suggest that the spectral changes in ν_{max} depend essentially on the α and AN parameters rather than the π^* parameter. Hence, the MLCT transition band values of the indicator complex reflect the solute–solvent interaction at the microscopic level, embodying both the specific and non-specific modes of interaction.

Binary solvent mixtures

The shifts in the ν_{max} values of the indicator complex measured in pure solvents and their aqueous and non-aqueous binary solvent mixtures (AB) at various molar fractions of the component A are listed in the ESI (Table S2). The ν_{max} values are shown as a function of the bulk molar fractions of the component A in Fig. 1 and 2. The functional relationship of ν_{max} *vs.* X_A is non-linear for all binary solvent mixtures in the current study. This finding is very similar to the partial vapor pressure with X_A plots for binary solvent mixtures.[28] It is well established that the non-linearity of the ν_{max} *vs.* X_A plots arises due to preferential solvation of the indicator complex, which is

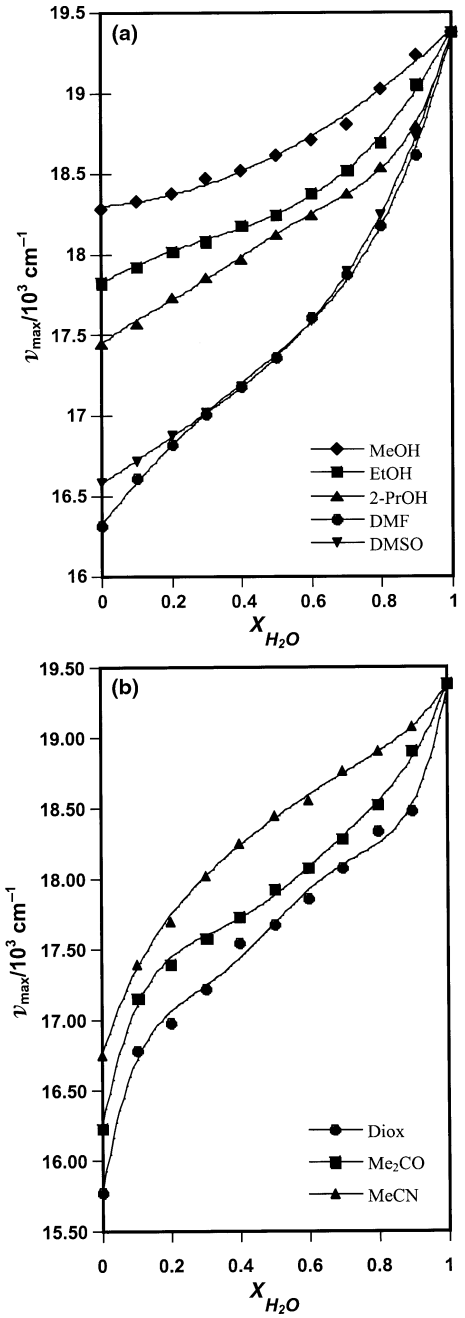


Fig. 1 Dependence of the ν_{max} values of the $Fe(phen)_2(CN)_2$ indicator complex on the bulk solution molar fraction of water (X_A) mixed with (a) EtOH, MeOH, 2-PrOH, DMF and DMSO, and (b) Diox, Me_2CO and MeCN.

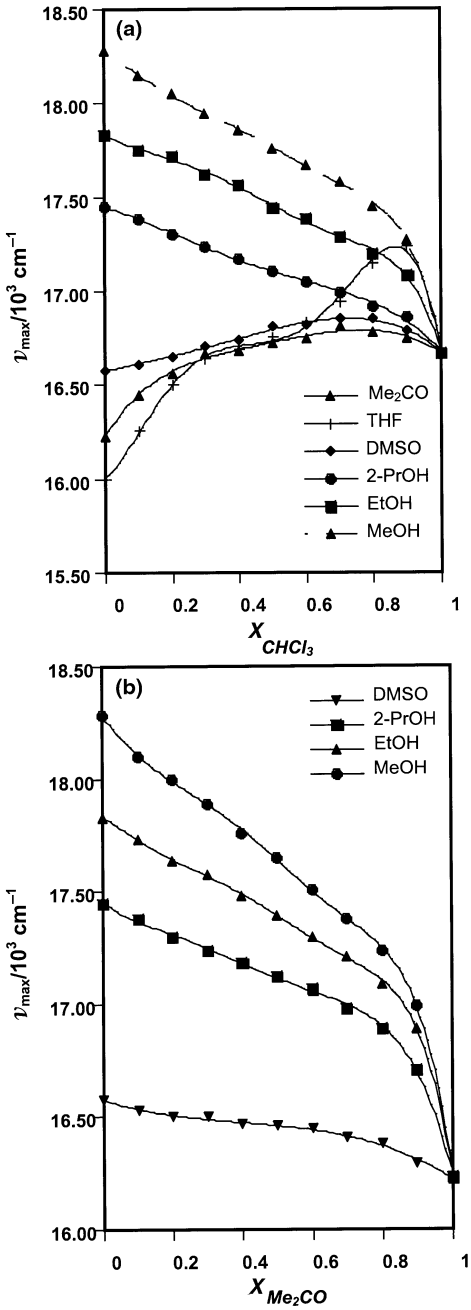


Fig. 2 Dependence of the ν_{max} values for the $Fe(phen)_2(CN)_2$ indicator complex on the bulk solution molar fraction of solvent (X_A) in (a) $CHCl_3$ and (b) Me_2CO binary solvent mixtures.

common, and because it modifies the neighborhood of the solute.[1,2,11,12]

Different criteria were used to assess the type and extent of the preferential solvation of the indicator complex in binary solvent mixtures, *viz.*, the local molar fraction (X_A^L), excess function (ΔX), iso-solvation point (X_B^{iso}) and preferential solvation constant ($K_{A/B}$) parameters.

The local molar fraction of the component solvents can be calculated using the relation[29]

$$X_A^L = 1 - X_B^L = (\nu_{AB} - \nu_B)/(\nu_A - \nu_B) \quad (2)$$

where ν_A and ν_B are the absorption frequencies in the pure solvents. The calculated values of the local molar fractions (X_A^L) are listed in the ESI (Table S3) and the functional relationship of X_A^L *vs.* the bulk molar fractions (X_A) are shown in Fig. 3–5. The deviation from ideality, straight lines which represent the situation where local and bulk molar fractions are the same, is a further indication of the specific interactions of the indicator complex with the components of the solvent mixture.[4,7,30] Two distinct patterns of preferential solvation for the indicator complex are observed in aqueous binary solvent mixtures (Fig. 3), negative deviation and dual behavior. Negative deviation is found in water mixed with alcohols (EtOH, 2-PrOH and MeOH), DMF or DMSO, while dual behavior (positive and negative deviations) is observed in water mixed with MeCN, Me_2CO or Diox. In non-aqueous binary solvent mixtures, negative and positive deviations are observed (Fig. 4 and 5). Negative deviation is found in Me_2CO–alcohol and $CHCl_3$–alcohol binary mixtures. However, positive deviation is observed in chloroform mixed with THF, DMSO or Me_2CO, and faint dual behavior is observed in Me_2CO–DMSO.

The type and extent of deviation from the straight line, excess function (ΔX; $\Delta X = X_A^L - X_A$), may be taken as a

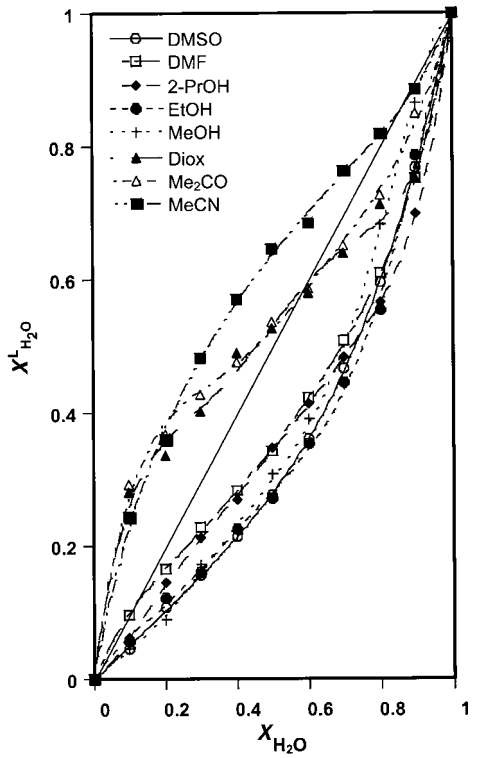


Fig. 3 X_A^L *vs.* X_A for various aqueous binary solvent mixtures, using $Fe(phen)_2(CN)_2$ as an indicator solute. The straight line represents ideal behavior.

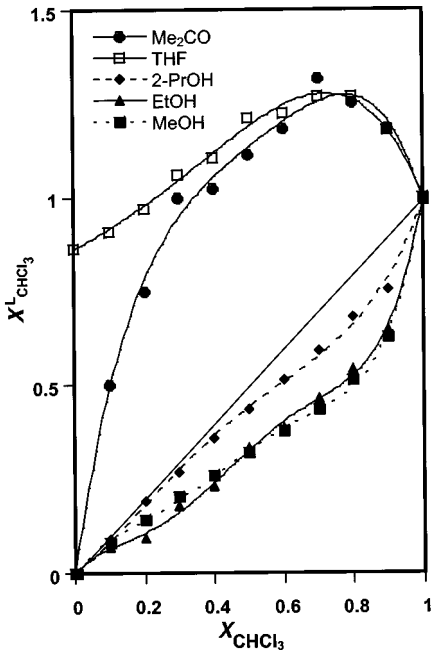


Fig. 4 X_A^L *vs.* X_A for various binary solvent mixtures of $CHCl_3$ with alcohols, THF, Me_2CO and DMSO, using $Fe(phen)_2(CN)_2$ as an indicator solute.

measure of preferential solvation. A positive value of ΔX indicates a preference for component A over component B, while a negative value signifies the reverse. A summation of ΔX values at all fractions can be used to quantify the extent of this preference (*vide infra*).

The iso-solvation point (X^{iso}) refers to the solvent composition in the bulk at which ν_{max} of the indicator complex in the binary solvent mixture lies midway between the ν_{max} values in the pure solvent components.[12] The calculated X_B^{iso} values for the indicator complex in different binary mixtures are given in Table 1. The type and extent of preferential solvation can be ascertained from the X_B^{iso} values. A negative deviation appears when $X_B^{iso} < 0.5$ and a positive deviation occurs when $X_B^{iso} > 0.5$, indicating a preference for component B over component A for the former situation and the opposite trend for the latter.[12] Table 1 shows values of $X_B^{iso} < 0.5$, for the indicator complex in water, $CHCl_3$ or Me_2CO mixed with alcohols, and the mixture Me_2CO–DMSO, indicating preferential solvation by component B.[12,31] However, values of $X_B^{iso} > 0.5$ are found in chloroform mixed with DMF, THF or Me_2CO, and methanol with MeCN or THF, signifying preferential solvation by component A.

A more quantitative estimate of the extent of preferential solvation of the indicator complex in binary solvent mixtures can be made by empolying the preferential solvation parameter $K_{A/B}$, using the thermodynamic model of Frankel *et al.*,[1]

Table 1 Preferential solvation parameters of the $Fe(phen)_2(CN)_2$ complex at various molar fractions of component A in different binary solvent mixtures at 25 °C

Binary solvent mixture (A–B)	$\Sigma\Delta X$		Deviation type	X_B^{iso}		$K_{A/B}$	
	$^+$ve[a]	$^-$ve		$^+$ve	$^-$ve	$^+$ve	$^-$ve
Water–MeOH		1.25	–		0.30		0.69
Water–EtOH		1.52	–		0.25		0.40
Water–2-PrOH		1.30	–		0.28		0.25
Water–DMF		1.09	–		0.31		0.33
Water–DMSO		1.51	–		0.27		0.37
Water–Diox	0.53	0.32	d[b]	0.90	0.11	1.30	0.46
Water–Me_2CO	0.60	0.19	d	0.89	0.15	1.24	0.55
Water–MeCN	0.97	0.01	d	0.75	0.06	1.46	0.67
MeOH–THF	1.04		+	0.69		1.34	
MeOH–MeCN	2.40		+	0.87		3.47	
$CHCl_3$–MeOH		1.53	–		0.22		0.14
$CHCl_3$–EtOH		1.54	–		0.25		0.23
$CHCl_3$–2-PrOH		0.62	–		0.42		0.44
$CHCl_3$–DMSO	13.39		+	0.86		2.76	
$CHCl_3$–THF	5.69		+	0.87		—	
$CHCl_3$–Me_2CO	4.82		+	0.89		4.10	
Me_2CO–MeOH		1.57	–		0.22		0.39
Me_2CO–EtOH		1.90	–		0.17		0.33
Me_2CO–2-PrOH		1.89	–		0.18		0.30
Me_2CO–DMSO		0.99	–		0.29		0.31

[a] $^+$ve preferentially solvated by solvent A; $^-$ve preferentially solvated by solvent B. [b] d dual behavior (+, −).

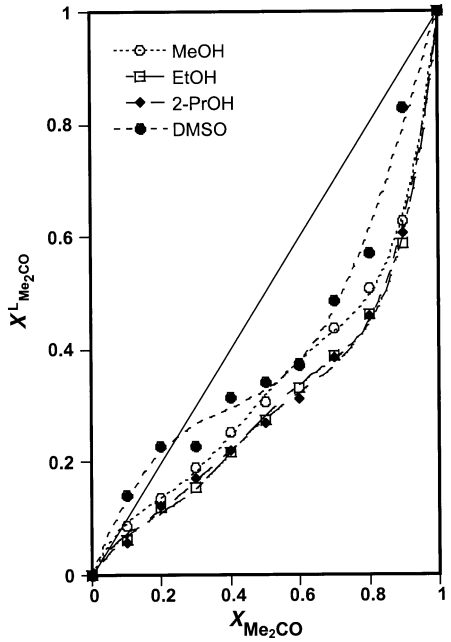


Fig. 5 X^L_A *vs.* X_A for various binary solvent mixtures of Me_2CO with alcohols and DMSO, using $Fe(phen)_2(CN)_2$ as an indicator solute.

according to the following equation:

$$K_{A/B} = \frac{(X^L_A/X^L_B)}{(X_A/X_B)} \quad (3)$$

where X^L_A and X^L_B represent local molar 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. The parameter $K_{A/B}$ measures the tendency of the indicator complex to be solvated with solvent A in comparison to solvent **B**. According to eqn. (3), a plot of (X^L_A/X^L_B) *vs.* (X_A/X_B) will give straight line with slope $K_{A/B}$, which represents the preferential solvation constant. $K_{A/B}$ can be obtained from Fig. 3–5 and the calculated values are given in Table 1. These $K_{A/B}$ values concerning preferential solvation are the same as those discussed above but they do allow a better inter-system comparison to be made. $K_{A/B} < 1$ indicates a preference for component **B** over component A, in contrast, $K_{A/B} > 1$ signifies the opposite trend.[12]

The conclusion given above can be extracted, for the indicator complex, from the data in Table 1. These data show that: (a) $K_{A/B} < 1$ in water, chloroform or acetone mixed with alcohols, water mixed with DMSO or DMF, and the mixture Me_2CO–DMSO, as well as at high molar fractions of water in aqueous mixtures of MeCN, Me_2CO or Diox. (b) Values of $K_{A/B} > 1$ are found in chloroform mixed with DMSO or Me_2CO, and mixtures of methanol with THF or MeCN, as well as at low molar fractions of water in aqueous mixtures of MeCN, Me_2CO or Diox. This indicates preferential solvation of the indicator complex by component **B** in the former case and A in the latter.

All possible combinations have been checked for the calculated preferential solvation parameters $K_{A/B}$, $\Sigma\Delta X$ and X^{iso}_B given in Table 1 using multiple regression analysis. The best fits obtained yield the following: $K_{A/B} = 1.77 + 0.73\Sigma\Delta X - 2.03\ X^{iso}_B$, $r = 0.999$ and $K_{A/B} = 0.66 + 0.06\Sigma\Delta X - 0.82X^{iso}_B$, $r = 0.83$; for non-aqueous and aqueous binary solvent mixtures, respectively. The correlation coefficient values can be used to judge the agreement between the different criteria chosen in the present work. The agreement is very good for chloroform and acetone systems and poor for aqueous systems, indicating the simplicity of the former systems and the complexity of the latter.

It was thought that correlations of the preferential solvation data given in Table 1 *vs.* well-known solvent parameters using multiple linear regression analysis might quantify the role which solvent–solvent interaction plays in the preferential solvation process. Hence, such treatments were carried out, the results of which are collected in Tables 2 and 3. According to the relative percentage contributions of the α, π^* and DN, AN parameters, it can be concluded that the values of $K_{A/B}$ are essentially affected by the hydrogen bond donor ability (α) and acceptor number (AN) parameters of the co-solvent, except for the acetone system, which is mainly affected by the polarity–polarizability (π^*) parameter. However, the $\Sigma\Delta X$ and X^{iso}_B values are found to be mainly affected by the π^* and donor strength (DN) parameters of the co-solvent, except for the chloroform system, which is found to be mainly dependent upon the α and AN parameters.

The positive signs of the AN, DN and α coefficients for the aqueous solvent system suggest that as the values of these solvent parameters increase, the extent of solvent–solvent and solute–solvent interactions increase. This can be ascribed to solvent–solvent interaction, which might lead to the formation of a new solvent species (S_{AB}) *via* donor–acceptor or hydrogen-bonding interactions. This new solvent species could have properties which are quite different from those of pure solvents A and **B**.[30] Scheme 2 suggests possible routes for the formation of S_{AB}; a 1 : 1 molar fraction ratio for solvents A and **B** was assumed for the sake of simplicity. The co-solvent which has a higher DN or lower AN, *e.g.* aprotic solvents, should interact with water according to route (a), which leads to a decrease in the extent of the water cluster. In contrast, the solvent which has a higher acceptor number and lower donor number, *e.g.* protic solvents such as alcohols,

Table 2 Parametric solvent coefficients on the extent of the preferential solvation (PS) of dicyanobis(1,10-phenanthroline)iron(II) complex in binary solvent mixtures, obtained from the multi-parametric equation: $PS = PS_0 + a\alpha + b\pi^*$

						Relative contribution (%)	
PS	System	PS_0	a	b	r	α	π^*
ΔX	aqueous	−1.28	1.35	−1.55	0.92	46.6	53.4
	$CHCl_3$	−6.84	−5.88	19.60	0.98	23.1	76.9
	Me_2CO	−3.22	0.26	2.23	0.97	10.4	89.6
X^{iso}_A	aqueous[a]	−0.12[b]	0.73	0.44	0.99	62.4	37.6
		0.64[c]	3.50	6.28	—	35.8	64.2
	$CHCl_3$	1.15	−0.81	−0.29	0.99	73.8	26.2
	Me_2CO	0.01	0.03	0.28	0.93	10.5	89.5
$K_{A/B}$	aqueous[a]	0.63[b]	1.42	−0.30	0.99	82.7	17.3
		−0.67[c]	7.00	−9.17	—	43.3	56.7
	$CHCl_3$	6.05	−4.75	−2.95	0.92	61.7	38.3
	Me_2CO	−0.04	0.22	0.35	0.98	38.9	61.1

[a] Two distinct types. [b] Protic solvent. [c] Aprotic solvent.

Table 3 Parametric solvent coefficients on the extent of the preferential solvation (PS) of dicyanobis(1,10-phenanthroline)iron(II) complex in binary solvent mixtures, obtained from the multi-parametric equation: $PS = PS_0 + aAN + bDN$

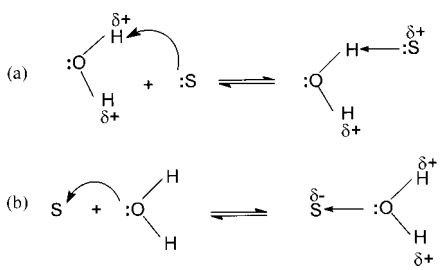
PS	System	PS_0	a	b	r	Relative contribution (%)	
						AN	DN
ΔX	aqueous	1.41	1.64	2.99	0.92	35.4	64.6
	$CHCl_3$	10.70	−12.60	−6.60	0.99	65.6	34.4
	Me_2CO	−5.54	1.70	5.04	0.99	25.2	74.8
X_A^{iso}	aqueous	−0.20	0.18	0.68	0.93	20.9	79.1
	$CHCl_3$	0.59	−1.04	0.84	0.99	55.3	44.7
	Me_2CO	−1.02	−0.73	1.36	0.91	34.9	65.1
$K_{A/B}$	aqueous[a]	−9.12[b]	8.11	4.73	0.98	63.2	36.8
		−0.59[c]	1.12	−0.83	—	57.4	42.6
	$CHCl_3$	6.44	−5.81	2.24	0.99	72.2	27.8
	Me_2CO	0.54	−0.55	0.13	0.92	80.9	19.1

[a] Two distinct types. [b] Protic solvent. [c] Aprotic solvent.

should interact with water molecules according to route (b), which strengthens the water clusters. This interpretation is supported by the data in Tables 2 and 3, which show splitting in the data for the aqueous systems into two groups, aprotic and protic. This finding could explain the complexity found for the aqueous system data.

The preferential solvation data and discussion given above clarify that, for mixed aqueous solvents containing alcohols, DMF and DMSO, the indicator complex is preferentially solvated by the organic component (**B**). Whereas, mixed aqueous solvents containing Diox, Me_2CO and MeCN show dual behavior; the indicator complex is preferentially solvated by water first (at low molar fractions of water), then by the organic component at high molar fractions of water. The preference for the organic component over water, despite water having a higher acceptor number, can be understood in terms of the strong self-association of water through solvent–solvent hydrogen bonding,[32] in addition to the considerably hydrophobic nature of the indicator complex over most of its structure. Furthermore, the water clusters are strengthened through the substitutional interaction of alcohols with these clusters,[12,33] which agrees with the proposed mechanism in Scheme 2 route (b). Consequently, the opportunity for water molecules to solvate the indicator complex will decrease and the number of hydrogen bonds will increase.

For the case of dual behavior, as the percentage of the organic component increases, the self-associated structure of water gradually breaks down and at a high molar fraction of the organic component, preferential solvation by water, through solute–solvent hydrogen bonding, is observed. This may be ascribed to the additional mixing of MeCN, Me_2CO and Diox with water,[34] since all these organic molecules function only as hydrogen bond acceptors, as described by the proposed mechanism in Scheme 2 route (a). These solvents cannot form part of the hydrogen-bonding network of water, as suggested from their lower α values,[2] which means that the organic solvent molecules exist in the space between the water clusters.[12,34] Hence, the water clusters becomes weaker with these organic solvents, which was observed as endothermic mixing.[35] Thus, the chance of the water molecules solvating the indicator complex will be enhanced as the molar fraction of the organic component of these mixtures increases. While in the water-rich region, free water molecules become less available for solvation owing to strong self-association and the formation of S_{AB} species through hydrogen bonding, so the organic component is preferred over water. On the other hand, in non-aqueous binary solvent mixtures, the indicator complex usually shows preference for the component which has the higher Lewis acidity (AN).



Scheme 2 Solvent–solvent interaction to form S_{AB} solvent species in aqueous (a) protic and (b) aprotic solvent mixtures.

Thus, in the mixed aqueous systems, the results are understandable in terms of the micro-heterogeneity of the binary mixture.[36] The breaking of the hydrogen-bonded network of water and formation of hydrogen bonds in aqueous aprotic solvent mixtures have been reported by other workers.[34,37,38] Similar preferential solvation characteristics were also observed for mesoionic compounds and Reichardt's pyridine betaine in this type of solvent mixture.[12,39] A theoretical study of preferential solvation in a number of two-component systems has also shown similar behavior.[32] Ultimately, the preferential solvation of the indicator complex in aqueous mixed solvents is determined by solute–solvent and solvent–solvent interactions, while solute–solvent interaction is more predominant in non-aqueous solvent mixtures.

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