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Notes

Extension of the Unified Solvation Model to Organometallic and Polycyclic Aromatic Probes

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Introduction

Recently a unified solvation scale of solvent polarity was developed which allows one to estimate the influence of nonspecific solvation on a wide variety of physicochemical properties of solutes[1] using eq 1, where S' is the solvent polarity

$$\chi = S'P + W \tag{1}$$

parameter, χ (having energy units) is the solvent dependent value of the physicochemical property of the solute, P is a measure of the susceptibility of the solute to solvation, and W is the value of χ when S' is zero. Values for S' have been established for over 50 solvents using data for more than 30 solutes.[3] New solutes and solvents are readily added.

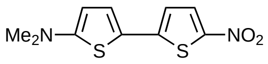
Nonspecific solvation involves the types of interactions treated with the reaction field or Kirkwood approach.[4] Solvent reorganization occurs to form a dynamic cavity surrounding the solute molecules. The size, shape, and charge distribution of the cavity are complimentary to those of the solute molecules. Solvent molecules comprising the cavity are oriented to optimize the interaction of the solvent with the probe. The solvent properties in the vicinity of the solute may be quite different from those of the solvent, so dipole moment, polarizability, or permitivity are often not good predictors of solvent effects.

Deviations from eq 1 occur whenever specific interactions (such as hydrogen bonding and charge-transfer interactions) or solute aggregation are present. One way of handling such systems is to recognize the existence of the specific interactions and then to treat the nonspecific solvation of the donor−acceptor adduct separately. The E and C approach[5] has been used to compute specific solvation involving hydrogen bonding solvents and donor molecule solutes.[3] For these cases, the unified solvation equation is modified to

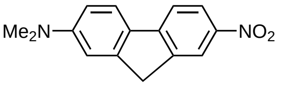
$$\chi = E_A'E_B^* + C_A'C_B^* + S'P + W \tag{2}$$

where E_A' and C_A' are the solvent acceptor parameters and E_B^* and C_B^* are the solute donor parameters. The terms ($E_A'E_B^*$ + $C_A'C_B^*$) relate to the specific solvation contribution to the formation of the hydrogen-bonded adduct and the terms ($S'P$ + W) to the contribution from nonspecific solvation of that adduct. More than 200 physicochemical measurements, were used to obtain E_B^* and C_B^* values for 24 solutes and E_A', C_A', and S' values for 14 protonic solvents. A similar approach has been used to study acceptor solutes dissolved in donor solvents.[6]

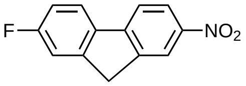
Chart 1



a. 5-(dimethylamino)-5′-nitro-2,2′-bithiophene, DMANBIT[9]



b. 2-(dimethylamino)-7-nitrofluorene, DMANF[10]



c. 2-fluoro-7-nitrofluorene, FNF[10]

The unified solvation scale also provides a useful way of probing more subtle molecular interactions. For example, the pattern of the deviations observed in the electronic transitions of 4-nitroaniline in a wide range of solvents suggests that charge transfer interaction occur.[6] Separating specific and nonspecific solvation has provided new insights into the influence of the solvent on electron transfer processes in metallocenes[7] and the role of ion-pair formation in the decarboxylation of benzisoxazole-3-carboxylate ions.[8]

A search of the recent literature[9−14] has produced 10 new solutes whose solvatochromism have been studied in detail. The objective of this paper is to use these ten solutes with varying geometrics to test the predictive ability of the unified solvation scheme. In so doing, new insights concerning the meaning of the probe E_B^* and C_B^* parameters result. The incorporation of these ten new solutes leads to the addition of eleven new or improved solvent S' parameters. The structural formulas of the three organic compounds, are given in Chart 1.

Energies are expressed in 10^3 cm^{-1}. The solvent (S', E_A', and C_A') and solute parameters (P, W, E_B^* and C_B^*) used in data fits have been reported previously.[15]

Results and Discussion

Nonspecific Solvation Interactions. The first set of solvent shifts analyzed involve solutes that are being solvated by nonspecific interactions. The results are displayed graphically for $W(CO)_4bpy$ and DMANBIT in Figure 1. The average deviations are 0.14 and 0.10. Similar quality fits result for all the probes and only the resulting P and W values are given in Table 1. All data fits are available as Supporting Information.

DMANBIT, DMANF, and FNF display positive (bathochromic or red) solvatochromic shifts in which the absorption peak

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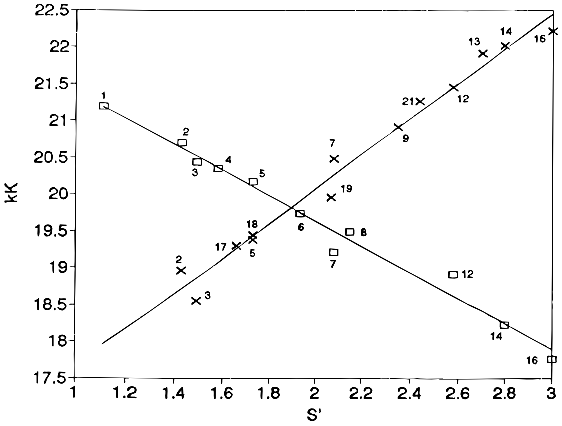

Figure 1. Experimental Transition Energy vs *S*′ for W(CO)$_4$bpy (□) and DMANBIT (×). Key: 1, C_6H_{12}; 2, $(C_2H_5)_3N$; 3, CCl_4, 4, $(n\text{-}C_4H_9)_2O$; 5, $(C_2H_5)_2O$; 6, $O(CH_2CH_2)_2O$; 7, $(CH_2)_4O$; 8, $CH_3OO_2C_2H_5$; 9, $(CH_2)_5CO$; 10, $CH_3COC_2H_5$; 11, $(C_2H_5O)_3PO$; 12, $(CH_3)_2CO$; 13, $CH_3CON(CH_3)_2$; 14, $HCON(CH_3)_2$; 15, $(CH_2)_4CO_2$; 16, $(CH_3)_2SO$. Key: kK = 10^3 cm^{-1}.

Table 1. Summary of Probe Parameters

probe	no. of solvents	*P*	*W*	E_B*	C_B*	av dev (% fit)[c]
W(CO)$_4$bpy	18	2.37	15.34	−2.12	1.42	0.15 (5)
W(CO)$_4$phen	16	2.24	15.70	−1.91	1.12	0.14 (5)
Mo(CO)$_4$bpy	16	2.15	16.51	−1.88	1.11	0.11 (4)
Cr(CO)$_4$bpy	16	2.36	14.68	−2.23	1.30	0.12 (4)
cis-Ru(phen)$_2$(CN)$_2$	13	1.11	16.99	0.83	0.47	0.12 (21)
Pt(bpy)Cl$_2$	7	1.86	20.58	*b*	*b*	0.09 (5)
CpMn(CO)$_2$C$_5$H$_5$N	5	1.29	23.59	*b*	*b*	0.04 (3)
DMANBIT[a]	16	−1.74	23.11	0.82	−0.15	0.09 (3)
DMANF[a]	16	−1.29	26.54	*b*	*b*	0.16 (7)
FNF[a]	16	−0.74	31.80	*b*	*b*	0.15 (10)

[a] Aromatic solvents omitted. [b] Measurements are not available in a sufficient number of hydrogen-bonding solvents. [c] Percent fit is 100 times the average deviation divided by the range of experimental values.

moves to longer wavelengths (smaller energies) as the polarity of the solvent, as measured by *S*′, increases. This behavior is typical of chromophores undergoing a $\pi \rightarrow \pi^*$ transition and corresponds to more extensive solvation of the excited state than the ground state. The dipole moment change of the probe functional group induced by the transition is in the same direction, but larger than the ground state dipole moment. All three of these probes undergo charge transfer interactions in π-solvents. The remaining solutes, all of which are coordination compounds containing 1,10−phenanthroline or 2,2′-bipyridine as a ligand, produce negative (hypsochromic or blue) shifts corresponding to an increased transition energy resulting from polar solvents stabilizing the ground state and/or destabilizing the excited state. In these cases, the probe transition moment dipole is in a different direction than the ground state dipole moment.

There is no evidence for charge transfer complexation of the carbonyl compounds with benzene or toluene solvent. Chlorobenzene deviates in the same direction for all of the coordination compounds and could have a small contribution from specific charge transfer interactions with the probe behaving as a π-donor.

Calculation Involving Acceptor Solvents. Six of the reported solutes have been studied in enough hydrogen bonding solvents to permit analysis with eq 2. Data in both hydrogen bonding and nonspecifically solvating solvents are combined in the analysis. The probe parameters resulting from these fits are also summarized in Table 1. The values for *P* and *W* are nearly identical to those obtained when the non-interacting solvents were analyzed separately with eq 1 and the average deviations are comparable. The complete fits are given in the Supporting Information. The E_B* and C_B* values of the probes should be regarded as tentative because the C_A'/E_A' ratios of the solvents employed are similar. They can be used with confidence to predict shifts for hydrogen bonding solvents with similar C_A'/E_A' ratios. One of the advantages of the data analysis with eq 2 is the factoring of the shift into specific and nonspecific contributions. For a given hydrogen bonding solvent, the contribution from the specific interaction is given by $E_A{}^*E_B + C_A{}^*C_B$. For example, the specific interaction in the case of methanol and W(CO)$_4$bpy corresponds to -1.03×10^3 cm^{-1}). In the case of the coordination compounds, the specific interaction decreases the spectral shift. This change is in the opposite direction as that from an increased solvent polarity. With DMANBIT the specific interaction for the acceptor solvents increases the shift, which is also in the opposite direction of an increase in solvent polarity for this probe.

Table 2. Refined and New *S*′ Values for Solvents[a]

solvent	no. of solutes	*S*′	solvent	no. of solutes	*S*′
$C_6H_3(CH_3)_3$	4	(1.54)	$CH_3CO_2\text{-}n\text{-}C_4H_9$	3	(1.99)
$(n\text{-}C_4H_9)_2O$	8	1.57	$(CH_2)_5CO$	10	2.35
$C_6H_5CH_3$	9	1.66	$ClCH_2CHCl_2$[c]	16	(2.35)
C_6H_5Cl	9	1.98	$C_2H_5COC_2H_5$	6	2.37
			$CH_3COC_2H_5$	7	2.50

[a] Fits were obtained using eq 1. Values for χ were obtained from the appropriate literature sources; *P* and *W* values were obtained either from this paper or ref 15. The results of the fits are given in the Supporting Information. [b] Those values of *S*′ based on fewer than six measurements are tentative and are enclosed by parentheses in the table. The *S*′ values for toluene and cyclohexanone are unchanged from earlier values but are included because a significant number of new probes were included in the calculation. [c] These solvents have the potential for hydrogen bonding and *S*′ may include a contribution from this effect.

Insights Concerning the Nature of the Specific Interaction from E_B* and C_B*. The signs of E_B* and C_B* have the potential of providing details about the nature of the specific interaction of the probe and the solvent. Unfortunately, most of the hydrogen bonding systems have similar C_A'/E_A' ratios leading to uncertainties in the E_B* and C_B* parameters. Before interpretations based on sign reversals are made, it should be shown that a poor fit results when E_B* and then C_B* are set at zero in a data fit.

The signs of the E_B* and C_B* values for the probes in Table 1 will be discussed in general terms to illustrate the information content. When the bond, P−H−X, formed from the specific interaction of the solvent H−X with the probe has its bond axis and bond polarity in the same direction relative to the probe as a noninteracting polar solvent, the solvent interaction with the transition moment dipole, will cause *P* and E_B* to have the same sign. This is the case for many of the reported probes parameters. When the bond axis dipole of the specific interaction is in a different direction than the nonspecific solvent−probe dipole−dipole orientation, *P* and E_B* will have opposite signs. This could occur, for example, in W(CO)$_4$bpy if the hydrogen bonding involved the carbonyl group or the π-system of bipy and the probe dipole lay along a line from the metal bisecting the two nitrogens. The metal−ligand transition into the bypy would create a dipole in a different direction than that of the dipole−dipole hydrogen bond interaction leading to destabilization of the excited state by the electrostatic component of the specific interaction.

The sign of C_B depends upon the influence of covalency in the hydrogen bond on the energy of probe donor atom involved in hydrogen bonding. This donor orbital is predominantly contributing to the nonbonding MO of the three-center hydrogen bond. The electrostatic component of the hydrogen bond interaction will lower the donor orbital energy, but the covalent component could lower or raise the donor orbital energy relative to the energy of this orbital in the absence of hydrogen bonding. The energy change is difficult to predict for it depends upon the donor orbital coefficients in the bonding and nonbonding MO's. The influence of the orbital energy on the sign of C_B* for the different probes would depend upon the type of transition involved. In the case of hydrogen bonding to bpy of $W(CO)_4$bpy, lowering the π-orbital energy and raising π^* would increase the transition energy and give a positive C_B. INDO results[16] predict that the specific hydrogen bonding interaction of water with pyrimidine, pyridazine, and pyrazine produce red shifts in the n → π^* transition. The nonspecific interaction produces a blue shift. Finally, the direction of the deviations for a given probe in correlations to S' will depend upon the magnitudes and signs of C_B* and E_B*.

Addition of New Solvents. The availability of P and W values for these new probes leads to new, or improved, values of S' for 11 solvents. The values of S' are summarized in Table 2.

Calculations

Electronic transition energies for each solute in different solvents were fit to eq 1 using the multivariable regression program for those solvents having well-established S' values. The individual deviations between the experimental and calculated energies were compared with the average deviation of the data as a whole. Classes of solvents having large deviations in the same direction were eliminated from the set and the fit was re-run using the remaining solvents. Patterns in the deviations of the classes of solvents which were eliminated suggest that both specific and nonspecific solvation are involved.

Hydrogen-bonding solvents were removed from all ten sets of data. Aromatic solvents were removed from the solute fits for DMANBIT, DMANF, and FNF but not the seven organometallic compounds. Charge transfer complexation is suggested in the organic solutes. Chloroform and methylene chloride gave erratic results and were eliminated from all fits. These solvents form weak hydrogen bonds, thus, producing a mixture of hydrogen-bonded and non-hydrogen-bonded solute species.

All ten of the solutes discussed above displayed significant deviations when hydrogen-bonding, acceptor solvents are fit to eq 1. Four-parameter regressions were run using eq 2[3] and S', E_A', and C_A' values taken from the literature.[3,15] At least five acceptor solvents were included in each fit.

Supporting Information Available: Tables showing the experimental data and the calculated values for all of the probes discussed in this article as well as a table of the systems used to calculate new S' values (7 pages). Ordering information is available on any current masthead page.

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