

## TWO REINTRODUCED SOLVATOCHROMIC INDICATORS FOR HYDROGEN BOND DONATION AND ACCEPTANCE

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**The behaviour of *cis*-dicyanodi-1,10-phenanthrolineiron(II) and acetylacetonato-*N,N,N',N'*-tetramethylethylenediaminocopper(II) perchlorate as solvatochromic indicators for the ability of solvents to donate a hydrogen atom or a pair of electrons, respectively, towards the formation of a hydrogen bond is examined by multivariable linear regressions and principal component analysis.**

### INTRODUCTION

The effect of solvents on the physical and chemical properties of solutes is a very important topic in chemistry. This effect has been explained in terms of the polarity/polarizability and the ability to form hydrogen bonds of the solvents. Many scales have been designed to describe these effects quantitatively,<sup>1</sup> some based on a single parameter and others on a multi-parameter approach. For example, Dimroth and Reichardt's  $E_T(30)$ ,<sup>2</sup> Kosower's  $Z^3$  and Winstein and Grunwald's  $Y^4$  are based on the single-parameter approach. On the other hand, Kamlet *et al.*<sup>5</sup> defined four parameters,  $\pi^*$ ,  $\delta$ ,  $\alpha$  and  $\beta$ , to describe the solvent effect. By means of these parameters (with the addition of others when the need arose), they and their co-workers succeeded in describing the solvent effects on the rates of reactions,<sup>6</sup> NMR chemical shifts<sup>7</sup> and IR,<sup>8</sup> UV<sup>9</sup> and fluorescence<sup>10</sup> spectra. Similarly, the solvatochromic parameters of solutes, which are the same physical entities as those of the solvents but may have numerically different values for  $\alpha$  and  $\beta$ , describe solvent-water partition coefficients,<sup>11</sup> aqueous solubilities<sup>12</sup> of solutes and chromatographic indices.<sup>11a,13</sup>

The general equation to rationalize the solvent effect is:<sup>6-13</sup>

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta + d\delta \quad (1)$$

where  $XYZ$  is one of these measures of the solvent effect,  $\pi^*$  measures the polarity/polarizability of the solvent,  $\alpha$  its aptitude to donate a hydrogen atom to form a hydrogen bond,  $\beta$  its tendency to provide a pair of electrons to such a bond and  $\delta$  modifies the polarizability effect measured by  $\pi^*$  for certain classes of solvents. These solvent parameters were calculated by

averaging the results of numerous spectral and kinetic experiments, in order to exclude any anomaly arising from the choice of any particular solute used as the probe.

The solvatochromic effect, i.e. the solvent-caused shift of  $\bar{\nu}$ , the peak frequency of the lowest energy UV-visible band of a dye solute, generally depends on all four parameters. However, the ideal indicator for a certain parameter must show a strong sensitivity for the property measured by it but none for those measured by the remainder of the parameters. In this respect, the  $\pi^*$  indicators are the easiest to handle, since the solvatochromic effect on indicators in non-hydrogen-bonding solvents depends only on the non-specific interactions of the medium. On the other hand, indicators suitable for the measurement of  $\alpha$  must be highly sensitive to the hydrogen atom donation ability and least sensitive to non-specific interactions and to the basicity of the solvents. The opposite should apply to the properties of the  $\beta$  indicators, which should be highly sensitive to the electron pair donation ability of the solvent and not sensitive to the other effects.

The generally used  $\beta$  indicators 4-nitrophenol (**1**) and 4-nitrobenzamine (**2**) are sensitive to both  $\pi^*$  and  $\beta$ , as shown by the multi-variable linear regressions:<sup>14,15</sup>

$$\bar{\nu}(\mathbf{1}) = 35 \cdot 045 - (1 \cdot 641 \pm 0 \cdot 205)\pi^* - (2 \cdot 882 \pm 0 \cdot 200)\beta - (0 \cdot 349 \pm 0 \cdot 118)\delta \quad (2)$$

$$(n = 46, r = 0 \cdot 9736, F_{3,43} = 212, \sigma = 0 \cdot 271)$$

$$\bar{\nu}(\mathbf{2}) = 31 \cdot 10 - 3 \cdot 14\pi^* - 2 \cdot 79\beta \quad (3)$$

where  $\bar{\nu}$  is given in  $10^{-3} \text{ cm}^{-1}$ . The ratio  $b/s$  measures the suitability of the dye to serve as a  $\beta$  indicator: the higher it is, the better is the indicator. For **1**  $b/s = 1 \cdot 76$  and for **2**  $b/s = 0 \cdot 88$ , hence by this criterion **1** is a better

$\beta$  indicator than 2. Likewise, the higher is the  $a/s$  (and  $a/b$ ) value of a dye, the better it functions as an  $\alpha$  indicator. The widely used Dimroth and Reichardt betaine 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenoxide (3) is a good  $\alpha$  indicator, with  $a/s = 1.09$  and  $a/b = 7.0$ .<sup>16</sup>

In this paper we reintroduce two indicators suggested previously<sup>17</sup> in a different manner, namely the iron complex *cis*-dicyanodi-1,10-phenanthrolineiron(II) (4)<sup>18</sup> as an  $\alpha$  indicator and the copper complex acetylacetonato-*N,N,N',N'*-tetramethylethylenediaminocopper(II) perchlorate (5)<sup>19</sup> as a  $\beta$  indicator.

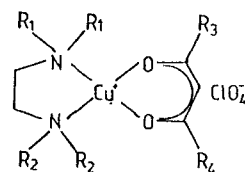
## RESULTS AND DISCUSSION

Multi-variable linear regression computations for the experimental values of  $\bar{\nu}(5)$  in 17 solvents<sup>17</sup> (some  $\bar{\nu}_{\max}$  measurements were conducted in our laboratory) as the dependent variable and the published solvatochromic parameters<sup>20,21</sup> of these solvents as the independent variables yielded the following equation from the data presented in Table 1:

$$\bar{\nu}(5) = 18.76 \pm 0.13 - (2.793 \pm 0.210)\beta \quad (4)$$

$$(n = 17, r = 0.960, F_{1,16} = 177, \sigma = 0.26)$$

It is seen that this copper complex, being one of a series of  $\beta$ -diketonatoethylenediaminocopper(II) complexes,<sup>22</sup> is most suitable as a  $\beta$  indicator since it is almost exclusively  $\beta$ -sensitive. Application of equation (4) to experimental spectroscopic results for 5 in aqueous acetonitrile solutions yielded  $\beta$  values<sup>23</sup> that matched the  $\beta$  values for these solutions obtained by means of equations (2) and (3) with indicators 1 and 2,



- 6:  $R_1-R_1 = (CH_2)_5, R_2-R_2 = (CH_2)_5, R_3 = R_4 = t\text{-Bu}$   
 7:  $R_1-R_1 = (CH_2)_5, R_2-R_2 = (CH_2)_5, R_3 = R_4 = CH_3$   
 8:  $R_1-R_1 = (CH_2)_5, R_2-R_2 = (CH_2)_5, R_3 = CH_3, R_4 = Ph$   
 9:  $R_1-R_1 = (CH_2)_5, R_2-R_2 = (CH_2)_5, R_3 = R_4 = Ph$   
 10:  $R_1-R_1 = (CH_2)_5, R_2-R_2 = (CH_2)_5, R_3 = CH_3, R_4 = CF_3$

respectively. This matching strongly supports the adequacy of equation (4).

Fukuda *et al.*<sup>22</sup> recently published electronic spectral data in seven solvents for compounds 6–10.

Application of Fukuda *et al.*'s data (Table 2) and the solvatochromic parameters of the solvents involved (Table 1) in multi-variable linear regressions showed that all the compounds 6–10 are exclusively  $\beta$ -sensitive (in all cases  $n = 7$ ):

$$\bar{\nu}(6) = 18.92 - (3.61 \pm 0.35)\beta; r = 0.9903, F_{1,6} = 101, \sigma = 0.20;$$

$$\bar{\nu}(7) = 19.90 - (3.51 \pm 0.28)\beta; r = 0.9951, F_{1,6} = 100, \sigma = 0.16;$$

$$\bar{\nu}(8) = 19.79 - (3.49 \pm 0.25)\beta; r = 0.9903, F_{1,6} = 110, \sigma = 0.17;$$

$$\bar{\nu}(9) = 19.69 - (3.39 \pm 0.29)\beta; r = 0.9868, F_{1,6} = 74, \sigma = 0.20;$$

$$\bar{\nu}(10) = 19.25 - (3.50 \pm 0.34)\beta; r = 0.9887, F_{1,6} = 44, \sigma = 0.20.$$

Table 1. Electronic spectral data  $\bar{\nu}_{\max}$  (in  $10^3 \text{ cm}^{-1}$ ), of compound 5 in various solvents and the solvatochromic parameters<sup>20,21</sup> of the latter

Solvent	$\bar{\nu}_{\max}$	$\pi^*$	$\alpha$	$\beta$	Ref.
2,2,2-Trifluoroethanol	18.94	0.73	1.49	0.00	— <sup>a</sup>
Nitromethane	18.80	0.85	0.22	0.06	17
1,2-Dichloroethane <sup>b</sup>	18.38	0.81	0.00	0.10	— <sup>a</sup>
Dichloromethane <sup>b</sup>	18.22	0.82	0.13	0.10	— <sup>a</sup>
Propylene carbonate	18.05	1.15	0.00	0.40	17
Acetone	17.51	0.71	0.08	0.48	17
Ethyl acetate	17.33	0.55	0.00	0.45	17
Acetonitrile	17.30	0.75	0.19	0.40	— <sup>a</sup>
Tetrahydrofuran	17.27	0.58	0.00	0.55	17
Propan-2-ol	17.00	0.48	0.76	0.84	— <sup>a</sup>
Methanol	16.89	0.60	0.98	0.66	— <sup>a</sup>
Ethanol	16.87	0.54	0.86	0.75	— <sup>a</sup>
Formamide	16.72	0.96	0.71	0.68	17
<i>N,N</i> -Dimethylformamide	16.58	0.88	0.00	0.69	17
<i>N</i> -Methylformamide	16.45	0.90	0.62	0.80	— <sup>a</sup>
Dimethyl sulphoxide	16.31	1.00	0.00	0.76	17
Hexamethylphosphoric triamide	15.80	0.87	0.00	1.05	— <sup>a</sup>

<sup>a</sup>  $\bar{\nu}_{\max}$  values measured in our laboratory.

<sup>b</sup>  $\delta = 0.50$  (otherwise  $\delta = 0$ ).

Table 2. Electronic spectral data,  $\bar{\nu}_{\max}$  (in  $10^3 \text{ cm}^{-1}$ ), of the copper complexes 5–10 in various solvents

Solvent	5	6	7	8	9	10
Dimethyl sulphoxide	16.31	16.1	15.7	15.8	15.7	15.3
<i>N,N</i> -Dimethylformamide	16.58	16.4	16.1	16.1	16.1	15.5
Methanol	16.89	16.8	16.7	16.7	16.7	16.1
Acetone	17.51	17.2	17.2	17.2	17.1	16.5
Acetonitrile	17.30	17.2	17.1	17.1	16.9	17.1
Nitromethane	18.80	18.8	18.5	18.3	18.3	17.8
1,2-Dichloroethane	18.38	19.2	18.8	18.5	18.3	17.2

The unique results of the exclusive  $\beta$ -sensitivity of compounds 5–10 poses the question of whether other factors exist which are not expressed by these correlations because they have not been included as independent parameters in the multi-variable linear regression calculations. Solutions to such problems are given by factor analysis (FA)<sup>24</sup> or principal components analysis (PCA)<sup>25</sup> methods. In our case, these methods should yield at least two factors, one corresponding to the constant term and the other to the  $\beta$ -term, and others, if they result from this analysis, to physical properties that have not been included in the regression analysis. PCA calculations applying the  $\bar{\nu}$  data for compounds 5–10 show that there are only two significant factors. Two factors are retained by the real error<sup>26</sup> and the factor indicator function (IND)<sup>27</sup> criteria, and these factors explain 97.2% of the variance. The PCA calculations confirm the peculiar lack of sensitivity of the copper complex cations towards non-specific interactions noted above.

This led us to examine the behaviour of the non-complexed sodium cation. Multi-variable linear regression computations were applied to Popov's<sup>28</sup> data on <sup>23</sup>Na NMR chemical shifts in infinitely dilute solutions of sodium iodide in organic solvents. They yielded the equation

$$\delta(^{23}\text{Na NMR, ppm}) = 16.43 - (18.40 \pm 2.20)\beta - (6.17 \pm 2.02)\delta \quad (5)$$

$(n = 15, r = 0.9433, F_{2,13} = 30, \sigma = 1.91)$

The *P* statistic of the independent variable  $\delta$  is 1.1%, which is large but still acceptable. This statistic is defined as the minimum number above which an independent variable cannot be included in a regression equation. The variable  $\delta$  is a solvent-family-dependent factor, having the value 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents and 0.0 for others. For this latter class of solvents the chemical shift of <sup>23</sup>Na<sup>+</sup> is, indeed, an exclusively  $\beta$ -sensitive parameter.

It should be noted that the spectral data for compounds 5–10 are also simple linear functions<sup>16,28</sup> of the donor number *DN*.<sup>29</sup> Fukuda *et al.*'s data<sup>22</sup> give the following regressions with  $n = 7$  for all the compounds

except 10, where the data for 1,2-dichloroethane were excluded:

$$\begin{aligned} \bar{\nu}(6) &= 19.01 - 0.103DN; r = 0.9836; \\ \bar{\nu}(7) &= 18.76 - 0.102DN; r = 0.9939; \\ \bar{\nu}(8) &= 18.52 - 0.091DN; r = 0.9937; \\ \bar{\nu}(9) &= 18.40 - 0.088DN; r = 0.9881; \\ \bar{\nu}(10) &= 18.16 - 0.097DN; r = 0.9830; \end{aligned}$$

These results conform to the equations of Marcus<sup>30</sup> and Taft<sup>31</sup> which show that the *DN* values and the  $\beta$  parameters are highly linearly correlated.

In contrast to the copper complex 5, the iron complex 4, designed to measure the  $\alpha$  of solvents, is not exclusively sensitive to a single parameter. Multi-variable linear regression calculations for the spectral data for 4 in various solvents (Table 3) yielded

$$\begin{aligned} \bar{\nu}(4) &= 15.636 + (1.210 \pm 0.216)\pi^* \\ &\quad + (2.664 \pm 0.113)\alpha - (0.772 \pm 0.176)\beta \quad (6) \\ (n &= 14, r = 0.9914, F_{3,11} = 191, \sigma = 0.172) \end{aligned}$$

Although 4 is not an exclusively  $\alpha$  indicator, the ratio  $a/s = 2.20$  is much higher than that of Dimroth and Reichardt's betaine 3, referred to above as the commonly used  $\alpha$  indicator. It is also better than that of other  $\alpha$  indicators, such as<sup>9c</sup> isoquinolinium-1-benzoyl-2-ethoxy-2-oxoethylide, with  $a/s = 1.64$ , 4-cyanofornyl-1-methylpyridinium oximate, with  $a/s = 1.26$ , or 5,5-dimethylpyrrolidine 1-oxide, with  $a/s = 1.49$ . The indicator *N,N*-dimethylthiobenzamide *S*-oxide has a higher value,  $a/s = 2.73$ , but this compound is rather unstable.

Multi-variable linear regression calculations can be used as an important tool to distinguish between different kinds of solute–solvent interactions. Application of the spectral data in Table 3 and including the data for the strong acids formic and trifluoroacetate gave an inadequate regression equation with an insufficient correlation coefficient,  $r = 0.7794$ . Exclusion of these acids yielded the excellent equation (6). Weaker acids, such as acetic acid, behave in this respect as ordinary organic solvents, capable of the donation of a hydrogen atom towards the formation of a hydrogen bond.

Table 3. Electronic spectral data,  $\bar{\nu}_{\max}$  (in  $10^3 \text{ cm}^{-1}$ ), of compound 4 in various solvents and the solvatochromic parameters<sup>20</sup> of the latter

Solvent	$\bar{\nu}_{\max}$	$\pi^*$	$\alpha$	$\beta$	Ref.
Formic acid	24.39	0.65	1.03	0.38	17
Water	19.61	1.09	1.17	0.47	17
Acetic acid	18.66	0.60	0.92	0.45	17
Formamide	18.32	0.96	0.71	0.68	17
Ethanol	17.95	0.54	0.86	0.75	— <sup>a</sup>
Propan-2-ol	17.48	0.48	0.76	0.84	— <sup>a</sup>
Nitromethane	16.95	0.85	0.22	0.06	17
Propylene carbonate	16.72	1.15	0.00	0.40	17
Acetonitrile	16.70	0.75	0.19	0.40	— <sup>a</sup>
Dichloromethane <sup>b</sup>	16.62	0.82	0.13	0.10	— <sup>a</sup>
Dimethyl sulphoxide	16.49	1.00	0.00	0.76	17
<i>N,N</i> -Dimethylformamide	16.25	0.88	0.00	0.69	17
Pyridine <sup>c</sup>	16.13	0.87	0.00	0.64	— <sup>a</sup>
Tetrahydrofuran	15.77	0.58	0.00	0.55	17
Hexamethylphosphoric triamide	15.77	0.87	0.00	1.05	— <sup>a</sup>

<sup>a</sup>  $\bar{\nu}_{\max}$  values measured in our laboratory.

<sup>b</sup>  $\delta = 0.50$ .

<sup>c</sup>  $\delta = 1.00$ .

Fourier transform IR spectra of the indicator 4 in a potassium bromide pellet and in the solvents dichloromethane and *N*-methylformamide show the two C≡N stretching bands at the same frequencies of 2080 and 2065  $\text{cm}^{-1}$ . In methanol and 2,2,2-trifluoroethanol it shows a broader band at 2080  $\text{cm}^{-1}$ . In formic acid, however, the C≡N band was shifted to 2027  $\text{cm}^{-1}$  and in sulphuric and trifluoroacetic acid even to 2016  $\text{cm}^{-1}$ . These shifts are rationalized as being due to the protonation of the indicator 4 to give  $[\text{Fe}=\text{C}=\text{NH}]^+$  groups, in which the C—M bond is longer. The strong hydrogen-bond-donor solvents methanol, 2,2,2-trifluoroethanol and *N*-methylformamide do not show this effect, since they only form hydrogen bonds with the cyano group and do not protonate it. Hydrogen bond formation and protonation can therefore also be distinguished by whether there is conformation or not to equation (6).

## EXPERIMENTAL

Multi-variable linear regression calculations, factor analysis and principle component analysis were conducted on the university VAX computer with the SAS program. The indicators 4 and 5 were prepared according to Shilt<sup>18</sup> and Fukuda and Sone.<sup>19</sup> Fourier transform IR spectra were recorded with a Bruker IFS 113v spectrometer and UV and visible spectra with a Perkin-Elmer Lambda 5 spectrophotometer.

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