WATER IN ORGANIC SOLVENTS AS STUDIED BY SOLVATOCHROMISM

By Mitsuhiko Hida, Hiroko Yoshida and Sadao Arai

(Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan)

Synopsis

Azonia betain dyes 2a–2c and 4-nitroanilines, 3 and 4, were used as solvatochromic indicators to investigate the behavior of water in organic solvents. The shift of the wavenumber of maximal absorption of these dyes by an addition of water in organic solvent was analyzed by assuming that water and solvent molecules selectively solvate a solute in Onsager cavity. It was considered that water around the dyes, 3 and 4, in aprotic solvent such as acetone or acetonitrile constitutes a cluster or other associated species, while water in a small amount solvates unimolecularly the azonia betain dyes in aprotic solvent. Solvatochromism in a binary mixture of solvents was discussed by using a selective solvation model.

1. Introduction

In a course of study of azonia-aromatic chemistry, we synthesized some merocyanine dyes (1a–1c).\(^1\)

\[
\begin{align*}
1a; & \text{R} = \text{H} \\
1b; & \text{R} = \text{Br} \\
1c; & \text{R} = \text{OCH}_3
\end{align*}
\]

By an addition of amine, such as piperidine, proton dissociation of hydroxyl group of these dyes gave the corresponding betain dyes (2a–2c). These betain dyes are colored by orange in water and by green in acetone. These large negative solvatochromism can be interpreted by assuming a resonance between two Kekule structures of the betain and merocyanine forms.

Since the betain form can be assumed to be more stable than the merocyanine form, the former (2) may contribute more than the latter (2') in the ground state, while the latter (2') may have larger weight than the former (2) in the excited state. Thus the dye will have more dipolar character in its ground state than in its excited state. Therefore an increase in polarity and hydrogen bonding character of an environment will cause an increase in the excitation energy. By an addition of water to acetone or acetonitrile solution of the azonia betain dyes (2) the color continuously changed from green to orange.

As shown in Fig. 1, blue shift in wavelengths of the maximal absorption is very large by an addition of a small amount of water. In this case it shifted by about 5 nm upon an addition of 1000 ppm of water. After the wavelength seems to approach a certain value by addition of water in the vicinity of 30 to 50\%, it shifted again largely by further addition of water. This suggests that the character of solvent surrounding the solute changes at the water content 30~50\% (v/v).

On the other hand, an addition of ethyl alcohol into acetone solution of the dye caused a monotonous blue shift (curve 2 in Fig. 1). Contrary to
water, ethyl alcohol does not seem to change the character of environment surrounding the solute.

These observations prompted us the study of the solvatochromic properties of the azonia betain dyes in a binary solvent mixture.

2. Experimental

2.1 Materials

The azonia dyes (1) were synthesized and purified as previously reported.1) As solvatochromic indicators, 4-nitroaniline (3) and N,N-dimethyl-4-nitroaniline (4) were used too. Both were of commercial origin (Tokyo Kasei Kogyo Co. Ltd., GR grade), and used without further purification.

Acetone was dried by Molecular shieve 4A and distilled and stored under nitrogen. Acetonitrile was heated with P2O5 for several hours, and then distilled two times under nitrogen. After further dehydration with calcium hydride, it was distilled and stored under nitrogen.

Water was distilled by use of a distillator made of copper.

2.2 Measurements

Absorption spectra were recorded on Hitachi Double Beam Photometer 220. Spectroscopic measurements were made on solutions of the indicators 3 and 4 (10⁻⁴ mol.dm⁻³). The spectra of azonia dyes (1) (10⁻⁴ mol.dm⁻³) were measured in the presence of piperidine (10⁻² mol.dm⁻³). Positions of the maximal absorption were determined as follows.

By using absorbances at three wavelengths at 0.5 nm intervals around the maximal absorption, a quadratic equation was fitted to the observed spectra. Position of the maximal absorption was determined by averaging the five observations of the maximum position of the above quadratic equation. All observations of the maximal absorption agreed to each other within less than 0.1 nm from the average.

3. Results and discussions

3.1 Langmuir-style change of wavenumber with composition of binary mixture of solvents

In many investigations of the solvation of ion and molecule, the solvent shell has been assumed, which may be resulted by the interactions between solute and solvent molecules. Solvation number is defined as a number of solvent molecules surrounding a solute molecule. However, the solvation number largely depends on solute and the method of measurement.

Considerable progress has been made in understanding the effect of solvent on a spectral property of solute using quantum mechanical perturbation theory.2) The calculation of the change of an electronic energy due to interaction between solute and solvent molecules has been carried out by assuming Onsager model to simplicity. In Onsager model the solute molecule in a spherical cavity is suffered by an effective electric field due to the dielectric character of solvent. The solvent molecule may be oriented variously around the solute. Since the orientation relaxation time of the solvent molecule is much longer than the time required for the excitation of the solute molecule by light absorption, the distribution of the solvent molecule does not change on electronic excitation of the solute molecule. Then an effective field, or the reaction field, can be defined by averaging the various interactions between the
solute and solvent molecules over the molecular distribution.

The quantitative understanding, however, can be attained only in the cases where the weak electrostatic interaction between solute and non-polar solvent molecules is operative. Those theoretical treatments of the solvatochromic character does not apply to the cases where specific short-range forces, such as hydrogen bonding, charge-transfer and other strong interactions between solute and solvent are operative.

Description of solvation of solute in solvent mixture is more complicated and a difficult undertaking in some cases of polar solvent mixtures.

Since theoretical tools may be a difficult undertaking for the solvatochromism of the azonia betain dyes in binary mixture of polar solvents (Fig. 1), a crude model is assumed to description of solvation of our dyes as mentioned below.

a. A solute molecule is surrounded by definite number of polar solvent molecules. Although the assumption of constant number of solvent molecule around the solute seems to be too crude an approximation for binary mixture of solvents, this assumption is tentatively adopted to simplicity.

b. Since solvent molecule is oriented around the solute in various distributions, the average distribution over various orientations is assumed to create a reaction field. However, an explicit expression of the reaction field is not necessary.

c. If the higher order perturbation by the reaction field is ignored, the excitation energy may change linearly with the strength of the reaction field. Thus the solvatochromic shift can be written by eq. (1).

\[
\delta R = \text{const.} \times (\text{strength of the reaction field } R) \tag{1}
\]

Here, \( \delta R \) denotes an increment of wavenumber by interaction with the reaction field.

d. In case of a binary mixture of solvents the overall reaction field, \( R \), is assumed to be made by a linear combination of the reaction fields of each solvent, \( R_A \) and \( R_B \) (eq. (2)).

\[
R = f_A R_A + f_B R_B \tag{2}
\]

Here, \( f_A \) and \( f_B \) denote the mole fractions of solvent A and B around the solute, respectively.

Even in cases where hydrogen bonding and other strong interactions are operative, eq. (2) is assumed to be valid.

By expressing \( \delta R \) of solvent A and B as \( \delta_A \) and \( \delta_B \) respectively, the solvatochromic shift can be written by eq. (3).

\[
\sigma - \sigma_0 = f_A \delta_A + f_B \delta_B \tag{3}
\]

Combining with eq. (1), eq. (3) can be rewritten by eq. (4).

\[
\sigma = f_A \sigma_A + f_B \sigma_B \tag{4}
\]

or, \( \Delta \sigma = \Delta \sigma_0 + f_0 \).

where \( \Delta \sigma = \sigma - \sigma_A \) and \( \Delta \sigma_0 = \sigma_B - \sigma_A \).

e. In many cases of binary solvent mixtures it has been found that the ratio of solvent molecules around the solute may be different from that in the bulk solution. Then, in a binary mixture of solvent a selective solvation is assumed. If any interaction between solvent molecules is assumed to be absent, solvent molecules competitively enter into the solvation shell from the bulk solvent region. When \( S_A \) and \( S_B \) denote numbers of solvent molecules A and B, respectively, in the solvation shell, and \( C_A \) and \( C_B \) denote mole concentrations in the bulk region, these can be related by eq. (6) in an equilibrium state.

\[
S_B/S_A = K(C_B/C_A) \tag{6}
\]

The value of \( K \) corresponds to “the index of selective solvation” of solvent B compared with solvent A.

Using eq. (6), the relationship between the solvatochromic shift (\( \Delta \sigma \)) and the solvent composition can easily be derived. We can write eq. (7) by using volume% (\( x \)) of solvent B for convenience,

\[
\Delta \sigma = \frac{(x/100) + (\tau_1 + \tau_2 x/100)}{(1 + \tau_1 + \tau_2)} \tag{7}
\]

or, \( \Delta \sigma = \frac{x}{(100/x)} \tag{8} \)

where \( \tau_1 = \frac{(1/K)(\sigma_A/\sigma_B)(M_A/M_B) \), \( \tau_1 + \tau_2 = 1 \), and \( \sigma = \) density and \( M = \) molecular weight.

Thus, Langmuir-style expression can be derived by the above assumptions. The index of selective solvation of solvent B, compared with solvent A, can be estimated from the slope \( (\tau_2) \) of a linear plots of \((1/\Delta \sigma)\) against \((100/x)\).

In some cases we found that the value of \( \tau_2 \) is very small and the better fit of the observations to Henry-style expression is obtained. 3)
Figures 2, 3, 4 and 5 show the changes of wavenumber with the amount of added second solvent (x % v/v). Solid lines represent the calculated values by eq. (7), except for the cases of the dye 4 in acetone-methanol and acetonitrile-methanol, where the shift of the wavenumber is too small to analyse the double reciprocal plot between $d\sigma$ and solvent composition ($x$).

Since the agreement with the observations is satisfactory, the model for the selective solvation, mentioned above, can be considered to be useful for the description of the solvatochromism of the dyes in polar solvents. The results obtained by using regression analysis are compared in Table 1. It can be revealed that alcohols are more preferable to acetone or acetonitrile for selective solvation of the dye except for 4.

In the case of binary mixtures of acetone-ethanol and acetonitrile-ethanol the spectral changes of the dye 4 are small in the region of small amount of ethanol. This result indicates that the values of the index of the selective solvation ($K$) of
Fig. 5 Plots of wavenumber vs. ethanol content in acetonitrile
curve 1: the dye (3), curve 2: the dye (4),
curve 3: the dye (2a), curve 4: the dye (2b)

Table 1 The results of regression analysis of the solvatochromism in binary mixture of solvents

<table>
<thead>
<tr>
<th>binary mixture</th>
<th>dye</th>
<th>correlation factor</th>
<th>index of selective solvation</th>
</tr>
</thead>
<tbody>
<tr>
<td>first solvent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>3</td>
<td>0.995</td>
<td>1.82</td>
</tr>
<tr>
<td>methanol</td>
<td>4</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>acetone</td>
<td>2a</td>
<td>0.983</td>
<td>5.31</td>
</tr>
<tr>
<td>ethanol</td>
<td>2b</td>
<td>0.987</td>
<td>5.33</td>
</tr>
<tr>
<td>acetone</td>
<td>3</td>
<td>0.997</td>
<td>5.92</td>
</tr>
<tr>
<td>methanol</td>
<td>4</td>
<td>0.997</td>
<td>0.19</td>
</tr>
<tr>
<td>acetone</td>
<td>2a</td>
<td>0.987</td>
<td>7.97</td>
</tr>
<tr>
<td>methanol</td>
<td>2b</td>
<td>0.994</td>
<td>7.83</td>
</tr>
<tr>
<td>acetone</td>
<td>3</td>
<td>0.995</td>
<td>2.97</td>
</tr>
<tr>
<td>methanol</td>
<td>4</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>acetone</td>
<td>2a</td>
<td>0.977</td>
<td>13.18</td>
</tr>
<tr>
<td>methanol</td>
<td>2b</td>
<td>0.990</td>
<td>11.80</td>
</tr>
<tr>
<td>acetone</td>
<td>3</td>
<td>0.999</td>
<td>1.93</td>
</tr>
<tr>
<td>methanol</td>
<td>4</td>
<td>0.991</td>
<td>0.166</td>
</tr>
<tr>
<td>acetone</td>
<td>2a</td>
<td>0.993</td>
<td>19.21</td>
</tr>
<tr>
<td>methanol</td>
<td>2b</td>
<td>0.990</td>
<td>19.29</td>
</tr>
</tbody>
</table>

*) The change of wavenumber is too small to analyse by a linear regression method.

acetone and acetonitrile relative to ethanol are much larger. Thus, the regression analysis using eq. (8) was carried out by selecting ethanol as first solvent. The dye 3 has the value of $K$ close to unity, then this dye seems to be solvated less selectively by solvents, contrary to the dye 4 which is more selectively solvated by polar aprotic solvents than by ethanol.

The solvatochromic shift of the azonia betain dyes, 2a and 2b, in acetone-ethanol also seems to follow the Langmuir-style solvation model, but their correlation factor was not so excellent. This is because the plots of $\Delta \sigma_a/\Delta \sigma$ vs. $100/x$ were, strictly speaking, not linear, but slightly upward curvature, although the deviations are rather small and almost comparable to experimental error. These results reflect that these azonia betain dyes cannot be solvated according to simple Langmuir-style model. Since correlation factors ($r$) increased using Freundlich-style correlation equations (eq.(9) for the dye 2a, and eq.(10) for the dye 2b), these dyes seem to be suffered by various selective solvations in aprotic solvent-ethanol.

$$\ln(\Delta \sigma_a/\Delta \sigma) = 0.274 \ln x - 0.221 \quad (9)$$
$$r = 0.996$$

$$\ln(\Delta \sigma_a/\Delta \sigma) = 0.273 \ln x - 0.157 \quad (10)$$
$$r = 0.999$$

3.2 The solvatochromism in a binary mixture of aprotic solvent and water

Figures 6 and 7 display the shifts of the maximal absorptions of the dyes by an addition of water in acetone or acetonitrile. The dyes 3 and 4 show that the maximal absorptions shifted according to Langmuir-style model (Figures 6(b) and 7(b)). Only a slight deviations were observed at higher concentration of added water in case of acetone-water mixture. Although these deviations are comparable to experimental error as shown by Table 2, it can be clearly observed that the wave number increased with increasing added water after reaching the minimum value. This tendency reflects that the reaction field is strengthened by an addition of water, but it is weakened after the maximum reaction field is attained.

A number of models, such as flickering cluster model of Franck and Wen, were developed to describe structure of water.4) We assumed that
Fig. 6 Plots of wavenumber vs. water content in acetone
(a): the indicator (2b), (b): the indicator (2c),
(c): the indicator (3), (d): the indicator (4)

Fig. 7 Plots of wavenumber vs. water content in acetonitrile
(a): the indicator (2b), (b): the indicator (2c),
(c): the indicator (3), (d): the indicator (4)
the solvation shell may be constituted of unimolecular water and aprotic solvent molecule at lower concentration of water, while at higher concentration water possesses a complicated structure, similar to liquid water, in a solvation shell. If slight deviations in Figures 6(b) and 7(b) can be ignored, the character of water in the solvation shell is considered to be unaltered over the whole concentration range of water. Since liquid water consists of cluster or other associated species, water in the solvation shell around the dye molecules, 3 and 4, may constitute complicated structure, such as cluster, even at lower concentration in aprotic solvent.

This consideration seems to be reasonable, because water is known to be liable to constitute cluster around a neutral aromatic compounds.5) The solvatochromic shifts of the azonia betain dyes, 2b and 2c, clearly differed from those of the dyes, 3 and 4 (Figures 6a and 7a). The wavenumber of those dyes, 2b and 2c, hypsochromically shifts by an addition of water. After the wavenumber approaches to a definite value with an addition of water, then it increases again with further addition of water. The plot of the wavenumber against water content possessed upward curvature in early stage of addition of water, while downward curvature at higher concentration range. This result may reflect that water in the solvation shell changes its structure in a range of 30 to 50% of water content.

Solid lines in Figures 6a and 7a represent results calculated using the Langmuir-style model. In these cases the least-squares correlation of the wavenumber with water content was carried out according to eq. (10), excluding the data which deviate from a fitted line at 95% confidence level.

\[(\sigma_w - \sigma_a)/(\sigma - \sigma_a) = \tau_1 + \tau_2 (100/\kappa)\]  

(10)

Here, \(\sigma_w\) is designated to wavenumber in imaginary water solvent following to the Langmuir-style model, and \(\sigma_a\) that in aprotic solvent. In Table 2 all parameters of the Langmuir-style model are summarized. The difference between \(\sigma_w\) and \(\sigma_a\) in liquid water (\(\sigma_1\)) is rather small in the cases of the dyes 3 and 4, while \(\sigma_w\) is more bathochromic about 2000 cm\(^{-1}\) than \(\sigma_1\) in the cases of the dyes 2b and 2c. Then it may be assumed that water solvates unimolecularly the dyes 2b and 2c at water content less than 30–50% in acetone or acetonitrile, while water in cluster form operates in solvent shell at higher concentration.

The reaction field by monomeric water may be weaker than that by associated water. Detailed comparison of the reaction fields of them in aprotic solvent may be made using LSER (Linear

<table>
<thead>
<tr>
<th>dye</th>
<th>range of water content (v%/%)</th>
<th>(\tau_1)</th>
<th>(\tau_2)</th>
<th>(\sigma_w) (10^3 \text{ cm}^{-1})</th>
<th>correlation factor</th>
<th>(K)</th>
<th>(\sigma) (water) (10^3 \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0–70</td>
<td>-0.249</td>
<td>-0.439</td>
<td>25.88</td>
<td>0.996</td>
<td>0.976</td>
<td>26.34</td>
</tr>
<tr>
<td>4</td>
<td>0–80</td>
<td>-0.389</td>
<td>-0.063</td>
<td>23.44</td>
<td>1.000</td>
<td>0.626</td>
<td>23.67</td>
</tr>
<tr>
<td>2b</td>
<td>0–30</td>
<td>0.0138</td>
<td>0.235</td>
<td>19.26</td>
<td>1.000</td>
<td>17.64</td>
<td>21.37</td>
</tr>
<tr>
<td>2c</td>
<td>0–30</td>
<td>0.0204</td>
<td>0.239</td>
<td>18.04</td>
<td>1.000</td>
<td>11.93</td>
<td>19.96</td>
</tr>
<tr>
<td>a) acetone/water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dye</td>
<td>range of water content (v%/%)</td>
<td>(\tau_1)</td>
<td>(\tau_2)</td>
<td>(\sigma_w) (10^3 \text{ cm}^{-1})</td>
<td>correlation factor</td>
<td>(K)</td>
<td>(\sigma) (water) (10^3 \text{ cm}^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>0–90</td>
<td>-0.338</td>
<td>-0.317</td>
<td>26.03</td>
<td>0.997</td>
<td>1.017</td>
<td>26.34</td>
</tr>
<tr>
<td>4</td>
<td>0–100</td>
<td>-0.492</td>
<td>-0.087</td>
<td>23.66</td>
<td>0.995</td>
<td>0.697</td>
<td>23.67</td>
</tr>
<tr>
<td>2b</td>
<td>0–50</td>
<td>0.0116</td>
<td>0.248</td>
<td>19.81</td>
<td>0.997</td>
<td>29.60</td>
<td>21.37</td>
</tr>
<tr>
<td>2c</td>
<td>0–50</td>
<td>0.0137</td>
<td>0.237</td>
<td>18.54</td>
<td>0.998</td>
<td>25.06</td>
<td>19.96</td>
</tr>
<tr>
<td>b) acetonitrile/water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3 Analysis of solvatochromism by LSER

Several empirical scales have been proposed in order to quantify solvent effect in systems which was beyond the reach of theoretical tools. Polarity scales have been developed on the basis of spectral change of some indicators; e.g., the Z-scale by Kosower, the E-k-scale by Walter, the E-T-scale by Dimroth and the π°-scale by Taft.

Many approaches to solvent effect on physical and chemical properties of solute have been made in the application of the principles of linear free energy relationships to solvent effect. Taft and his coworkers proposed a multi parameter expression (eq. (10)), using three different scales which is assumed to be independent of each other and determined empirically; the polarity scale, π°, and a scale of solvent hydrogen bonding donor and the β scale of solvent hydrogen bonding acceptor.

\[ \sigma = a \pi^° + b \alpha + c \beta + \sigma_o \]  

(11)

The π° scale is based on the solvatochromic shift of the π−π° transitions of indicators. The average values are normalized so that π° of cyclohexane = 0.00 and π° of DMSO = 1.00. The β scale is determined by the enhanced displacement due to hydrogen bonding interaction using couple of indicator. The analysis was carried out on a couple 4-nitroaniline and N,N-diethyl-4-nitroaniline, and another couple 4-nitroanisole and 4-nitrophenol. This scale was determined also using the medium effects on physical properties of several indicators, such as 4-fluorophenol and 4-substituted and unsubstituted-2-nitroaniline.

The α scale was determined using 13C-nmr shift of phenyl methyl sulfoxide and 19F-nmr of 4-fluoracetophenone, and electronic spectral shifts of several indicators. However, it was rather difficultly formulated, because some unknown polarizability terms of hydrogen bonding of donor solvent are possibly included and the effect of weak self-association of such solvent cannot be excluded.

Table 3 shows the solvatochromism of the dyes 2a to 2c and 3 and 4. The absorption spectra of 2a-2c can be recorded only in polar solvents, because these dyes are insoluble in nonpolar solvent. Coefficients of eq. (11), a, b and c, and correlation factors are compared in Table 4, excluding data of the dyes 2a-2c in water which deviate from the regression line. The standard deviations between the observed and calculated values were 0.15 × 10³ cm⁻¹ in case of the dyes 2a-2c (number of data = 15) and 0.26 × 10³ cm⁻¹ in case of the dyes, 3 and 4 (number of data = 22). The fit is rather good but not so excellent, since these deviations are about 1% of the observed value, larger than the experimental error.

The observed values of 2a and 2c in water obviously deviate from the regression line at 95% confidence level, while the observed values of 3 and 4 in water agreed well with the calculated values (Table 5).

Table 3 The solvatochromism of the dyes

<table>
<thead>
<tr>
<th>solvent</th>
<th>maximal absorption/10³ cm⁻¹ of dyes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>31.15</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>30.41</td>
</tr>
<tr>
<td>benzene</td>
<td>29.15</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>28.89</td>
</tr>
<tr>
<td>acetone</td>
<td>27.33</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>27.47</td>
</tr>
<tr>
<td>methanol</td>
<td>27.03</td>
</tr>
<tr>
<td>ethanol</td>
<td>26.98</td>
</tr>
<tr>
<td>water</td>
<td>26.34</td>
</tr>
</tbody>
</table>

* insoluble
** rather unstable

Table 4 Parameters of LSER

<table>
<thead>
<tr>
<th>dye</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>σo/10³cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>−3.238</td>
<td>−0.662</td>
<td>−2.660</td>
<td>31.22</td>
</tr>
<tr>
<td>4</td>
<td>−3.429</td>
<td>−0.698</td>
<td>0.079</td>
<td>28.24</td>
</tr>
<tr>
<td>2a</td>
<td>3.603</td>
<td>4.538</td>
<td>0</td>
<td>12.64</td>
</tr>
<tr>
<td>2b</td>
<td>3.274</td>
<td>4.729</td>
<td>0</td>
<td>12.631</td>
</tr>
<tr>
<td>2c</td>
<td>2.109</td>
<td>4.200</td>
<td>0</td>
<td>12.316</td>
</tr>
</tbody>
</table>

Table 5 Comparison of the calculated and observed wavelengths

<table>
<thead>
<tr>
<th>dye</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>obs./nm</td>
<td>471</td>
<td>468</td>
<td>501</td>
<td>379</td>
<td>422</td>
</tr>
<tr>
<td>calc./nm</td>
<td>461</td>
<td>464</td>
<td>516.5</td>
<td>378</td>
<td>421</td>
</tr>
</tbody>
</table>
Each parameter as defined by eq. (12).

\[
\begin{align*}
\pi^* \% &= \frac{\alpha}{\pi^* / \Sigma \times 100} \\
\alpha \% &= \frac{\beta}{\alpha / \Sigma \times 100} \\
\beta \% &= \frac{\gamma}{\beta / \Sigma \times 100}
\end{align*}
\]

where \(\Sigma = a \pi^* + b \alpha + c \beta\)

As is evident from Table 6, the solvatochromic effects of acetone and acetonitrile are mainly controlled by their polar character. In cases of alcohols the solvent effect on the dye 3 is controlled by both polar and hydrogen bonding-accepting characters, while the dye 4 is mainly affected by the polar character of solvent.

All azonia betain dyes are mainly affected by the hydrogen bonding-donating character of alcohols. The solvent effects of water on the dyes, 3 and 4, are mainly controlled by the polar character of the solvent. In cases of the dyes 2a–2c in water, the deviations from regression line increased, as the contribution of hydrogen bonding character of solvent rises (Table 5). This result leads us the idea that liquid water around these dyes possesses larger \(\alpha\)-value and smaller \(\pi^*\)-value than the assumed value by Taft.\(^{10}\)

If \(\pi^*\) and \(\alpha\)-values of water around the dyes 2a–2c are assumed to be 0.253 and 1.693, respectively, the calculated wavelengths of these dyes are 471 nm, 468 nm and 501 nm, respectively. Those are close to the observed values listed in Table 5.

As mentioned above (Table 2), the imaginary water solvent which unimolecularly solvates possesses weaker reaction field than liquid water. By comparing \(\sigma_w\) with \(\sigma\) of liquid water, \(\pi^*\)- and \(\alpha\)-values of the imaginary water can be obtained as 0.321 ± 0.05 and 1.260 ± 0.08. These values can give \(\sigma_w(2b) = (19.64 \pm 0.3) \times 10^3\) cm\(^{-1}\) and \(\sigma_w(2c) = (18.28 \pm 0.3) \times 10^3\) cm\(^{-1}\). Therefore it can be concluded that the weak reaction field of the imaginary water solvent around the azonia betain dyes is mainly due to its low hydrogen donating ability.

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References

3) The details will be reported near future.
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ソルバトクロミズムから見た有機溶媒中の水

東京都立大学工学部　飛田満彦　吉田穂子　荒井良夫

アソニアベタイン色素 2a～2c および 4-ニトロアニリン類 3 および 4 を指示薬として、有機溶媒中における水の挙動について検討した。有機溶媒中に水を添加した際の、これら色素の最大吸収波数変化を、Onsagerキャビティ中にある溶媒に対する水および溶媒の競争的選択性溶媒モデルを仮定して解析した。その結果、次のことが明らかとなった。

アセトン、アセトニトリルのような非プロトン性溶媒中での色素 3 および 4 のまわりの水はクラスター状の状態で溶媒和する。一方、色素 2a～2c に対しては同じ溶媒中小量の水は分子状の離散状態で溶媒和する。同様な選択性溶媒モデルにより非プロトン性溶媒とアルコールとの混合溶媒系を解析し、水の場合と比較した。

また、これらの溶媒中における反応場を Taft らの提案した LSER（線型溶媒和エネルギー関係）を用いて解析し、それぞれの色素に対する溶媒の反応場について考察した。