Further Study on the Forms of Umbelliferone in Excited State. Part II

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Dedicated to Professor Dr. A. Schmillen on his 65th Birthday

The assumption [1] that there exist two excited tautomeric forms of umbelliferone in ethanol-aqueous solutions is compared with experimental results. Agreement is achived by assuming that the equilibrium between the two forms is dependent on the polarity of the solvent.

1. Introduction

Paper [1], presents the umbelliferone emission and absorption spectra in ethanol-aqueous solutions. Two sharply-marked emission spectra about 405 nm and 485 nm, and an isoemission point between them were observed when the water content was changed from 1–10%. At the same time no changes of the absorption spectra were seen in any of the tested solutions.

The phenomenon was interpreted as the result of an equilibrium between two tautomeric forms of the umbelliferone molecule in the excited state S. The suggested excited tautomeric forms clearly exhibit differences in their electron clouds and dipole moments. (The calculations were carried out by the PPPCI method.) The phototautomer with the larger separation of the charges has a considerably larger calculated dipole moment (4.26 D) than the other one (2.61 D).

2. Theoretical Considerations

In papers [2, 3] it was established that there exists an equilibrium of conformers dependent on the properties of the medium and on the polarity of the solution in particular.

Abraham [2] derived an equation for the difference of the energies of two forms in solution. If the term due to quadrupole interaction is ignored, the equation is

$$\Delta E^{\mathrm{S}} = \Delta E^{\mathrm{V}} - (\mu_{\mathrm{A}}^2 - \mu_{\mathrm{B}}^2) \cdot a^{-3}\{x(1-lx)^{-1} + b\, f_{\mathrm{e}}[1-\exp(-c/2)]\}, \quad (1)$$

where ΔE^{S} and ΔE^{V} are the energy differences between the two forms in solution (S) and vapour (V), μ_{A}, μ_{B} and μ_{S} are the dipole moments of the two forms and the solvent molecule, "a" is the radius of the spherical cavity of the Onsager reaction field theory and

$$x = (\varepsilon - 1)/(2\varepsilon + 1), \quad l = 2\alpha/a^3$$

where, ε is the dielectric constant of the binary solvent, α the mean polarizability of the dissolved molecule,

$$c = (\mu_{\mathrm{A}} - \mu_{\mathrm{B}}) \cdot \mu_{\mathrm{S}}/r^3\, kT\,,$$
$$f_{\mathrm{e}} = [(\varepsilon - 2)(\varepsilon + 1)/\varepsilon]^{1/2}$$

and "r" the mean distance between the point dipoles of dissolved molecules and 6 solvent molecules in an octahedral arrangement.

In Eq. (1) the first term in the braces is due to the interaction between the polarizable dipolar molecule (with $l > 0$) and the surrounding dielectric solvent, and the second term represents the energy of the electrostatic dipole-dipole interaction between the solute and solvent molecules averaged over all possible orientations of molecules.

For a binary solvent, the mean square dipole moment is given by

$$\mu_{\mathrm{S}}^2 = x_1\, \mu_1^2 + x_2\, \mu_2^2$$

where x_1 and $x_2 = 1 - x_1$ are the mole fractions of the solvent constituents.

The population ratio of the two forms in the state of thermodynamic equilibrium is

$$N_{\mathrm{A}}/N_{\mathrm{B}} = \exp(\Delta S^{\mathrm{S}}/k) \cdot \exp(-\Delta E^{\mathrm{S}}/kT)\,, \quad (2)$$

where ΔS^{S} and ΔE^{S} are the entropy and the energy differences of the respective forms in the solution.

From Eqs. (2) and (1) we obtain the relation

$$\ln(N_{\mathrm{A}}/N_{\mathrm{B}}) = (T\,\Delta S^{\mathrm{S}} - \Delta E^{\mathrm{V}}/kT) + (\mu_{\mathrm{A}}^2 - \mu_{\mathrm{B}}^2)/a^3\, kT \cdot \{x(1-lx)^{-1} + b\, f_{\mathrm{e}}[1-\exp(-c/2)]\}\,. \quad (3)$$

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Thus, if ΔS^{S} is supposed to be independent of x_1, the dependence of

$$\ln(N_{\mathrm{A}}/N_{\mathrm{B}}) \quad \text{on}$$
$$\{x(1-l\,x)^{-1} + b\,f_{\mathrm{e}}[1-\exp(-c/2)]\}$$

should be linear.

Our work aims at examining this dependence for the tautomeric equilibrium of umbelliferone in the state S_1, in aqueous-ethanol solutions with a water content of 1–10 volume%.

The population ratio of the tautomeric forms, i.e. of the excited umbelliferone (A) and the phototautomer (B) for each of the solutions was calculated from their emission spectrum [1].

The intensity of fluorescence F for solutions with no chemical reaction in the excited state can be presented as

$$F(\lambda,\lambda')\,\mathrm{d}\lambda' = w\,I_0(\lambda)\cdot k(\lambda)\cdot c\,\Phi_0\,f_{\mathrm{Q}}(\lambda')\,\mathrm{d}\lambda', \quad (4)$$

where

λ is the exciting wavelength,
λ' the wavelength of the emission spectrum which is being analized,
w the gauge constant,
I_0 the intensity of the exciting light,
$k(\lambda)$ the absorption coefficient of the solution,
c the concentration of the solute,
Φ_0 the quantum efficiency of luminescence, and
f_{Q} the quantum normalized distribution function.

If there occur two different luminous forms in the excited state, and the emission spectra of these are sufficiently separated so that there are two wavelengths λ'_{A} and λ'_{B} for which the emission signal comes from one of them only, then

$$F_{\mathrm{A}}(\lambda,\lambda'_{\mathrm{A}})\,\mathrm{d}\lambda'_{\mathrm{A}} = w\,I_0(\lambda)\,k(\lambda)\,c\,\Phi_0^{\mathrm{A}}\,f_{\mathrm{Q}}^{\mathrm{A}}(\lambda'_{\mathrm{A}})\,x_{\mathrm{A}}\,\mathrm{d}\lambda'_{\mathrm{A}}, \quad (4\mathrm{a})$$

$$F_{\mathrm{B}}(\lambda,\lambda'_{\mathrm{B}})\,\mathrm{d}\lambda'_{\mathrm{B}} = w\,I_0(\lambda)\,k(\lambda)\,c\,\Phi_0^{\mathrm{B}}\,f_{\mathrm{Q}}^{\mathrm{B}}(\lambda'_{\mathrm{B}})\,x_{\mathrm{B}}\,\mathrm{d}\lambda'_{\mathrm{B}}, \quad (4\mathrm{b})$$

where x_{A}, $x_{\mathrm{B}} = 1 - x_{\mathrm{A}}$ are the mole fractions of respective forms.

If we substitute

$$w\,I_0(\lambda)\,k(\lambda)\,\Phi_0^{\mathrm{A}}\,f_{\mathrm{Q}}^{\mathrm{A}}(\lambda'_{\mathrm{A}})\,c = K_{\mathrm{A}},$$
$$w\,I_0(\lambda)\,k(\lambda)\,\Phi_0^{\mathrm{B}}\,f_{\mathrm{Q}}^{\mathrm{B}}(\lambda'_{\mathrm{B}})\,c = K_{\mathrm{B}},$$

then

$$F_{\mathrm{A}}(\lambda,\lambda'_{\mathrm{A}}) = K_{\mathrm{A}}\,x_{\mathrm{A}}, \quad (5\mathrm{a})$$
$$F_{\mathrm{B}}(\lambda,\lambda'_{\mathrm{B}}) = K_{\mathrm{B}}\,x_{\mathrm{B}}. \quad (5\mathrm{b})$$

From the above two equations we obtain thus

$$F_{\mathrm{B}}(\lambda,\lambda'_{\mathrm{B}}) = K_{\mathrm{B}} - (K_{\mathrm{B}}/K_{\mathrm{A}})\,F_{\mathrm{A}}(\lambda,\lambda'_{\mathrm{A}}). \quad (6)$$

3. Calculated Results

A plot of $F_{\mathrm{B}}(\lambda,\lambda'_{\mathrm{B}})$ against $F_{\mathrm{A}}(\lambda,\lambda'_{\mathrm{A}})$ for $\lambda'_{\mathrm{B}} =$ 485 nm and $\lambda'_{\mathrm{A}} = 405$ nm, with $\lambda = 324$ nm and $c = 5\cdot 10^{-5}$ m/l in solutions of 3, 5, 7, 8, 10 volume% water in ethanol is presented in Figure 1. The straight line in Fig. 1 is a least-squares fit. From its slope $K_{\mathrm{B}}/K_{\mathrm{A}}$ can be determined, and then $x_{\mathrm{A}}/x_{\mathrm{B}}$ for each solution from the equation

$$x_{\mathrm{A}} = (1 + F_{\mathrm{B}}/F_{\mathrm{A}}\cdot K_{\mathrm{A}}/K_{\mathrm{B}})^{-1}. \quad (7)$$

$K_{\mathrm{B}}/K_{\mathrm{A}} = 7.545$ and the $\ln x_{\mathrm{B}}/x_{\mathrm{A}}$ values listed in Table 1 were obtained.

Next the values of

$$x(1-l\,x)^{-1} \quad \text{and} \quad f_{\mathrm{e}}[1-\exp(-c/2)],$$

were calculated for two cases:

a) Constant parameters

$$\mu_{\mathrm{A}} = 2.61\ \mathrm{D}, \quad \mu_{\mathrm{B}} = 4.26\ \mathrm{D}, \quad l = 1/2, \quad T = 293\ \mathrm{K}.$$

The radius "a" was evaluated on the assumption that the $a \simeq r$ and using the simplified formula

$$4/3\pi\,a^3 = M/N\,\varrho,$$

where M is the molecular weight, N Avogadro's number and ϱ the density of the dissolved substance. Thus we have obtained $a^3 = 5.212$ cm³.

Table 1.

Molar conc. of H_2O	Vol. conc. of H_2O	ε	μ_{s}	$y = x(1-lx)^{-1}$	f_{e}	$z = f_{\mathrm{e}}\cdot(1-\exp(-c/2))$	$y + 0.4\,z$	$\ln x_{\mathrm{B}}/x_{\mathrm{A}}$
0.091	0.03	28.6	1.719	0.6216	5.2469	2.5699	1.6496	− 0.435
0.146	0.05	31.5	1.73	0.6255	5.5169	2.7082	1.7087	− 0.657
0.196	0.07	33.9	1.74	0.6284	5.7307	2.8275	1.7592	− 0.820
0.220	0.08	34.9	1.746	0.6295	5.8174	2.8790	1.7811	− 1.1267
0.270	0.10	37.5	1.7551	0.6318	6.0371	2.9968	1.8306	− 1.5708

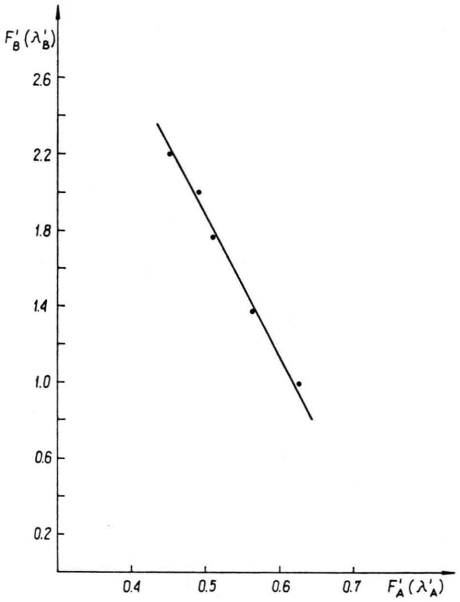

Fig. 1. Plot of $F'_B(\lambda_B)$ versus $F_A'(\lambda_A)$ for umbelliferone ($c = 5 \cdot 10^{-5}$ M/l) in ethanol with 3, 5, 7, 8, 10 volume % of water content; exciting wavelength $\lambda = 324$ nm. The emission signals for the two forms are taken from very accurately measured emission spectra (the same spectra have been given in Ref. [1]) for the wavelengths $\lambda'_A = 405$ nm (A form) and $\lambda'_B = 485$ nm (B = phototautomer form).

b) The parameters change with the composition of the solution (Table 1).

From the slope of the straight line in Fig. 2, $(\mu_B^2 - \mu_A^2)/a^3kT = 5.77$ was obtained. The theoretical value of this expression with $\mu_B = 4.26$ D and $\mu_A = 2.61$ D becomes 5.38. The correctness of $(\mu_B^2 - \mu_A^2)/a^3kT$ is limited due to an about 10% error in the evaluation of "a".

4. Concluding Remarks

The present work involves a number of simplifying assumptions:

1) the entropy ΔS^S remains constant, independently of the solvent polarity;

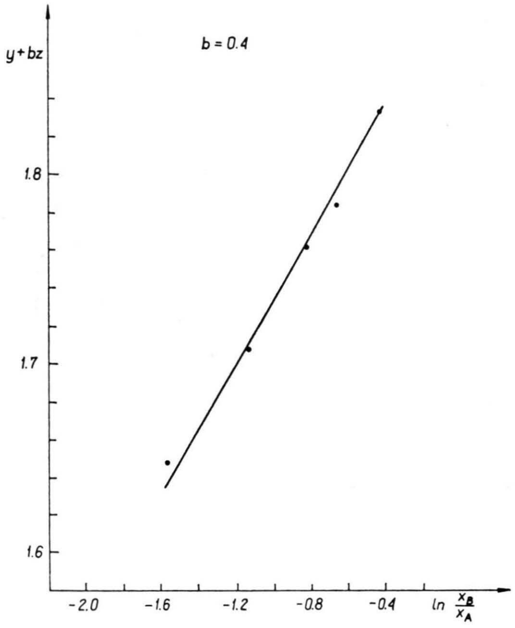

Fig. 2. Plot of $y + 0.4z$ versus $\ln x_B/x_A$.

2) the quadrupole interactions are neglected;
3) a complicated radial distribution is replaced by an octahedral solvent cage model with constant dimensions.

Nevertheless, the possibility of obtaining a straight line (Fig. 2) with parameter $b \neq 0$ shows that the dipole-dipole interaction with the polar solvent molecules plays a decisive role in the stabilization of the assumed tautomeric forms in ethanol-aqueous solutions.

Thus, the present calculation corroborates our hypothesis [1] about the existance of two tautomeric forms of umbelliferone in the excited state which are in an equilibrium.

Acknowledgement

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[3] M. Kobayashi and S. Kawabata, Spectrochim. Acta **33a**, 549 (1977).