

## Short Communication

## Solvent effects on the fluorescence of coumaric acids

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The polarity of the solvent substantially affects the fluorescence of many compounds. Attempted correlations between the fluorescence maximum of the compound and various theoretically or empirically derived parameters of solvent polarity have met with varying degrees of success [1, 2]. The most successful polarity parameters, at least as far as predicting fluorescence maxima are concerned, are the Reichardt-Dimroth  $E_T(30)$  parameter [2] and closely related Kosower  $Z$  value [3, 4]. These parameters are derived from the solvent dependence of the energy of the absorption maximum of negatively solvatochromic dyes (*i.e.* dyes whose absorption maximum shifts to higher energy in solvents of increasing polarity). However, the dye used to obtain the  $E_T(30)$  values has no hydrogen atoms capable of participating in hydrogen bonding and thus the absorption maximum would not be expected to be sensitive to the hydrogen bond accepting ability of the solvent. As part of our continuing work on arylethylenes we have undertaken a detailed study of the excited state behaviour of several coumaric acids and have found that the energy  $E_F$  of the fluorescence maximum showed a strong solvent dependence. Our results indicate that, in addition to the  $E_T(30)$  parameter, the hydrogen bond strength between the solute and the solvent is a significant factor in determining  $E_F$ .

The coumaric acids (Tokyo Kasei and BDH) were used as received and the solvents were of the purest available grade and were dried over calcium chloride or molecular sieves where necessary. The steady state and time-resolved fluorescence instrumentation and measurement techniques have been described previously [5].

Cinnamic acid (*trans*-3-phenyl-2-propenoic acid), methyl cinnamate and *p*-methoxycinnamic acids were found to be non-fluorescent in all solvents studied ( $\phi_F < 5 \times 10^{-5}$ ). *p*-coumaric acid (4-hydroxycinnamic acid) was weakly fluorescent and the dianion had a fluorescence lifetime of 25 ps in water as measured on a picosecond laser-streak camera system. The observed emission maximum (440 nm) is in agreement with previous results [6, 7]. *o*-methoxycinnamic acid (OM), *m*-methoxycinnamic acid (MM), *m*-coumaric acid (MC) and *o*-coumaric acid (OC) were found to be fluorescent in most of

TABLE 1

Photophysical data for coumaric acid derivatives

Solvent <sup>a</sup>	Absorption maximum (nm)		Fluorescence maximum (nm)			$E_T(30)^b$ (kJ mol <sup>-1</sup> )	$E_H^c$ (kJ mol <sup>-1</sup> )	
	OC	OM	MC	OC	MM			OM
1	318	326	— <sup>d</sup>	— <sup>e</sup>	368	373	136	0
2	321	317.5	370	372	362	368.5	145	23.3
3	322	320	375	375	369	376	151	21.3
4	321	319	377	376	369	376	156	24.0
5	321	319	376	378	371	379	159	19.8
6	320	318	380	379	372	375	167	19.6 <sup>f</sup>
7	325	318	400	395	379	388	183	29.1
8	319	316.5	394	394	388.5	395	192	17.6
9	322.5	321	397	397	388	396	195	18.9
10	324	320	404	405	393	387	203	—
11	321	316	427	427	405	406.5	232	—
12	322	320	— <sup>e</sup>	470	446	441	264	—
$\phi_F$			0.22	0.02	0.07	0.01		

<sup>a</sup>1, carbon tetrachloride; 2, diethyl ether; 3, dioxan; 4, tetrahydrofuran; 5, ethyl acetate; 6, methyl acetate; 7, dimethylformamide; 8, acetonitrile; 9, propylene carbonate; 10, 2-propanol; 11, methanol; 12, water.

<sup>b</sup>From ref. 8.

<sup>c</sup>From ref. 9.

<sup>d</sup>Insoluble.

<sup>e</sup>Non-fluorescent.

<sup>f</sup>From ref. 10.

the solvents studied and were used to investigate the relationship between  $E_F$  and  $E_T(30)$ . The fluorescence of OM and MM has not previously been characterized and MC was previously thought to be non-fluorescent since it does not fluoresce in water [7]. Table 1 details the fluorescence maximum of these compounds in the solvents and also the absorption maximum of OM and OC (it should be noted that the lowest absorption maximum of MC and MM is not resolvable at high solvent polarities). The quantum yields  $\phi_F$  of fluorescence for these compounds in ether are also tabulated. The fluorescence spectra were independent of excitation wavelength in all solvents and there was no evidence for the existence of photophysically distinct conformational species as reported for diarylethylene derivatives [5].

The data plotted in Fig. 1 show that a reasonable correlation exists between  $E_F$  and  $E_T(30)$  for MC. However, on closer inspection it is apparent that  $E_F$  in strong hydrogen bond acceptors is consistently lower than expected while  $E_F$  in weaker acceptors is higher. Unlike the dye from which the  $E_T(30)$  parameter is derived, the coumaric acids have hydrogen atoms available on the phenolic hydroxyl group and/or the carboxylic acid group which can participate in hydrogen bonding with the solvent. These consider-

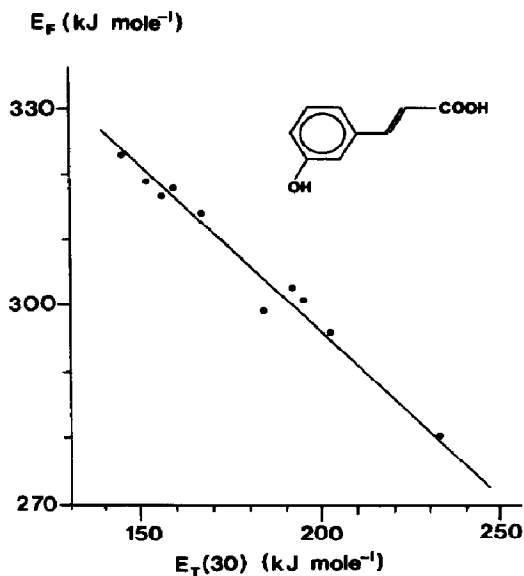


Fig. 1. Plot of the fluorescence maximum of MC vs. the  $E_T(30)$  solvent polarity parameter.

ations encouraged us to attempt a least-squares fit to an equation of the form

$$E_F = a + b_1 E_T(30) + b_2 E_H$$

where  $E_H$  is the strength of the phenol-solvent hydrogen bond [9] and  $a$ ,  $b_1$  and  $b_2$  are constants. In order to exclude any effects due to the hydrogen bond accepting ability of the solutes, only the data obtained in aprotic solvents were used. The results of the fit are presented in Table 2 and show that a marked improvement in correlation results when the strength of the

TABLE 2

Least-squares fitting results in solvents 1-9

$y$	$y = a + b_1 E_T(30)$			$y = a + b_1 E_T(30) + b_2 E_H$			
	$a$ (kJ mol <sup>-1</sup> )	$b_1$	$r^2$ <sup>a</sup>	$a$ (kJ mol <sup>-1</sup> )	$b_1$	$b_2$	$r^2$ <sup>a</sup>
$E_F(\text{MM})$	378	-0.36	0.891	379	-0.40	+0.32	0.977
$E_F(\text{OM})$	373	-0.36	0.929	374	-0.40	+0.25	0.983
$E_F(\text{MC})$ <sup>b</sup>	390	-0.46	0.917	410	-0.49	-0.72	0.994
$E_F(\text{OC})$ <sup>b</sup>	384	-0.43	0.954	396	-0.44	-0.42	0.986
SS(OM) <sup>c</sup>	-11	+0.43	0.964	-10	+0.42	+0.08	0.968
SS(OC) <sup>b,c</sup>	-9	+0.41	0.979	-7	+0.41	-0.09	0.980

<sup>a</sup>Square of the correlation coefficient.

<sup>b</sup>Excluding solvent 1.

<sup>c</sup>Stokes shift.

hydrogen bonding is incorporated as a variable. The improvement in fitting produced by including the hydrogen bond accepting ability of the solvents was statistically significant at the 95% confidence level for all the coumaric acids studied and significant at the 99% level for MC and MM. The fluorescence maximum of MC in particular could be specified by  $E_T(30)$  and  $E_H$  to within error limits of  $\pm 1$  nm, suggesting that there are no other solute-solvent interactions which affect the fluorescence maximum in these solvents. In contrast, there was no marked improvement in correlation between the Stokes shift of OM or OC with  $E_T(30)$  when  $E_H$  was incorporated as a variable (see Table 2). This observation is in agreement with previous reports [11, 12] that the Stokes shifts of phenols and aromatic carboxylic acids are not sensitive to hydrogen bond formation provided that no excited state proton transfer occurs. The  $b_1$  term for the coumaric acid derivatives is large and is indicative of a considerable charge transfer component in the excited state [2].

For the compounds studied ionization of the carboxylic acid group results in a blue shift of the lowest absorption band (e.g. 14 nm for OC) while ionization of the phenolic hydroxyl group leads to a considerable red shift of the absorption band (e.g. 55 nm for OC). Since the process of donating a proton to form a hydrogen bond can be considered as a partial ionization [13], these observations suggest that the absorption and emission maxima of coumaric acids will be blue shifted by hydrogen bonding through the carboxylic acid group and red shifted by hydrogen bonding through the phenol. For OM and MM only the carboxylic acid group proton is available to participate in hydrogen bonding with the solvent, and thus there should be a blue shift in fluorescence with solvents of increasing hydrogen bonding strength. However, in MC and OC the phenolic proton can participate in hydrogen bonding as well and an overall red shift in the fluorescence maximum with increasing hydrogen bonding strength of the solvent might be expected since the emission spectra of coumaric acids are much more sensitive to ionization of the phenol than to ionization of the carboxylic acid group. Hence, we would expect  $E_F$  to be positively correlated with  $E_H$  for OM and MM and negatively correlated with  $E_H$  for OC and MC, in agreement with the experimental results.

Consideration of the strength of hydrogen bonding between the solute and the solvent has resulted in a marked improvement in the correlation between the  $E_T(30)$  polarity parameter and the energy of the fluorescence maximum for coumaric acids. We feel that this observation may be generally applicable and may help to describe the solvent dependence of fluorescence from other solutes.

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