ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 108 (1997) 283–288

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Spectral properties of coumarin derivatives substituted at position 3. Effect of polymer matrix

M. Kaholek, P. Hrdlovič *

Polymer Institute, Slovak Academy of Sciences, Dubravska cesta 9, 842 36 Bratislava, Slovak Republic

Received 28 January 1997; accepted 6 February 1997

Abstract

The spectral properties of coumarin (2H-1-benzopyran-2-one) derivatives substituted at position 3 with bulky substituents, such as phenyl, phenylthio and benzylthio, were investigated in solvents of different viscosity and in polymer matrices. In order to evaluate the heavy atom effect, some derivatives were substituted by bromine at positions 6 and 8. The absorption spectra exhibit a broad band with a maximum at 340 nm (log $\epsilon \approx 4$) which is not influenced by the medium. Coumarin derivatives in solvents of low viscosity exhibit broad band fluorescence with a low quantum yield of 0.005 and a lifetime shorter than 0.1 ns. In solvents of higher viscosity and in polymer films, the quantum yields are 0.05–0.2 higher and the lifetime is increased by approximately 2 ns. On the basis of the spectral data, the rate constant of radiationless deactivation k_{nr} is 10^{11} s^{-1} in solution and 4×10^8 s^{-1} in the polymer matrix. The activation energy of the radiationless process in 3-phenylcoumarin is about 34 kJ mol^{-1} in glycerol. The activation energy of viscosity change of glycerol is 72 kJ mol^{-1}. This comparison indicates that the torsional rotation of the substituent at position 3 is partially influenced by the friction viscosity of the medium. © 1997 Elsevier Science S.A.

Keywords: Activation energy; Coumarin; Fluorescence; Polymer matrix; Radiationless process; Solvent effect; Substituents at position 3

1. Introduction

Coumarin (2H-1-benzopyran-2-one) and its derivatives occur widely in nature. Many natural and synthetic derivatives of coumarin are used in different applications in chemistry, biology, medicine and physics, mainly as a result of their luminescence properties. For this reason, considerable attention has been paid to the preparation of coumarin derivatives substituted at different positions and their spectral characteristics have been studied. Recently, it has been shown that the luminescence properties of the 4-alkyl and 7-alkoxy derivatives of coumarin are strongly dependent on the medium [1]. In viscous glycerol, a higher quantum yield of emission was determined than in methanol. A large Stoke's shift was observed for the derivative with a dimethylamino group at position 3 as a result of intramolecular charge transfer (ICT) [2]. Several workers have recommended that coumarin derivatives substituted at positions 3, 4, 6, 7 and 8 are suitable for use as dyes for lasers [3–7]. The most effective laser dyes are coumarins substituted at position 7 with electron-donating groups, such as hydroxyl, alkoxyl and amine, with electron-accepting groups at positions 3, 4 and 6.

Experimental studies and theoretical calculations have shown that the lowest excited state S_1 of unsubstituted coumarin has $n\pi^*$ character. Substitution of coumarin at positions 3–8 produces a change in the character of the S_1 state and a higher fluorescence yield. Different radiationless mechanisms leading to the deactivation of the lowest excited state and competing with fluorescence include ICT [2], the formation of a twisted intramolecular charge transfer (TICT) state [6,8] and a change from the planar to pyramidal configuration of the amino group [6]. In spite of the numerous studies, the role of the photophysical deactivation processes operating in substituted coumarins is not well understood.

In this paper, the spectral characteristics of coumarin derivatives substituted at position 3 with bulky groups, such as phenyl, phenylthio and benzylthio, are presented. In order to evaluate the heavy atom effect, some derivatives were substituted at positions 6 and 8 by bromine. The spectral properties were investigated in solution and in polymer matrices in order to compare the effect of different environments.

---

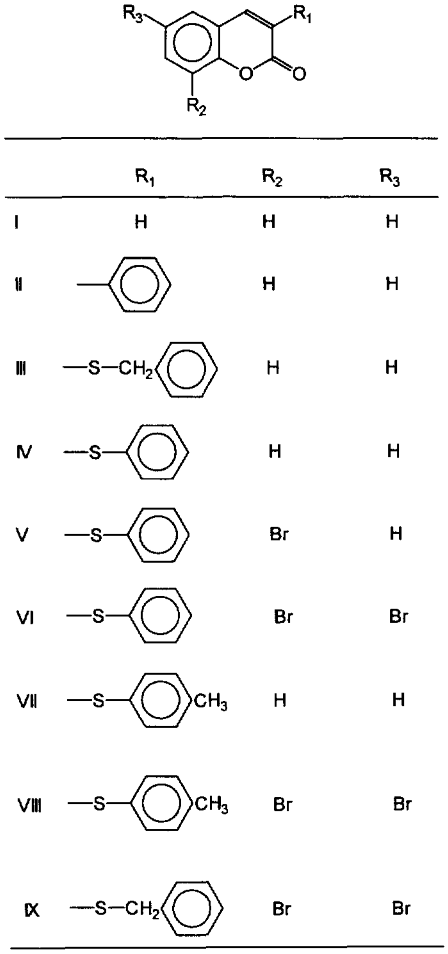
* Corresponding author. Tel.: +42 7 373448; fax: +42 7 375923; e-mail: upolhrdl@savba.sk

PII S1010-6030(97)00081-6

2. Experimental details

Coumarin (2H-1-benzopyran-2-one) (**I**) was a commercial product (Aldrich, Steinheim, Germany). The coumarin derivatives (Scheme 1) substituted at positions 3, 6 and 8 were prepared at the Department of Organic Chemistry, Faculty of Science, Comenius University, Bratislava and were as follows: 3-phenylcoumarin (**II**) (melting point (m.p.), 135–138 °C), 3-benzylthiocoumarin (**III**) (m.p., 162–164 °C), 3-phenylthiocoumarin (**IV**) (m.p., 117–119 °C), 3-phenylthio-6-bromocoumarin (**V**) (m.p., 179–180.5 °C), 3-phenylthio-6,8-dibromocoumarin (**VI**) (m.p., 150–153 °C), 3-(4-methylphenylthio)coumarin (**VII**) (m.p., above 350 °C), 3-(4-methylphenylthio)-6,8-dibromocoumarin (**VIII**) (m.p., 194–196 °C) and 3-benzylthio-6,8-dibromocoumarin (**IX**) (m.p., 174–178 °C). The purity of the coumarin derivatives was controlled by spectroscopy and thin layer chromatography (TLC).

Anthracene was zonally refined. Quinine sulphate was an analytical reagent (Lachema, Brno, Czech Republic). Cyclohexane and ethanol were of UV spectroscopy grade (Merck, Darmstadt, Germany). Chloroform (Mikrochem Ltd., Bratislava, Slovak Republic), tetrahydrofuran (BDH, Poole, UK) and glycerol (Lachema, Brno, Czech Republic) were analytical reagents. Butene oil (Hyvis 3) was a commercial product (BP Chemicals Ltd., London, UK).



Scheme 1. Structure of coumarin derivatives.

Polymer films were prepared by casting from solution. Polystyrene (PS, Vestyron, Huls AG, Germany), poly(methyl methacrylate) (PMMA, Diacon, ICI, UK) and polyvinylchloride (PVC, Neralit, Spolana Neratovice, Czech Republic) were used as polymer matrices. The doped compound was dissolved in polymer solution (5 g per 100 ml) and cast on a glass plate (26 mm × 38 mm). The solvent was allowed to evaporate slowly. The thickness of the film was 50 μm.

The absorption spectra were measured on an M-40 spectrometer (C. Zeiss, Jena, Germany). The emission spectra were taken on an MPF-4 spectrofluorometer (Perkin–Elmer, Norwalk, CO, USA) which was connected through an A/D converter and interfaced to a microcomputer [9]. The emission spectra of the solutions were measured in a right angle arrangement. The emission spectra of the polymer films were recorded in a front face arrangement in a solid sample holder. The quantum yield was determined relative to anthracene in solution and in a polymer matrix. The quantum yield of anthracene in solution was checked with quinine sulphate. The absolute quantum yields of coumarin derivatives were determined assuming that anthracene fluorescence is independent of the medium. The quantum yield was determined according to the relationship [10]

$$\Phi_\mathrm{F} = \Phi_\mathrm{F}^\mathrm{S} \frac{\int_0^\infty I_\mathrm{F}(\nu)\mathrm{d}\nu}{\int_0^\infty I_\mathrm{F}^\mathrm{S}(\nu)\mathrm{d}\nu} \left(\frac{1-10^{-A^\mathrm{S}}}{1-10^{-A}}\right)\left(\frac{n}{n^\mathrm{S}}\right)^2\left(\frac{2-r_n^\mathrm{S}}{2-r_n}\right) \qquad (1)$$

where $\Phi_\mathrm{F}^\mathrm{S}$ is the quantum yield of anthracene as standard, which was assumed to be 0.25 for all environments. For the relative quantum yields, the value of $\Phi_\mathrm{F}^\mathrm{S}$ for anthracene was set to unity. The integrals $\int_0^\infty I_\mathrm{F}(\nu)\mathrm{d}\nu$ and $\int_0^\infty I_\mathrm{F}^\mathrm{S}(\nu)\mathrm{d}\nu$ are the areas under the emission curves of the investigated compound and standard and A and A^S are the absorbances, n and n^S are the refractive indices and r_n and r_n^S are the anisotropies of emission on excitation by unpolarized light for the investigated compound and standard respectively.

The emission decay was measured on a LIF 200 apparatus (LTB GmbH, Berlin, Germany) which operates as a stroboscope. The output was digitized in an A/D converter and transferred to a microcomputer [11]. The decay curves were evaluated by the phase plane method [12]. The standard deviation $G^{1/2} = \Sigma[(I_\mathrm{cal} - I_\mathrm{exp})^2/n]^{1/2}$ characterized the quality of fitting. A standard deviation $G^{1/2}$ higher than 5% indicates that a monoexponential function does not fit the decay satisfactorily.

3. Results and discussion

The influence of the medium (solvent, micelles, polymer matrix) on the spectral properties is determined by the extent

Table 1
Spectral characteristics of coumarin derivatives substituted at position 3 in solution and in polymer matrices

Compound[a]	Medium[b]	λ_a (nm)	log ϵ	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\tilde{\nu}$ (cm^{-1})	Φ_F^c	τ_F (ns)	$G^{1/2}$
II	Cy	328	4.07	332	397	5300	0.064		
	E	328	4.09	330	401	5650	0.140		
	Gly–E (9 : 1)	328	4.09	340	405	5800	0.86		
	Gly			337	405		3.83		
	BO (Hyvis 3)	328	3.73	342	398	5400	0.96		
	PS	333	3.85	347	404	5300	0.82	0.2	
	PMMA	328	3.84	348	399	5400	0.85		
	PVC	333	3.85	350	416	6000	1.89	0.5	2.9
III	Cy	339	3.97	355	403	4700	0.0084		
	E	339	4.24	354	442	6900	0.0067		
	Gly–E (9 : 1)	337	3.99	356	430	6400	0.114		
	PS	339	3.90	353	415	5400	0.12		
	PMMA	339	3.70	345	406	4900	0.21		
	PVC	339	3.65	345	409	5000	0.24		
IV	Cy	333	3.93	345	464	8500	0.0052		
	E	339	4.04	351	521	10300	0.0028		
	Gly–E (9 : 1)	339	3.87	353	510	9900	0.043		
	PS	339	3.88	351	468	8100	0.26	1.4	8.1
	PMMA	339	3.64	345	466	8000	0.65	2.8	7.2
	PVC	339	3.59	350	469	8200	0.50	2.4	6.2
V	Cy	339	4.00	345	465	8000	0.0032		
	E	345	4.15	356	539	10400	0.0016		
	Gly–E (9 : 1)	343	3.84	370	520	9900	0.017		
	PS	345	3.99	357	473	7800	0.33	1.8	8.9
	PMMA	345	3.71	350	470	7700	0.73		
	PVC	345	3.78	355	475	7900	0.36	2.5	4.3
VI	Cy	345	4.16	355	479	8100	0.0033		
	E	345	4.20	361	519	10771	0.0010		
	Gly–E (9 : 1)	345	3.89	382	465	7481	0.055		
	PS	345	3.99	359	482	8200	0.31	2.4	5.2
	PMMA	345	4.05	355	475	7900	0.93	3.00	4.60
	PVC	345	4.07	360	487	8450	0.48		
VII	Cy	333	4.05	350	472	8800	0.0042		
	E	339	4.07	353	548	11200	0.0026		
	Gly–E (9 : 1)	339	3.96	360	534	10800	0.015		
	PS	339	3.89	351	477	8500	0.30	2.0	7.7
	PMMA	339	3.71	345	475	8400	0.59	2.8	7.6
	PVC	339	3.84	352	468	8100	0.65	2.7	5.5
VIII	Cy	345	4.24	355	499	8900	0.0015		
	E	345	4.27	361	576	11600	0.00033		
	Gly–E (9 : 1)	344	3.09	361	540	10500	0.051		
	PS	345	3.86	357	499	8900	0.37	2.4	6.9
	PMMA	345	3.97	355	494	8700	0.76	3.1	6.1
	PVC	351	3.94	357	504	8600	0.40		

[a] Compounds are shown in Scheme 1.
[b] Cy, cyclohexane; E, ethanol; Gly, glycerol; BO, butene oil; PMMA, poly(methyl methacrylate); PS, polystyrene; PVC, polyvinylchloride.
[c] Quantum yield relative to anthracene.

of interaction between the solute and the solvent. For weak interaction (associated with low solubility), the influence of the medium is negligible. In the extreme case, the solute exhibits characteristics typical of the gaseous phase. For strong, specific solute–solvent interactions, large shifts in the spectral bands and changes in intensity are observed. In polymer matrices, the viscosity of the matrix plays a role in addition to the polar effects common with low viscosity solvents. The standard preparation of polymer films by casting from solution may lead to complications due to different degrees of aggregation of the dopant; however, the final films are optically transparent.

The absorption spectra of coumarin derivatives show a broad band in solvents (cyclohexane, ethanol) and polymer matrices in the long-wavelength region without vibrational structure (Table 1). The band is red shifted by 20 nm relative to parent coumarin on substitution at position 3. Further substitution at positions 6 and 8 shifts the band slightly bathochromically (5 nm). Derivatives containing thio substituents at position 3 exhibit an absorption maximum at about 340 nm

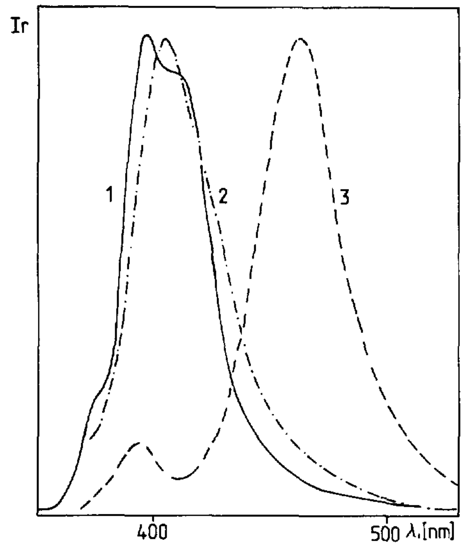


Fig. 1. Emission spectra of 3-phenylcoumarin (1.26×10^{-5} mol dm^{-3}) (1), 3-benzylthiocoumarin (1.01×10^{-4} mol dm^{-3}) (2) and 3-phenylthiocoumarin (1.12×10^{-4} mol dm^{-3}) (3) in cyclohexane.

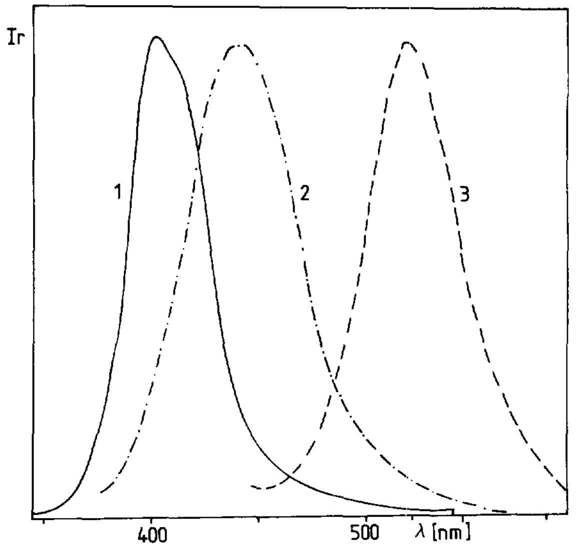


Fig. 2. Emission spectra of 3-phenylcoumarin (1), 3-benzylthiocoumarin (2) and 3-phenylthiocoumarin (3) in ethanol.

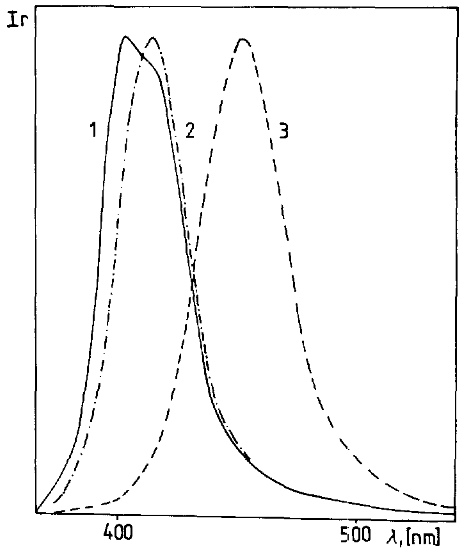


Fig. 3. Emission spectra of 3-phenylcoumarin (1), 3-benzylthiocoumarin (2) and 3-phenylthiocoumarin (3) in a polystyrene matrix.

with log $\epsilon \approx 4$. The determination of the molar extinction coefficient in polymer films is associated with higher error than that in solution and the log ϵ values exhibit a larger scatter.

The emission spectrum of unsubstituted coumarin is very weak [13] and, in our experimental apparatus, was not registered in solution or in a polymer matrix. Substitution of coumarin by phenyl at position 3 increases the fluorescence, and the quantum yield relative to anthracene is in the range 0.05–2 (Table 1). The fluorescence maximum in non-polar cyclohexane and polar ethanol is at 400 nm (Stoke's shift is around 5500 cm^{-1}) and the intensity is low. In polar ethanol, it is slightly higher than in cyclohexane. Substitution with a phenylthio group at position 3 results in a larger Stoke's shift of about 8500 cm^{-1} (Fig. 1). This emission is even more shifted in polar ethanol ($\Delta\tilde{\nu} \approx 10\,000\ \mathrm{cm}^{-1}$), but is less intense (Fig. 2). The large Stoke's shift indicates that the emission does not originate from a Franck–Condon transition. Stabilization of this state in polar ethanol indicates some ICT. This state, however, is partially quenched by polar solvents [2]. The emission spectra of the 3-substituted coumarins in a polystyrene matrix are shown in Fig. 3.

In general, the quantum yields of the substituted coumarins relative to anthracene are in the range 0.003–0.65, being lowest in ethanol and highest in PMMA films (Table 1). Substitution at positions 6 and 8 by bromine does not influence the shape and intensity of fluorescence. Similarly, substitution with methyl in the phenylthio group does not influence the emission. Substitution with a benzylthio group at position 3, which has a methylene bridge between the sulphur and phenyl group, exhibits the same effect as the phenyl group. The Stoke's shift is about 5000 cm^{-1}. The shift is larger in polar ethanol (about 7000 cm^{-1}), indicating that this compound is more sensitive than 3-phenylcoumarin. Substitution with bromine at positions 6 and 8, in combination with 4-methylphenylthio and 3-benzylthio, decreases the intensity of fluorescence.

The fluorescence lifetimes of all the derivatives under study are below the resolution limit of the LIF 200 apparatus (less than 0.1 ns). In polymer matrices, the fluorescence decay is substantially slower for derivatives substituted at position 3. The lifetime is in the range 0.2–3 ns as measured by the simple phase plane method. In most cases, the standard deviation $G^{1/2}$ is larger than 5%, indicating some deviation from a monoexponential function. Derivatives with phenyl and benzylthio groups at position 3 exhibit a shorter lifetime than those with a phenylthio group at position 3 in a polymer matrix. Substitution with bromine does not influence the lifetime of the substituted coumarins, i.e. bromine does not affect the radiation and radiationless processes based on lifetime measurements. However, the intensity measurements indicate some effect.

The rate constant (k_r) of the radiation process (fluorescence) can be estimated from the intensity of the absorption band using the formula [5] approximated from the Stickler and Berg exact relationship [14]

$$k_r = 10^4 \epsilon \quad (2)$$

where ϵ is the molar decadic extinction coefficient. Its value is 10^4 dm^3 mol^{-1} cm^{-1} for most derivatives substituted at position 3 and, therefore, the rate constant for the radiation process is about 10^8 s^{-1}.

The fluorescence lifetime is given by the relationship

$$\tau_F = \Phi_F / k_r \quad (3)$$

Since the lowest quantum yield of fluorescence of coumarin derivatives is about 0.005, the lifetime based on this simple calculation is about 5×10^{-11} s. This is clearly below the time resolution of the LIF 200 instrument (half-width of the nitrogen laser, 0.5 ns).

The rate constant of the radiationless process is given by

$$k_{nr} = (1 - \Phi_F) / \tau_F \quad (4)$$

The rate constant of the radiationless process for coumarin derivatives is therefore around 2×10^{10} s^{-1}. Assuming that the quantum yield of fluorescence of anthracene Φ_F^S is equal to 0.25 and is independent of the medium, and employing Eqs. (2)–(4), k_r, τ_F and k_{nr} for the derivatives of coumarin can be obtained and are summarized in Table 2. The calculated values of k_r, τ_F and k_{nr} for the solvents and polymer matrices set the limits. The calculated and measured values of τ_F are in good agreement. The scatter of the values of ϵ and Φ_F in the polymer matrices is rather high; therefore, it is not possible to determine any differences between the matrices. It seems that k_{nr} is slightly higher in PS than in the other matrices. A higher value of k_{nr} indicates that the PS matrix is less rigid if the rest of the solvent is the same for PMMA and PVC.

An analysis of the radiation and radiationless processes indicates that the substituent at position 3 influences the radiationless process which is sensitive to the medium. This conclusion is supported by the fact that no dependence of the luminescence on the medium was observed for parent coumarin. The radiationless deactivation of the electronic energy is associated with the rotation of this group. Clearly, there is a correlation between the frequency of rotation and the radiationless rate constant k_{nr}, but our data do not allow this relationship to be established.

To gain some insight into this process, the activation energy of the radiationless process was determined. For this purpose, the temperature dependence of the quantum yield or the fluorescence lifetime can be used. Since the fluorescence lifetime of coumarin derivatives in a polymer matrix is about 2 ns and the decrease in the lifetime due to a change in temperature is difficult to measure, the determination of the activation energy based on the temperature dependence of the quantum yield is preferred. From Eqs. (2)–(4), and assuming that the quantum yield is substantially lower than unity, the ratio $k_{nr}(T_2)/k_{nr}(T_1)$ can be approximated by $\Phi_F(T_1)/\Phi_F(T_2)$.

The dependence of the relative quantum yield on the temperature was determined in the temperature range 20–60 °C for 3-phenylcoumarin in viscous polar glycerol, a glycerol–ethanol mixture (9 : 1) and non-polar butene oil (Fig. 4). 3-Phenylcoumarin was chosen because it exhibits the most intense luminescence in glycerol. The activation energy of

Table 2
Photophysical constants of coumarin derivatives substituted at position 3

Compound	Medium[a]	ϵ (dm^3 mol^{-1} cm^{-1})	Φ_F^b	k_r (s^{-1})	τ_F (ns)	k_{nr} (s^{-1})
II	Cy	1.2×10^4	0.016	1.2×10^8	0.13	7.5×10^9
	E	1.2×10^4	0.035	1.2×10^8	0.29	3.3×10^9
	Gly–E (9 : 1)	1.2×10^4	0.215	1.2×10^8	1.8	4.4×10^8
	PS	6.9×10^3	0.213	6.9×10^7	3.09	2.5×10^8
	PMMA	7.1×10^3	0.473	7.1×10^7	6.67	8.0×10^7
	PVC	7.1×10^3	0.205	7.1×10^7	2.89	2.8×10^8
III	Cy	9.3×10^3	0.0021	9.3×10^7	0.023	4.3×10^{10}
	E	1.7×10^4	0.0016	1.7×10^8	0.0094	1.1×10^{11}
	Gly–E (9 : 1)	9.8×10^3	0.0285	9.8×10^7	0.29	3.4×10^9
	PS	7.9×10^3	0.03	7.9×10^7	0.38	2.5×10^9
	PMMA	5.0×10^3	0.053	5.0×10^7	1.06	9.0×10^8
	PVC	4.5×10^3	0.06	4.5×10^7	1.3	7.2×10^8
IV	Cy	8.5×10^3	0.0013	8.5×10^7	0.015	6.6×10^{10}
	E	1.1×10^4	0.0007	1.1×10^8	0.0064	1.6×10^{11}
	Gly–E (9 : 1)	7.4×10^3	0.011	7.4×10^7	0.149	6.6×10^9
	PS	7.6×10^3	0.065	7.6×10^7	0.85	1.1×10^9
	PMMA	4.4×10^3	0.163	4.4×10^7	3.7	2.2×10^8
	PVC	3.9×10^3	0.125	3.9×10^7	3.2	2.7×10^8

[a] The symbols are the same as in Table 1.

[b] Calculated using Φ_F (Table 1) assuming 0.25 for the quantum yield of anthracene in all media.

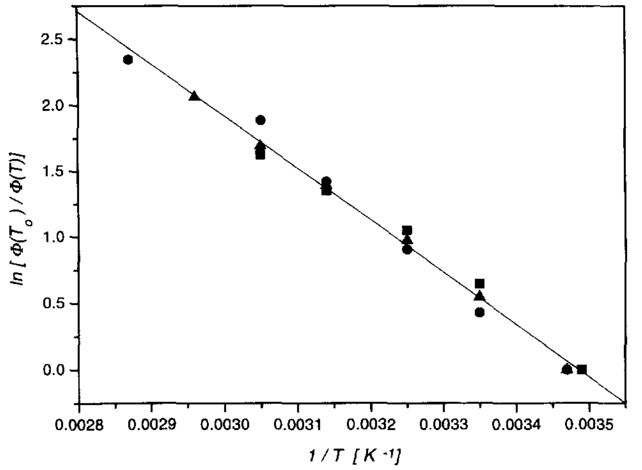


Fig. 4. Dependence of ln($\Phi(T_0)/\Phi(T)$) on $1/T$ for 3-phenylcoumarin in glycerol (●), a glycerol–ethanol mixture (9 : 1) (▲) and butene oil (■).

the radiationless process E_a is 34 kJ mol^{-1} for glycerol, 33 kJ mol^{-1} for a glycerol–ethanol mixture and 30 kJ mol^{-1} for butene oil. A decrease in emission indicates an increase in the rate of the radiationless process. Since E_a for this process is the same in both polar glycerol and non-polar butene oil, the polarity of the solvent does not affect the process. The activation energy of the change in viscosity is 73 kJ mol^{-1} for glycerol and almost the same for the glycerol–ethanol mixture [15]. A comparison of these values shows that the activation energy of the radiationless process is only half of the activation energy for the viscosity change. This means that the radiationless process is determined partially by the macroviscosity of the medium. Consequently, other factors influence the frequency of rotation of the substituent at position 3 in addition to the friction viscosity of the medium.

In conclusion, the luminescence properties of the coumarin derivatives under study are dominated by the character of the substituent at position 3 and the medium.

Acknowledgements

The authors thank the Grant Agency "VEGA" of the Slovak Republic for financial support through grant 2/1014/96.

References

[1] J.R. Heldt, J. Heldt, M. Ston, H.A. Diehl, Spectrochim. Acta, Part A 51 (1995) 1549.
[2] A. Gáplovský, P. Hrdlovič, J. Donovalová, P. Hrnčiar, J. Photochem. Photobiol. A: Chem. 59 (1991) 221.
[3] T.L. Arbeloa, F.L. Arbeloa, M.J. Tapia, J.L. Arbeloa, J. Phys. Chem. 97 (1993) 4704.
[4] B.B. Raju, T.S. Varadarajan, J. Phys. Chem. 98 (1994) 8903.
[5] B.B. Raju, T.S. Varadarajan, J. Photochem. Photobiol. A: Chem. 85 (1995) 263.
[6] T.L. Arbeloa, F.L. Arbeloa, J.L. Arbeloa, J. Lumin. 68 (1996) 149–155.
[7] B.B. Raju, T.S. Varadarajan, Laser Chem. 16 (1995) 109.
[8] K. Rechthaler, G. Köhler, Chem. Phys. 189 (1994) 99.
[9] G. Moyze, J. Mlýnek, D. Jurčák, P. Hrdlovič, Chem. Listy 86 (1992) 57.
[10] A. Kawski, A. Kubicki, B. Kubliňsky, J. Photochem. Photobiol. A: Chem. 79 (1993) 161–167.
[11] D. Jurčák, J. Mlýnek, G. Moyze, P. Hrdlovič, Chem. Listy 83 (1989) 531.
[12] J.N. Demas, A.W. Adamson, J. Phys. Chem. 57 (1971) 2463.
[13] J.S.S. de Melo, R.S. Becker, A.L. Maçanita, J. Phys. Chem. 98 (1994) 6054.
[14] S.J. Stickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814.
[15] R.C. Weast, Handbook of Chemistry and Physics, 58th ed., The Chemical Rubber Company, 1977–1978.