

39. What is the 'Solvent' Effect on the Electronic Spectra of a Solute in a Polymer Matrix?

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Dedicated to the memory of Professor *Heinrich Labhart*

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Summary

The theory of solvent-induced shifts of the absorption and fluorescence band spectra of a solute is well known and has been tested for a multitude of systems. However, there are only few applications to polymers. By a direct comparison of the spectral shifts in liquid solvents with those in polymers it is possible to determine the microenvironment of the solutes in polymers within the frame of this theory. Polyethylene terephthalate as fabric and film was chosen as model polymer. The spectral shifts of 15 fluorescing solutes in this polymer as well as in 10 solvents with widely differing refractive indices n and permittivities ϵ were measured and fitted to the equations given by the theory of the solvent effect. It is found that interactions with the permanent dipoles of polyethylene terephthalate may be neglected within the limits of accuracy attainable for this polymer and the chosen solutes. Dispersion forces dominate the solvent effect. The refractive indices effective at the site of the solute molecules are $n = 1.66$ for the fabric and $n = 1.70$ for the film.

Introduction. - The solvent effect of liquid solvents on the electronic spectra (electronic spectral shift) of a solute has been dealt with comprehensively by *Mataga & Kubota* [1] and by *Liptay* [2]. These authors also survey the fundamental contributions by *Bayliss* [3], *Ooshika* [4], *Lippert* [5], *McRae* [6], and by *Longuet-Higgins & Pople* [7]. In this connection, the meaning of the term 'solvent effect' is the solvent dependence of the wave number of the electronic absorption and emission bands. Numerous applications have revealed to what extent the observed and calculated spectral shifts agree.

However, direct comparisons of the solvent effects on absorption and fluorescence spectra in liquid solvents and solid matrices are rare, although extensive work has been done, e.g. on the pressure dependence of electronic spectra in compressed plastic media (*Offen* [8], *Nicol* [9]) as well as in fluid solvents (*Robertson et al.* [10]). It is the aim of this investigation to close this gap.

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The title question has not only a scientific interest, but also a practical background. In order to characterize a fluorescent whitening agent applied on a substrate, its reflectance spectrum (spectral radiance factor) is measured and resolved into an absorption and emission (fluorescence) spectrum according to the method of *Eitle & Ganz* [11]. This could be simplified considerably if liquid solvents were found which give rise to identical spectra, *i.e.* if substrate-like solvents existed. In the ideal case not only the absorption and fluorescence band shapes would be identical in solution and on the substrate, but the intensities would be unaltered, too. We shall not discuss intensities however, but shall deal only with *normalized* spectra.

The concept of a substrate-like solvent (SLS). - As a first approach to find a SLS it seems quite obvious to choose the chemically most similar environment for the solute molecule. When immersed in such a fluid medium the solute should show similar unshifted spectra. For polyacrylonitrile such a SLS could be acetonitrile. For polyethylene terephthalate (polyester) benzoic acid ethyl ester or terephthalic acid dibutyl ester suggest themselves as SLS. Solutions of the corresponding oligomers could also be envisaged as SLS. As shown below chemically related SLS often lead to spectral shifts as compared to the spectrum in the corresponding polymer and, therefore, are of no help to the solution of the problem.

Theory of the solvent effect in liquids. - The theory of the solvent effect enables us to calculate the relative spectral shifts of absorption and fluorescence spectra in different solvents by second order perturbation theory assuming the point dipole approximation [1] [2]. Specific interactions between solute and solvent as *e.g.* hydrogen bonds or the formation of charge transfer complexes are not allowed for.

According to this theory the relative spectral shift is caused by solute-solvent interactions. The effective electric field at the solute is approximated by the *Onsager* reaction field. In this model the solvent is described by its permittivity and refractive index, the solute by its dipole moment in the ground and excited state and by its polarizability.

Using numerous approximations the wave numbers of the maxima of the absorption and emission (fluorescence) spectra, $\tilde{\nu}_A^{\max}$ and $\tilde{\nu}_E^{\max}$, and the spectral shifts of the maxima, $\Delta\tilde{\nu}_A^{\max}$ and $\Delta\tilde{\nu}_E^{\max}$, relative to their position for the free molecule in the electronic and vibrational ground state $\tilde{\nu}_0$ are given by eqs. (1) and (2), respectively (*cf.* eqs. 8-55 and 8-56 by *Mataga & Kubota* [1] or eqs. 100 and 101 by *Liptay* [2]):

$$\Delta\tilde{\nu}_A^{\max} = \tilde{\nu}_A^{\max} - \tilde{\nu}_0 = \delta_A - Bp - C\mu_0(\mu_e - \mu_0)f \quad (1)$$

$$\Delta\tilde{\nu}_E^{\max} = \tilde{\nu}_E^{\max} - \tilde{\nu}_0 = -\delta_E - Bp - C\mu_e(\mu_e - \mu_0)f \quad (\tau_R \ll \tau_E) \quad (2)$$

where $p = (n^2 - 1)/(2n^2 + 1)$ and $f = [(\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]$. B and C are functions of the solute itself. The terms δ_A and δ_E correct for taking the wave numbers of the maxima of the absorption and emission spectra instead of the 0,0-transition. The magnitude of the solute dipole moments in the ground and excited electronic states are μ_0 and μ_e . Eqs. (1) and (2) correspond to those by *Mataga & Kubota* [1], if the f^2 term is neglected.

The *Stokes* shift is given in this approximation by

$$\bar{\nu}_A^{\max} - \bar{\nu}_E^{\max} = (\delta_A + \delta_E) + C(\mu_e - \mu_o)^2 f \quad (\tau_R \ll \tau_E) \quad (3)$$

Absorption spectra are due to an electronic transition from the ground equilibrium state to the *Franck-Condon* excited state, *i.e.* the molecular configuration of the solute and solvent in the ground equilibrium state is retained. The reorientation of the solvent molecules to the equilibrium excited state takes the time τ_R , the orientation relaxation time. If the average lifetime τ_E of the solutes in the excited state is much smaller than τ_R emission starts from the *Franck-Condon* excited state and the right-hand side of eq. (2) has to be replaced by the right-hand side of eq. (1) with $-\delta_E$ instead of $+\delta_A$. This, however, is the exception for liquid solvents at room temperature. The lifetime τ_E for allowed transitions is of the order of 10^{-9} s.

Polymers as environment for the solute molecule. - Synthetic polymers generally consist of crystalline and amorphous regions. It is widely accepted that solute molecules will migrate to the amorphous part in the course of the dyeing process [12]. A typical concentration for a dye or fluorescent substance is 0.1 weight-percent. This is in the range of or below the concentrations of the impurities in an ordinary synthetic polymer. Such impurities may be polymerization initiators, plasticizers, scavengers, water, solvents, white pigment (TiO_2) and the like. Even for a highly purified polymer one may ask what the environment of the solute molecule looks like. Does it behave like a somewhat viscous liquid or is it practically rigid during the relevant time scale for a fluorescing molecule ($\tau_R \leq 10^{-9}$ s), all measurements being made at room temperature?

More insight may be obtained by investigating the mobilities of solutes in polymers. In dielectric studies of the mobility of polar molecules in polystyrene *Davies & Edwards* [13] come to the conclusion that at 80° all the solute molecules investigated, which come in varying sizes and shapes, display their full dipole moment in polystyrene. For camphor with an essentially spherical shape the orientation relaxation time at 20° in polystyrene is $\tau_R = 38 \times 10^{-12}$ s as compared with the low viscosity solvent heptane, where $\tau_R = 7 \times 10^{-12}$ s. In contrast, the relaxation times of all the other bulkier molecules examined are much longer ($\tau_R \cong 10^{-6}$ s). The concentration range for the solutes was around 10 weight-percent.

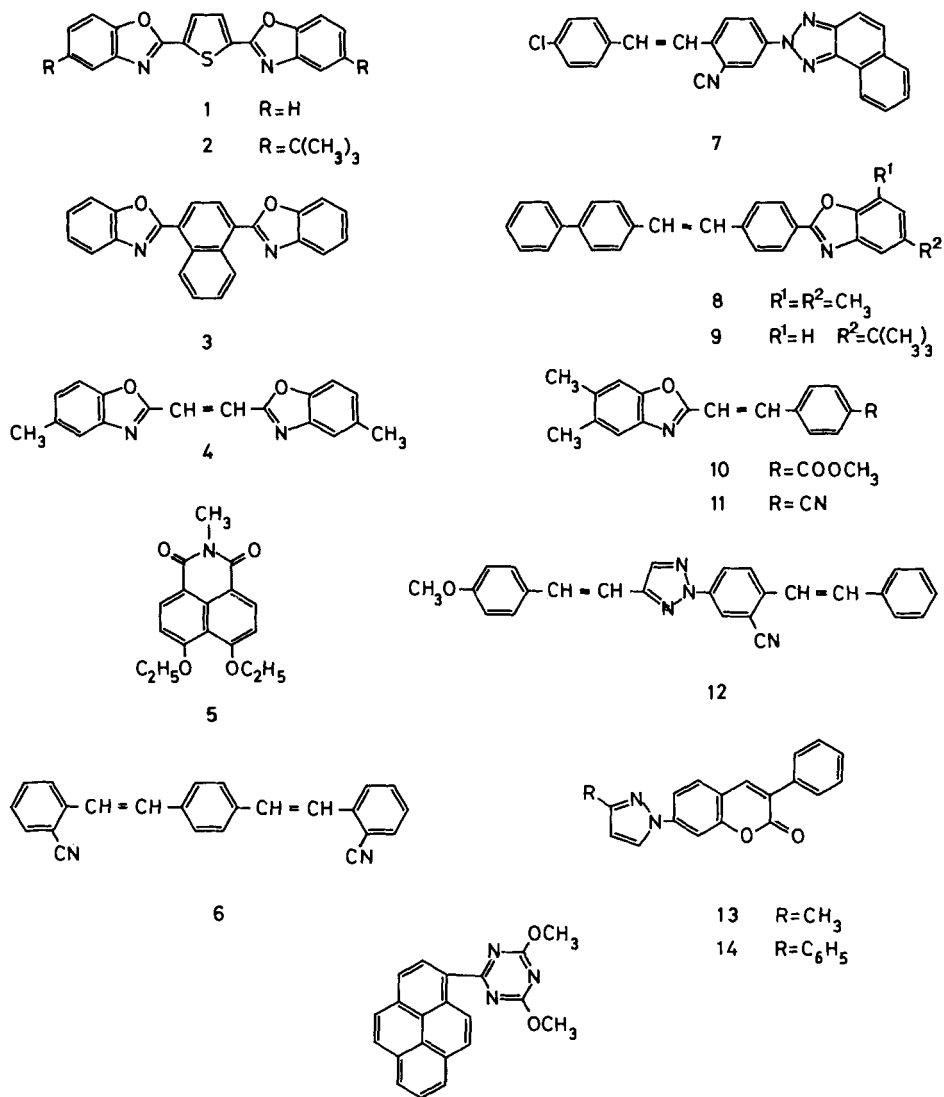
This investigation demonstrates that it is an open question whether dyes and fluorescing molecules with internal degrees of freedom actually have relaxation times $\tau_R < 10^{-9}$ s at room temperature in polymers with nonpolar or polar groups. Of course it is not a prerequisite that the solute relaxes within a nanosecond but that the entire system solute plus immediate environment does so. If after the dyeing process the solute occupies the most mobile sites in the polymer (which is not a far-fetched idea), the microscopic orientation relaxation time at those sites might be considerably shorter than the overall relaxation time of the polymer as derived from the frequency spectrum of the dielectric loss factor.

For this investigation we chose polyethylene terephthalate (a polyester, PES). The properties of this polymer with polar ester groups are relatively well known. Its dielectric properties have been described by *Reddish* [14] and others [15]. The polyester was dyed as a fabric and as a film. As fluorescing solute molecules 15 fluorescent whitening agents, most of them commercially well known, were chosen.

Experimental Part

Solutes. - Highly purified samples of fluorescent whitening agents for polyester (PES) [16] were used as solutes. These compounds have a longest wavelength absorption band which is clearly separated from the PES absorption. Structural formulae and numbering of compounds are given in Table 1.

Table 1. Fluorescent compounds used for electronic spectral shift measurements



Solvents and polymers. - A list of the liquid solvents used is contained in *Table 2* together with their relevant physical constants. Solute concentrations were varied from $5 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M. No concentration dependence of the spectra was observed. The solutions were protected from light except during measurement. No efforts were made to degas them.

Two types of polymeric materials were used in this investigation: transparent *Mylar* films, type B (*DuPont*) with a thickness of 25 μ m and polyester fabric, *Dacron-54* (*ICI*) with approximately 1 weight-percent white pigment TiO_2 . The refractive indices n and permittivities ϵ cited in *Table 2* are published values which refer to the untreated polymers. No values for the refractive indices and permittivities of dyed films or fabrics could be found in the literature, though structural changes of polymeric materials are well known to occur during the different dyeing procedures [17].

Table 2. *Solvents and polymers: Origin and physical properties*

Solvent	Symbol	Origin, Purity	n_D^a	ϵ^a	p^f	f^f
Acetic acid ethyl ester	AEE	<i>Merck</i> , Uvasol	1.370	6.02	0.184	0.400
Hexane	HEX	<i>Merck</i> , Uvasol	1.372	1.9 ^c	0.185	0.004
Cyclohexane	CYH	<i>Merck</i> , Uvasol	1.424	2.02	0.203	-0.001
<i>N,N</i> -Dimethylformamide	DMF	<i>Merck</i> , Uvasol	1.427	36.7 ^e	0.203	0.665
Toluene	TOL	<i>Merck</i> , Uvasol	1.494	2.38	0.225	0.024
Terephthalic acid dibutyl ester	TBE	synthesized, distilled ^g	1.496 ^b	5.64 ^b	0.226	0.315
Benzoic acid ethyl ester	BEE	<i>Fluka</i> , purum	1.503	6.1 ^b	0.228	0.334
Chlorobenzene	CLB	<i>Fluka</i> , puriss. p.a.	1.523	5.62	0.234	0.301
Benzoic acid benzyl ester	BBE	<i>Fluka</i> , purum	1.568	5.3 ^b	0.247	0.262
1-Chloro-naphthalene	CLN	<i>Fluka</i> , puriss.	1.633 ^b	5.0 ^b	0.263	0.214
Polyester fabric, <i>Dacron 54</i>	FABR	<i>ICI</i>	1.53-1.73 ^c	3.2-4.3		
Polyester film, <i>Mylar</i>	FILM	<i>Du Pont</i>	1.64 ^d	3.25 ^d		

^a) *R. C. Weast*, 'Handbook of Chemistry and Physics' 52nd Ed., The Chemical Rubber Co., Cleveland 1971-1972. Values refer to 25°.

^b) n_D was measured with a *Zeiss* refractometer, ϵ with a Dekameter DK03 (manufactured by Wissenschaftlich-Technische Werkstätten, Weilheim i.OB) at 1.8 MHz, in the cell DFL ls. Values refer to 25°.

^c) *P.-A. Koch* in Landolt-Börnstein, «Physikalische, chemische und technische Zahlenwerte», 6. Aufl., IV. Band, Springer, Berlin 1955, 344. Fibres show birefringence. Values refer to light polarized parallel and normal to stretching direction of the fibre, respectively.

^d) *Mylar*, Polyester Folie, Technische Information M-1F, M-4C, DuPont, Düsseldorf 1974.

^e) *Chr. Reichardt*, «Lösungsmittel-Effekte in der organischen Chemie» Verlag Chemie, Weinheim Bergstrasse 1969, 162.

^f) For definitions of p and f see eqs. (1) and (2).

^g) B.p. 156-158°/0.1 Torr, purity 99.2-99.7% by gas chromatography.

The dyeing procedures. - *Mylar* films were dyed by immersion in methylene chloride solutions of the solutes at room temperature for 1-2 days. (Typically, 0.1 g of film corresponding to 4 pieces of $3 \times 2.5 \times 0.0025$ cm³ in a solution of 25 mg of the solute in 3-5 ml CH_2Cl_2 was used.) The dyed films were carefully rinsed with methanol and air-dried in the dark for 2 days. Solute concentrations in the films, as determined by chloroform extraction, were 0.05-0.1 weight-percent, corresponding to $1-2 \cdot 10^{-3}$ M solutions.

The dyeing of the PES fabric was performed by a thermofixation process, in which the fabric was subjected to dry heat at 170°-210° for 30 s after applying the disperse fluorescent whitening agent by padding. Solute concentrations were determined by chlorobenzene extraction to be in the range of 0.05-1.4 weight-percent or approximately 10^{-3} M.

Absorption spectra. - The spectra of the liquid solutions and of the transparent PES films were recorded with a *Cary-14* spectrophotometer. Absorption spectra of opaque PES fabrics were obtained from reflectance measurements. PES fabrics (8 layers) were diffusely illuminated in an integrating sphere

by a 900 W high pressure xenon lamp. The short wavelength portion of this light is cut off sequentially by appropriate filters according to the procedure of *Eitle & Ganz* [11], so as to exclude fluorescence while recording the reflectance spectrum with a *Beckman ACTA M-VI* spectrometer (bandwidth 2 nm). The reflectance spectra were converted to absorption spectra by the *Kubelka-Munk* formulae.

Wave numbers of absorption maxima were determined with an accuracy of $\pm 80 \text{ cm}^{-1}$.

Fluorescence spectra. - The measurement of the fluorescence spectra was performed on a *Hitachi-Perkin Elmer MPF-2A* spectrofluorimeter with an excitation wavelength of 365 nm. A bandwidth of 4 nm was chosen for excitation and detection. Fluorescence detection was normal to the cell or sample surface. Dilute solutions ($5 \cdot 10^{-6}$ - $1 \cdot 10^{-5} \text{ M}$) were irradiated at an angle of 90° to the detection beam whereas solutions of higher concentrations or solid samples were irradiated at an angle of 30° . It was ascertained that the wave numbers of the fluorescence maxima were not influenced by reabsorption. Spectra were corrected for the instrument's spectral response.

Within the series of spectra of some compounds in certain solvents, resolution of vibrational structure changed markedly. Considering the fact that δ_E should be a constant for each compound, values of $\bar{\nu}_{E}^{\text{max}}$ for structured spectra were found by appropriately comparing these spectra with less resolved ones of the same overall halfwidth.

Wave numbers of fluorescence maxima were determined with an accuracy of $\pm 100 \text{ cm}^{-1}$.

Statistics. - $s_{r_2}^2$ is an unbiased estimate of the variance of the deviations from the population regression plane. The standard errors of the estimates of the 3 parameters of the two-dimensional linear regressions are calculated by well known procedures [18] using the values of s_{r_2} for eqs. (8) and (9), respectively. They are multiplied by the appropriate value $t_{0.05}$ of the two-tailed t-distribution chosen for the number of degrees of freedom (d.f.) for s_{r_2} ($t_{0.05} = 2.37$ for 7 d.f.). The resulting figures are given as 95% confidence limits of the parameters in eqs. (8) and (9). s_{r_1} is the sample standard deviation from the linear one-dimensional regression given in eq. (5). The 95% confidence limits inserted in eq. (5) are derived in an analogous manner for $t_{0.05} = 2.31$ for 8 d.f.

f_{PES} is an estimate of the point at which the regression line intersects the fixed abscissa $y=0$. As above the error figure quoted is the 95% confidence limit of f_{PES} . It is calculated by deriving its standard deviation and multiplying it by $t_{0.05} = 2.31$ for 8 d.f.

Results and Discussion. - The wave numbers of the maxima of the longest wavelength band of the absorption spectra and the emission (fluorescence) spectra of 15 different solutes in 10 different liquid solvents as well as in polyethylene terephthalate (polyester, PES) fabric and film are given in *Tables 3 and 4*. These data were fitted to eqs. (1) to (3) by linear and multiple linear regression analysis.

Analysis of the results lead to a qualitative statement about the orientation relaxation time τ_R in polyethylene terephthalate. The quantities $f = [(\varepsilon - 1)/(\varepsilon + 2) - (n^2 - 1)/(n^2 + 2)]$ and ε as well as $p = (n^2 - 1)/(2n^2 + 1)$ and n effective at the site of the solute molecules in the polyester were determined subsequently.

First, we determined the magnitude of f_{PES} with the help of the *Stokes* shift as defined in eq. (3). For this purpose the *Stokes* shifts of the 15 solutes i in 10 different solvents j were calculated relative to the *Stokes* shift in polyester fabric. This was not done separately for each of the 15 different solutes. Instead, in order to homogenize the data and to take full advantage of having so many solutes their *Stokes* shifts were summed up and averaged, yielding eq. (4).

$$\begin{aligned}
 yi &= \frac{1}{15} \sum_{i=1}^{15} [(\bar{\nu}_{A,ij}^{\text{max}} - \bar{\nu}_{A,i\text{PES}}^{\text{max}}) - (\bar{\nu}_{E,ij}^{\text{max}} - \bar{\nu}_{E,i\text{PES}}^{\text{max}})] \\
 &= \left[\frac{1}{15} \sum_{i=1}^{15} C_i (\mu_c - \mu_o)_i^2 \right] f_j = \left[\frac{1}{15} \sum_{i=1}^{15} C_i (\mu_c - \mu_o)_i^2 \right] f_{\text{PES}} \quad (\tau_R \ll \tau_E) \quad (4)
 \end{aligned}$$

The left hand side of eq. (4) corresponds to the dependent variable, f_j to the independent variable. The sums in brackets on the right-hand side of eq. (4) are constants to be determined by linear regression analysis. They are assumed to

Table 3. Maxima of the absorption spectra [1000 cm^{-1}] for the 15 solutes i in 10 solvents j as well as for polyethylene terephthalate fabric and film (POLYESTER FABR and FILM)

i \ j	1	2	3	4	5	6	7	8	9	10	POLYESTER	
	AEE	HEX	CYH	DMF	TOL	TBE	BEE	CLB	BBE	CLN	FABR	FILM
1	27.47	27.55	27.43	27.17	27.14	26.95	26.88	26.88	26.81	26.67	26.81	26.67
2	27.03	27.14	27.10	26.77	26.74	26.63	26.60	26.60	26.46	26.32	26.46	26.46
3	27.03	26.88	26.92	26.88	26.67	26.63	26.63	26.53	26.42	26.18	26.21	25.95
4	28.01	28.13	28.01	27.70	27.66	27.40	27.55	27.43	27.32	27.10	27.17	27.17
5	26.81	27.17	27.17	26.35	26.74	26.49	26.46	26.63	26.32	26.18	26.21	26.14
6	27.59	27.70	27.62	27.25	27.36	27.03	27.17	27.10	26.85	26.70	26.67	26.56
7	27.36	27.36	27.29	27.10	26.95	26.92	26.99	26.81	26.74	26.53	26.60	26.63
8	27.82	27.97	27.97	27.40	27.55	27.40	27.40	27.40	27.17	26.95	26.74	26.74
9	27.86	28.01	28.01	27.47	27.55	27.36	27.51	27.40	27.21	27.03	26.85	26.81
10	28.57	28.49	28.41	28.17	28.09	28.01	28.01	27.93	27.82	27.59	27.59	27.59
11	28.49	28.25	28.25	28.33	28.05	28.01	27.93	27.93	27.70	27.55	27.55	27.55
12	28.01	27.93	28.09	27.70	27.70	27.47	27.55	27.59	27.32	27.17	26.88	26.95
13	28.78	28.82	28.82	28.41	28.25	28.37	28.37	28.25	28.09	27.78	27.59	27.59
14	28.21	28.17	28.13	27.86	27.78	27.55	27.12	27.62	27.51	27.25	27.06	27.10
15	27.62	27.51	27.55	27.55	27.21	27.17	27.17	27.21	27.06	26.88	26.67	26.60
$\frac{1}{15} \sum_{i=1}^{15} \bar{\nu}_{A,i}^{\max}$	27.78	27.81	27.79	27.47	27.43	27.29	27.29	27.29	27.12	26.93	26.87	26.83

Table 4. Maxima of the fluorescence spectra [1000 cm^{-1}] for the 15 solutes i in 10 solvents j as well as for polyethylene terephthalate fabric and film (POLYESTER FABR and FILM)

i \ j	1	2	3	4	5	6	7	8	9	10	POLYESTER	
	AEE	HEX	CYH	DMF	TOL	TBE	BEE	CLB	BBE	CLN	FABR	FILM
1	23.81	23.98	23.70	23.42	23.53	23.42	23.39	23.28	23.17	22.99	23.20	23.09
2	23.50	23.58	23.36	23.00	23.09	23.02	23.04	22.88	22.83	22.35	22.83	22.83
3	23.33	23.50	23.36	22.99	22.99	22.91	22.88	22.88	22.73	22.52	22.73	22.68
4	24.10	24.60	24.24	23.42	24.01	23.87	23.70	23.64	23.47	23.04	23.67	23.53
5	23.31	24.10	23.95	22.88	23.31	23.09	23.04	23.09	22.96	22.60	22.99	22.88
6	23.50	23.92	23.70	23.15	23.20	23.12	23.00	23.09	22.88	22.57	22.88	22.68
7	23.92	24.10	23.95	23.53	23.56	23.53	23.47	23.42	23.31	23.09	23.26	23.15
8	23.87	24.15	23.95	23.31	23.56	23.42	23.39	23.36	23.20	23.00	23.09	22.94
9	23.81	24.15	23.98	23.20	23.58	23.45	23.39	23.36	23.23	23.00	23.15	22.99
10	23.47	24.27	24.15	22.62	23.64	23.31	23.20	23.31	23.12	22.73	23.31	23.09
11	23.28	24.13	23.98	22.42	23.47	23.01	22.91	22.99	22.88	22.42	23.31	23.04
12	22.94	24.93	24.69	19.31	24.21	23.20	22.73	23.47	23.09	22.86	23.36	23.28
13	23.39	23.87	23.78	22.94	23.42	23.15	23.09	23.20	23.04	22.78	23.09	22.73
14	23.36	23.67	23.50	22.78	23.15	23.04	22.99	22.96	22.86	22.57	22.88	22.73
15	23.92	24.69	24.39	23.15	23.92	23.75	23.53	23.53	23.53	22.83	23.47	23.64
$\frac{1}{15} \sum_{j=1}^{15} \bar{\nu}_{E,i}^{\max}$	23.57	24.11	23.91	22.81	23.51	23.29	23.18	23.23	23.09	22.76	23.15	23.02

depend entirely on the solutes and not to change from solvent to solvent. The regression equation is given by

$$y = (1.29 \pm 0.56) f + (0.002 \pm 0.180) \quad (5)$$

$s_{f1} = 2.27$ (cf. experimental part: Statistics).

For polyester fabric $y = 0$ and from eq. (5) it follows that

$$f_{\text{PES}} = (-0.001 \pm 0.140)$$

This result was derived on the assumption that the orientation relaxation time τ_R is shorter than the average lifetime τ_E of the solutes in the excited state ($\tau_R \ll \tau_E$). $f_{\text{PES}} \approx 0$ means that $\varepsilon \approx n^2$ for polyester fabric. This implies that at room temperature practically no orientation polarization due to the ester and terminal hydroxy groups in polyethylene terephthalate at the site of the solute molecules occurs within the relevant time, either for absorption or for fluorescence. A small, *i.e.* hindered, reorientation of polar groups in a polymer taking place very rapidly ($\tau_R \ll 10^{-9}$ s) is improbable and contradicts experience [19]. The assumption that $\tau_R \ll \tau_E$ is therefore discarded.

For $\tau_R \gg \tau_E$ eq. (2) is no longer valid, as explained before. It has to be replaced by eq. (1) with $-\delta_E$ instead of $+\delta_A$. The Stokes shift no longer depends on f , for the last term on the right-hand side of eq. (3) vanishes and the same is true for eq. (4). Consequently, we have to reinterpret the linear regression eq. (5) which gives zero

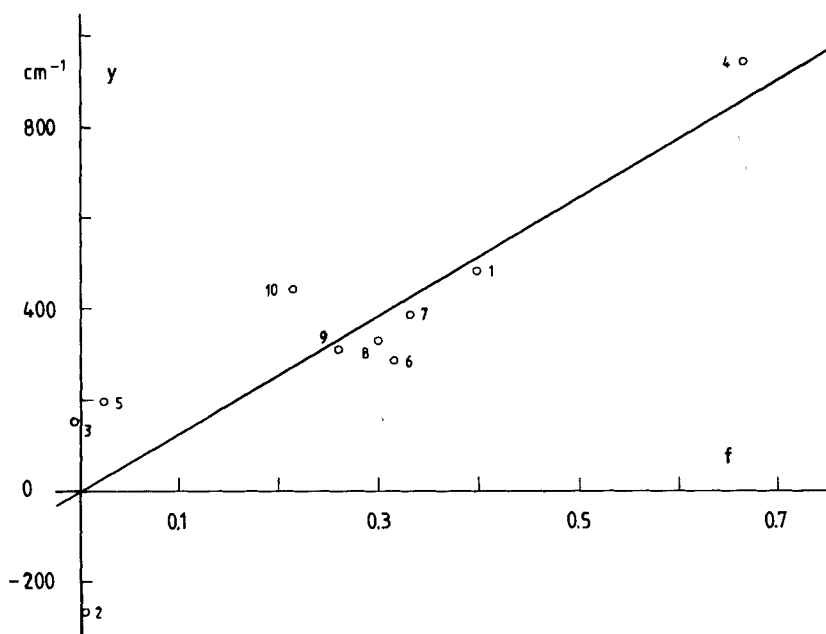


Fig. 1. Graphical representation of the linear regression eq. (5). The average Stokes shift y_j in the solvents $j = 1$ to 10 (cf. Table 2) relative to that in polyethylene terephthalate fabric is plotted as a function of f_j according to eq. (4)

within the limits of error for the corresponding term. We conclude from this result that this model is the correct one ($\tau_R \gg \tau_E$). Considering the *Stokes* shifts, the magnitude of f_{pES} cannot be determined.

Dielectric measurements on polyethylene terephthalate support this conclusion. At 25° and 1 GHz, ϵ falls off to 2.8 (at 1 MHz $\epsilon = 3.0$) [15] which is not significantly larger than n^2 (cf. Table 2). Its dielectric loss factor has a maximum near 100 kHz, that is $\tau_R \approx 10^{-6}$ s.

In Figure 1 the linear regression eq. (5) is shown for the 10 solvents examined. Each point represents the average *Stokes* shift of the 15 solutes measured in the respective solvent relative to the average *Stokes* shift in polyester fabric.

One of the aims of this investigation was to arrive at good estimates of the parameters p and f for polyester fabric and film and to calculate from these parameters the refractive index n and the permittivity ϵ (at low frequency) effective at the site of the solutes. For this purpose the data of the absorption and fluorescence spectra were subjected separately to multiple linear regression analysis according to eqs. (1) and (2). Again, this was not done separately for the 15 different solutes i in consideration of the aforementioned reasons. Instead, they were summed up and averaged.

$$\frac{1}{15} \sum_{i=1}^{15} \bar{v}_{A,ij}^{\max} = \frac{1}{15} \sum_{i=1}^{15} (\bar{v}_o + \delta_A)_i - \left(\frac{1}{15} \sum_{i=1}^{15} B_i \right) p_j - \left(\frac{1}{15} \sum_{i=1}^{15} [C \mu_o (\mu_e - \mu_o)]_i \right) f_j \quad (6)$$

$$\frac{1}{15} \sum_{i=1}^{15} \bar{v}_{E,ij}^{\max} = \frac{1}{15} \sum_{i=1}^{15} (\bar{v}_o - \delta_E)_i - \left(\frac{1}{15} \sum_{i=1}^{15} B_i \right) p_j - \left(\frac{1}{15} \sum_{i=1}^{15} [C \mu_e (\mu_e - \mu_o)]_i \right) f_j \quad (7)$$

$$(\tau_R \ll \tau_E)$$

This results in the regression equation

$$\frac{1}{15} \sum_{i=1}^{15} \bar{v}_{A,ij}^{\max} = (29\,940 \pm 360) - (11\,080 \pm 1\,600) p_j - (330 \pm 200) f_j \quad (8)$$

$s_{r_2}^A = 0.053$ (cf. experimental part: Statistics).

$$\frac{1}{15} \sum_{i=1}^{15} \bar{v}_{E,ij}^{\max} = (26\,280 \pm 750) - (11\,670 \pm 3\,300) p_j - (1\,470 \pm 400) f_j \quad (9)$$

$s_{r_2}^E = 0.109$ (cf. experimental part: Statistics).

For polyester the coefficient of the last term in eq. (9) has to be replaced by the one in eq. (8) if $\tau_R \gg \tau_E$ as has been made plausible in the discussion above. This coefficient, however, is more than 30 times smaller than that of the p -term. As p and f are of the same order of magnitude for polar solvents, this shows that for polyethylene terephthalate with a small or zero f value, the contribution to the solvent

effect due to the f term (or for that matter, ϵ) is *a fortiori* negligible compared to the p term.

Reddish [14] studied the dielectric properties of polyethylene terephthalate in the crystalline and amorphous states in dry and wet conditions. At 20° and 100 Hz he found for the permittivity ϵ values between 3.16 and 3.85. Even for the extremely low value of the refractive index $n=1.574$ as quoted by *Reddish* for the amorphous polymer, f will not assume a value above 0.16. The contribution due to the f term for polyethylene terephthalate is therefore well within the uncertainty of the p term and negligible for all reasonable values of ϵ and n of this polymer.

In principle it should be possible to decide whether there is a noticeable contribution to the solvent shift due to the f term, in other words, whether f_{PES} has a value slightly different from zero, as is suggested from dielectric measurements. Suitable solute molecules must have large dipole moments in the ground state, μ_0 , and large differences $\mu_c - \mu_0$. Absorption measurements with such molecules, which have been used *e.g.* by *Lippert et al.* [5], would result in much larger coefficients of f and, therefore, facilitate a decision.

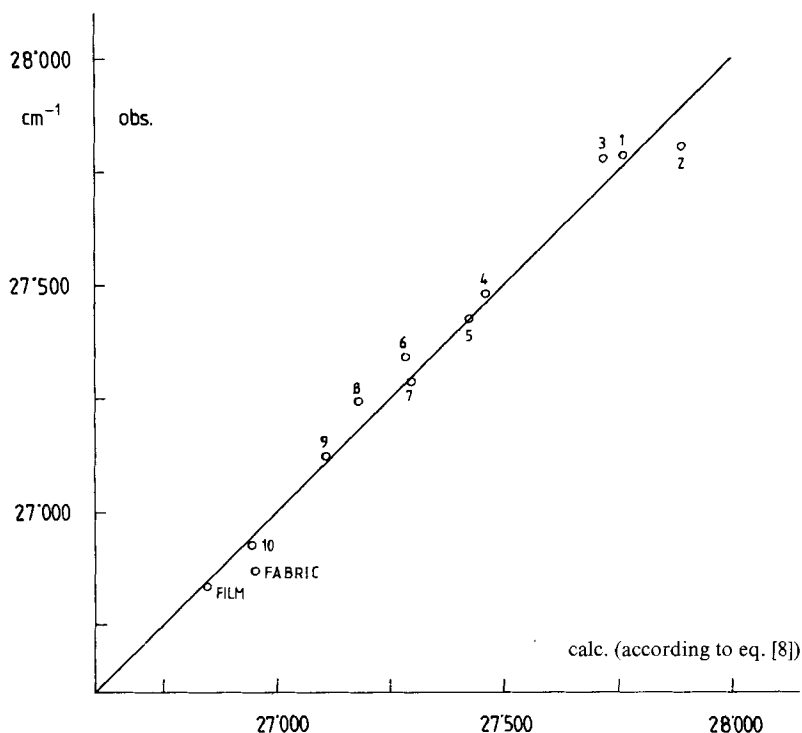


Fig. 2. Plot of observed vs. calculated wave numbers of the average absorption maxima $\frac{1}{15} \sum_{i=1}^{15} \bar{\nu}_{A,ij}^{\max}$ in the solvents $j=1$ to 10 (cf. Table 2) as well as in polyethylene terephthalate FABRIC ($n=1.66$, $f=0$) and FILM ($n=1.70$, $f=0$)

The coefficients of p in eqs. (8) and (9), which should be identical in this approximation, agree within the confidence limits. The value of approximately $\mu_e/\mu_o = 4.5$ for the ratio of the coefficients of f in these equations is not unreasonable for such an average of 15 different solutes.

Figures 2 and 3 show the observed wave numbers for the absorption and fluorescence maxima vs. the ones calculated according to eqs. (8) and (9), respectively. The neglect of the f^2 term seems to be justified for this choice of solutes and solvents, judging from the excellent fit to the multiple linear regression equations. Only for solutes with very different dipole moments in the ground and excited state as well as with a large μ_o could this term become important.

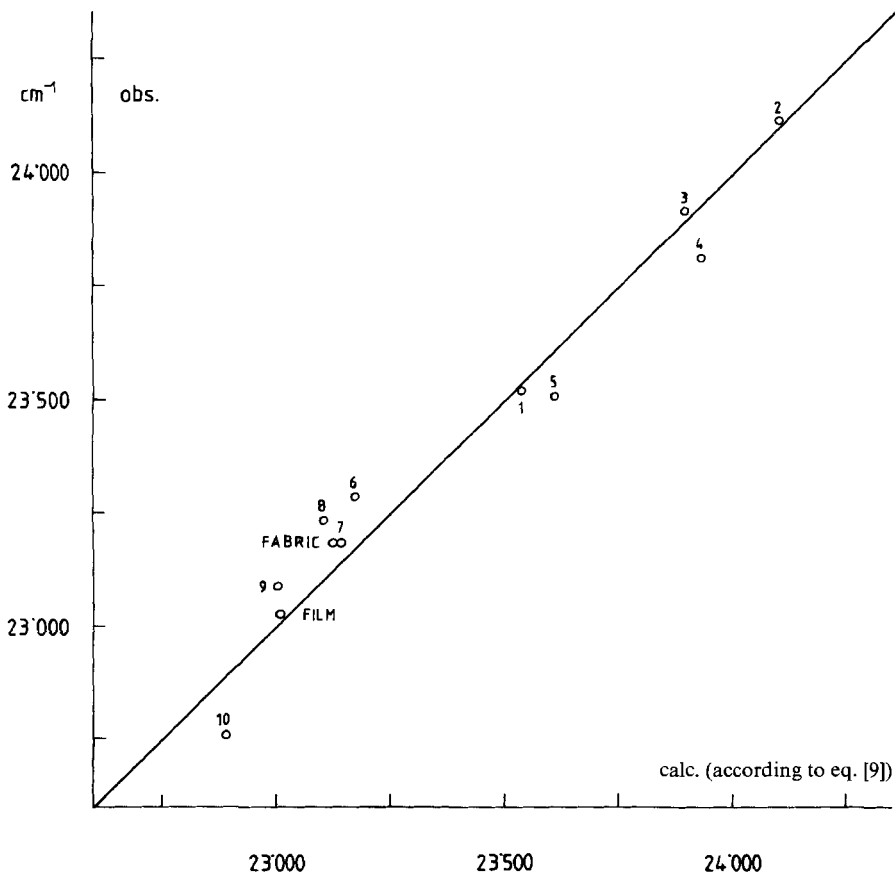


Fig. 3. Plot of observed vs. calculated wave numbers of the average fluorescence maxima $\frac{1}{15} \sum_{i=1}^{15} \bar{\nu}_{E,i}^{max}$ in the solvents $j = 1$ to 10 (cf. Table 2) as well as in polyethylene terephthalate *FABRIC* ($n = 1.66$, $f = 0$) and *FILM* ($n = 1.70$, $f = 0$)

The data for polyethylene terephthalate calculated with $n=1.66$ for polyester fabric and $n=1.70$ for polyester film ($f_{\text{PES}}=0$) closely fit the averaged observed wave numbers in this polymer. The data are compatible with those given in the literature (*cf. Table 2*). The close fit of the polyester data augurs well for other polymers. With a sufficiently high number of solutes differing in their properties it should be possible to determine the effective refractive indices in a meaningful way, too. Extrapolating from the findings in polyethylene terephthalate we believe that in general the f value for polymers may be neglected. As far as may be judged from the scant data of *Nicol, Wild & Yancey* [9] this seems also to be the case for 9-cyano-anthracene in polymethylmethacrylate. The data for this compound in polyacrylonitrile films are less conclusive.

The concept of substrate-like solvents may be discussed by reference to *Figures 2 and 3*. Solvents with chemically similar structure such as phthalic acid dibutyl ester and benzoic acid benzyl ester are of limited help. Occasionally they reproduce the fluorescence spectra in polyester relatively well because they compensate for their lower refractive indices with higher effective permittivities than polyester. The absorption spectra, however, are badly reproduced. Nonpolar solvents with a refractive index equal to that in polyester would be the best possible choice. The large refractive index needed, however, is always accompanied by absorption in or near the visible region. This seriously impedes their use as solvents for dyes and fluorescent whitening agents.

Conclusions. - The model polymer polyethylene terephthalate in the form of dyed polyester fabric and film was used to show under what conditions the theory of the (liquid) solvent effect may be applied to the electronic spectra of solutes in this polymer. As a consequence of the long orientation relaxation time τ_R no reorientation of the environment of the solute molecules occurs during their lifetime in the excited state τ_E . The solvent effect on the fluorescence spectra becomes identical with the one on the long wavelength absorption bands. Because $f = [(e - 1) / (e + 2) - (n^2 - 1) / (n^2 + 2)]$ is small for polyethylene terephthalate, and because its coefficient is usually small for common solutes, this term may generally be neglected. The spectral shift in this polymer and very probably in others, too, is dominated by the dispersion term.

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