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Contribution of the fluorescence spectroscopy to the determination of binary phase diagrams of mesomorphic mixtures. I. Investigation of a system-alkylcyanobiphenyl/phenyl-cyclohexanecarboxylate

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Abstract. — The study of the spectral distribution and intensity of the fluorescence of binary mesomorphic mixtures as a function of the temperature is presented as a convenient method for obtaining phase diagrams. For a mixture of a given composition, the fluorescence intensity measured in the frequency range of the monomer and of the excimer emission, shows two types of discontinuities at the phase transitions. Ratio $I_M/I_D$ ranging from 0 to $\infty$ can be obtained as a function of the composition, of the temperature, and of the nature of the phase. Monomer fluorescence ($I_M$) is characteristic of the crystalline and of the $SB$ phases while in the $S_{A1}$, $N$ and the $I$ phases, excimer fluorescence ($I_D$) is predominantly observed. The emission spectra can detect simultaneously the presence of molecular association, the degree of order and the molecular mobility of the phase involved.

1. Introduction.

Photophysical processes in alkyl- and alkoxycyanobiphenyl derivatives have been widely investigated in our laboratory in solution [1] as well as in neat phases [2, 3] in order to characterize migration and energy transfer in liquid crystals.

In the neat mesomorphic or isotropic phase, the alkoxy compounds (COB) emit only excimer fluorescence centred at 380 nm whatever the phase involved: smectic, nematic, or isotropic up to $20^\circ$C above the N-I transition. Monomer fluorescence only, is observed in the crystalline phase. Excimer fluorescence is a structureless emission band observed in systems containing aromatic units. It corresponds to the radiative deactivation of an excited dimer, the excimer, formed by collisional interaction of an excited and an unexcited molecule. Excimer formation requires parallelism and close proximity ($\pm 0.35 \text{ nm}$) of the interacting aromatic chromophores. Monomer fluorescence corresponds to the radiative deactivation of an excited chromophore which does not interact with neighbouring molecules neither in the ground nor in the excited state. The alkylox substituted cyanobiphenyl derivatives behave like their alkoxy homologs but the $\lambda_{\text{max}}$ of the excimer emission is shifted to shorter wavelength when the temperature is raised up.

In binary mesomorphic mixtures of a fluorescent and a non fluorescent compound, monomer and excimer fluorescence can be observed simultaneously. Their relative importance depends on temperature and on concentration.

This paper is the first part of a general study of the fluorescence of binary mesomorphic mixtures performed in order to separate temperature and concentration effects on excimer formation in the different mesophases. Liquid crystalline binary mixtures of the fluorescent alkylcyanobiphenyl (9CB) and of
the non fluorescent phenyl-cyclohexanecarboxylate (5H5) have been investigated. In these systems, when the mole fraction of 5H5 increases, the antiparallel pairing of the cyanomolecules breaks up, preventing excimer formation: monomer and excimer fluorescence can thus be obtained simultaneously and related to the temperature and to the nature of the phase involved. In this work, the study of the spectral distribution and of the intensity of the fluorescence as a function of the temperature is mainly presented as a convenient method for obtaining phase diagrams of binary mesomorphic mixtures. The comprehensive discussion of the photophysical processes involved will be discussed elsewhere.

2. Experimental.
The mixtures studied were

\[
\begin{align*}
9CB & : \text{CH}_3\left(\text{CH}_2\right)_6\overset{\bigcirc}{\bigcirc}\text{CN} \\
9CB/5H5 & \\
5H5 & : \text{C}_9\text{H}_{11}\overset{\text{H}}{\bigcirc}\text{C}-\text{O}\bigcirc\text{C}_5\text{H}_{11}
\end{align*}
\]

The 9CB was purchased from BDH Chemicals Ltd, Poole, Dorset; U.K. after three recrystallization in MeOH, it was shown to be free from impurities by HPLC and spectrofluorimetry. The 4-pentylphenyl-trans-4'-pentylcyclohexane-1-carboxylate (5H5) was used without further purification.

The two components were mixed under stirring in the isotropic phase and then allowed to cool down. This operation was repeated two or three times before use.

The fluorescence spectra were measured with a spectrofluorimeter MPF-2A from Perkin-Elmer. A thin layer of mesogen is spread between two quartz plates which are then inserted in a thermostated copper block. The excitation wavelength is 280 nm. All the spectra are obtained with frontal excitation.

The phase diagram of the binary system 9CB/5H5 was obtained with a polarising microscope Laboval (Zeiss) equipped with a Mettler FP52 heating stage and a FP5 control unit (3 °C/min) and by DTA analysis (Dupont Thermal Analyser DTA 990, 2 °C/min).

3. Results and discussion.

3.1 Compilation of the phase diagram with the polarizing microscope. — Mixture of mesogenic materials with large difference in polarity are known to form in many cases an injected smectic mesophase, generally of type A [4-6] and sometimes of type B or E [7, 8]. This is confirmed by figure 1 obtained by microscopic examination for 9CB in 5H5 [9]. According to Gray et al. the smectic phase observed for 90 % of 9CB in 5H5 is a bilayer SA phase stabilized by the interactions of the strong terminal dipoles ('). The injected phase formed at high 5H5 weight fraction is a monolayer SA phase (SA1). The thermal stability maximum of the SA1 mesophase corresponds for this system to 30 weight % of the polar component.

3.2 Simplified kinetic treatment for the formation of excimer in solution. — The kinetic scheme for a monomer — excimer system is shown below using Birks’ notations for the rate parameters [11].

\[
\begin{align*}
\text{Scheme 1 (1).} \\
M \overset{\text{M*}}{\rightarrow} M + h\nu_{FM} & \quad k_{FM} \\
M^* \rightarrow M + kT & \quad k_{GM} \\
M + M^* \rightarrow D^* & \quad k_{DM} \\
D^* \rightarrow M + M^* & \quad k_{MD} \\
D^* \rightarrow M + M + h\nu_{FD} & \quad k_{FD} \\
D^* \rightarrow M + M + kT & \quad k_{GD}
\end{align*}
\]

For steady state illumination and under photostationary conditions, the following relation is obtained:

\[
\frac{I_M}{I_D} = \frac{k_{FM}(k_{MD} + k_D)}{k_{FD}k_{DM}[M]} \quad (1)
\]

where \(I_M\) and \(I_D\) are the monomer and excimer fluorescence intensity. This equation shows that \(I_M/I_D\) increases when the concentration of \(M\) decreases.

(1) X-ray diffraction shows however some interdigitated character of the bilayer phase which can be considered as a \(S_{A1}\) smectic phase according to the classification of Bordeaux's group [10].

(2) Conversion to the triplet state has been neglected.
smaller than $k_{D}$ while the reversed is observed at high temperature. The sequence of activation energies is generally

$$E_{FM} < E_{FD} < E_{D} < E_{DM} = E_{MD}.$$  \hspace{1cm} \text{(2)}$$

As a consequence, $I_{M}/I_{D}$ increases with decreasing temperature at low temperature and increases with increasing temperature at high temperature. A minimum value of $I_{M}/I_{D}$ is thus observed in the intermediate range.

It can also be shown that when there is an overlapping of the spectral distribution of monomer and excimer fluorescence, there exists a narrow frequency range $\nu_{i}$ common to both emissions where the following conditions are verified at constant temperature [12, 13].

$$\frac{I_{M}}{I_{D}} = 1, \quad \frac{dI_{M}}{d[M]} = \frac{dI_{D}}{d[M]} = 0.$$  \hspace{1cm} \text{(3)}$$

This corresponds to the existence of a concentration independent isoemissive point. It implies that the same kinetic scheme is valid in the whole concentration range. In some particular cases a temperature independent isoemissive point can also be observed at constant concentration of the fluorescent chromophore. It corresponds in a narrow frequency range to the conditions:

$$\frac{I_{M}}{I_{D}} = 1, \quad \frac{dI_{M}}{dT} = \frac{dI_{D}}{dT} = 0.$$  \hspace{1cm} \text{(4)}$$

The kinetic meaning of the temperature independent isoemissive point is complicated. It will be discussed elsewhere [14]. The frequency at which either the temperature or the concentration independent isoemissive point is observed is characteristic of the photophysical processes involved in the particular concentration or temperature range.

3.3 EFFECT OF THE CONCENTRATION OF THE ALKYLICYANOBIPHENYL ON THE FLUORESCENCE SPECTRA AT CONSTANT TEMPERATURE. — The fluorescence spectra of different binary mixtures are given in figure 2, for 9CB in 5H5 at 30, 45 and 75 °C. They are given in arbitrary units in order to show the evolution of the $I_{M}/I_{D}$ ratios as a function of the weight fraction of the luminescent chromophores. The absolute values of $I_{M}$ and $I_{D}$ of the different spectra can thus not be compared. At 30 °C, for high
CB content (weight % of 9CB > 60 %) the emission is centred at 380 nm and is attributed to excimer emission. For low CB weight fraction (< 10 %) the emission spectrum is centred at 336 nm and is attributed to the monomer. For intermediate CB content (10-60 %) the monomer and the excimer emissions are observed simultaneously. These observations are thus in agreement with equation 1. Similar increase of $I_M/I_D$ with decreasing concentration of the luminescent chromophore is observed at 45 and 75 °C.

3.4 EFFECT OF THE TEMPERATURE ON THE FLUORESCENCE SPECTRA AT CONSTANT WEIGHT FRACTION. — A mixture of 5H5 and 9CB containing 15 weight % of 9CB was chosen for a systematic investigation of the successive phases by DTA analysis, microscopic examination and fluorescence spectroscopy. Two types of experiments have been performed:

In a first heating run, the mesomorphic mixture is spread on a quartz plate, warmed up in the isotropic phase and then allowed to cool down and to crystallize in a refrigerator. Different properties are then measured on heating the sample at controlled rate from the crystalline to the isotropic state.

— The phase transitions are determined by DTA and DSC analysis (2 °C/min) and controlled by microscopic examination (3 °C/min).

— The fluorescence intensity is measured respectively at $\lambda_a = 310$ nm (in the monomer range) and at $\lambda_a = 470$ nm (in the excimer range) as a function of the temperature (3 °C/min).

— The spectral distribution of the fluorescence is recorded at different temperatures.

The sample used here above in the first heating run is allowed, when in the isotropic phase (75 °C) to cool down to room temperature. At this temperature crystallization does not occur. The sample is then reheated; the phase transition temperatures, the fluorescence intensity and the spectral distribution of the fluorescence are then measured as summarized above in the first heating run; this constitutes the second heating run.

3.4.1 First heating run.
3.4.1.1 DSC and DTA analysis. — The phase transition temperatures of the two components as well as their enthalpies measured by DSC are given in table I. From these data, the liquidus curves of the phase diagram can be calculated using the Schröder-Van Laar equation [15].

$$\ln X_A = - \frac{\Delta H_A}{R} \left( \frac{1}{T} - \frac{1}{T_A} \right)$$

where $\Delta H_A$ and $T_A$ are the melting heat and the melting point of the pure component A, $T$ is the melting point of the mixture containing $X_A$ moles of A and $R$ is the gas constant.

### Table I. — Temperatures (°C) and corresponding enthalpies (J/gr) of the phase transitions for 9CB and 5H5.

<table>
<thead>
<tr>
<th></th>
<th>9CB</th>
<th></th>
<th>5H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - SAd</td>
<td>41.9</td>
<td>117.3</td>
<td></td>
</tr>
<tr>
<td>SAd - N</td>
<td>46.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>N - I</td>
<td>48.6</td>
<td>4.6</td>
<td></td>
</tr>
</tbody>
</table>

First heating run

<table>
<thead>
<tr>
<th></th>
<th>9CB</th>
<th></th>
<th>5H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C - N</td>
<td>36.3</td>
<td>83.9</td>
<td></td>
</tr>
<tr>
<td>N - I</td>
<td>46.2</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

Second heating run

<table>
<thead>
<tr>
<th></th>
<th>9CB</th>
<th></th>
<th>5H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sg - N</td>
<td>27.3</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>N - I</td>
<td>46.2</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

As shown in figure 3, the eutectic composition is obtained between 21 and 22 °C for a binary mixture containing ~ 38 weight % of 9CB. These values are in good agreement with the experimental data [14]. Concerning the ester (5H5), this compound is crystalline below 36 °C and nematic above this temperature, it presents however on cooling a monotropic SG transition at 27°C as indicated in table I and in figure 3.
The phase transitions of a sample of 5H5 containing 15 weight % of 9CB have been observed by DTA and are given in figure 4A. The S_{Al}-N transition is observed at 41 °C and the N-I transition at 48.9 °C. Two other peaks are detected: a first sharp one at 21 °C corresponding to the melting of the eutectic mixture and a second broad one with a maximum at 31 °C corresponding to the melting of the excess solid. Small letters a to i have been used to characterize the interesting temperature ranges. They will be used later on in the text.

3.4.1.2 Continuous recording of the fluorescence intensity at constant wavelength as a function of the temperature. — The fluorescence intensities have been recorded continuously as a function of temperature at \( \lambda_a = 310 \text{ nm} \) in the monomer emission and at \( \lambda_a = 470 \text{ nm} \) in the excimer emission range. They are given in figure 5A where different discontinuities corresponding to the phase transitions reported in the DTA diagrams are observed. Range a-b is characteristic of the crystal-S_{Al} transition at the eutectic temperature. At b, the system is composed of a non fluorescent solid (5H5) and a S_{Al} phase at the eutectic composition. The S_{Al} phase contains a higher weight % of 9CB than the initial mixture as indicated in figure 3. After b, the temperature of the sample rises and the concentration of 9CB decreases in the S_{Al} phase (range b-c). As a consequence, the contribution of the excimer fluorescence decreases in agreement with equation (1). At point c, melting of 5H5 crystals is complete; the system is homogeneous S_{Al}. Ranges d-e and f-g are characteristic of the S_{Al}-N and N-I transitions respectively. They can be interpreted as resulting from changes of intensities correlated to changes of refractive index on passing from a phase to another.

3.4.1.3 Spectral distribution of the fluorescence as a function of temperature. — The spectral distribution of the mixture containing 15 weight % of 9CB at representative temperature is given in figure 6. It will be correlated with the temperature ranges given in figures 4A and 5A. At 20 °C (below a) the fluorescence is that of the crystalline 9CB. At 23 °C (point b), the fluorescence is emitted by the S_{Al} phase at the eutectic composition. The spectral distribution is completely modified. It corresponds to the excimer with a small contribution of monomer at 330 nm. At 28 °C (between b and c), the fluorescent S_{Al} phase contains less 9CB; this results in an increase of \( \frac{I_m}{I_D} \) in agreement with equation (1). Point c of figures 4A and 5A corresponds to the end of melting.
of 5H5. From this point, the weight fraction of 9CB in the fluorescent phase is constant and the subsequent modifications of the fluorescence spectrum are then controlled only by the temperature and (or) by the organization of the phase involved. At 36, 45 and 75 °C, the phases are respectively S_{AI}, N and I.

An increase of $I_M/I_D$ is observed as the temperature increases. At 75 °C, the fluorescence spectrum is predominantly that of the monomer. It is related to an important excimer dissociation in agreement with equation (1) and inequality (2).

If the fluorescence spectra are more systematically investigated as a function of the temperature, four domains can be differentiated as reported in the following figures. Figure 7_A gives the spectral modifications observed in range a-b. The fluorescent species is crystalline 9CB at 18 °C. At 21 °C it is pure S_{AI} phase at the eutectic composition. At intermediate temperature, contributions of crystalline 9CB and pure S_{AI} phase at the eutectic composition are observed (19 °C). Their relative importance depends on the extend of melting. Figure 7_B corresponds to range b-c of figure S_{AI}. The progressive decrease of 9CB weight fraction in the S_{AI} phase corresponds to a progressive increase of $I_M/I_D$. A weight fraction independent isoemissive point is situated at 364 nm. It corresponds to the conditions of equation (3). Figure S_{AI} is characteristic of the S_{AI} phase at constant composition (range c-d) and of S_{AI}-N transition. The ratio $I_M/I_D$ remains constant. An enhancement of intensity of both $I_M$ and $I_D$ is observed. In the nematic phase (Fig. 8_B) the total fluorescence intensity is nearly constant although a small decrease of the contribution of the excimer fluorescence is observed. A decrease in the total intensity occurs at the N-I transition in agreement with the measurements at one wavelength reported in figure 5. In the isotropic phase beyond g (Fig. 9) excimer dissociates with increasing temperature as usually observed for excimer forming systems at high temperature. As a consequence, $I_M/I_D$ increases with temperature in agreement with equation (1) and inequality (2). A temperature independent isoemissive point situated at $\lambda = 350$ nm is observed. It corresponds to the conditions given in equation (4).

3.4.2 Second heating run.

3.4.2.1 DTA analysis. — If the sample used during the first heating run is allowed to cool down from the isotropic phase and then reheated figure 4_B three peaks are now present. The first one at 30 °C is characteristic of a monotropic transition. Careful examination between crossed polars indicates a S_{B}-S_{AI} transition characterized by the so-called bars (parallel bands appearing during the S_{B}-S_{AI} transition). The S_{AI} - N and the N-I transition corresponds to those given in figure 4_A.
3.4.2.2 Continuous recording of the fluorescence intensity at constant wavelength as a function of the temperature. — The fluorescence intensity measured at \( \lambda_a = 310 \text{ nm} \) and at \( \lambda_a = 470 \text{ nm} \) as a function of the temperature is given in figure 5B. Range h-i (S\(_B\)-S\(_{A1}\) transition) is characterized by monomer-excimer conversion. Between d'-e' and f'-g' the expected S\(_{A1}\)-N and the N-I transition do occur.

3.4.2.3 Spectral distribution of the fluorescence as a function of temperature. — The spectral distribution of the mixture containing 15 weight % of 9CB at characteristic temperatures during the second heating run are given in figure 10. Below h (25 °C), the fluorescence of the sample is that of the monomer. This monomer fluorescence is representative of the S\(_B\) phase while excimer fluorescence is the main emission in the S\(_{A1}\) phase. In the S\(_B\) phase the molecular axes are orthogonal to the layers with hexagonal arrangement of the molecular axes within the layers. The S\(_B\) phase is more ordered and rigid than the S\(_{A1}\) phase with its random arrangement of the molecular axes within the layers. Excimer formation requires the presence of pairs of chromophores which obey very strict requirements of relative geometrical situation. These pairs, which can either form during the life-time of the excited state or be preformed at defects and act as energy traps are thus present in larger amount in the S\(_{A1}\) phase than in the S\(_B\) phase. At 36, 46 and 79 °C, the fluorescence spectra are representative of the S\(_{A1}\), N and I phases respectively.

If temperature effect is more accurately investigated during the second heating run, four domains can also be described. The monomer fluorescence of the S\(_B\) phase is observed between 21 and 30 °C (Fig. 11). At 30 °C, the monomer fluorescence begins to decrease while excimer fluorescence increases. Between 30.5 and 33 °C (range h-i) monomer-excimer conversion detects the S\(_B\)-S\(_{A1}\) transition. A temperature independent isoemissive point is observed at 369 nm (Fig. 11). In the S\(_{A1}\) phase (range i-d') the ratio \( I_M/I_D \) is constant and has the same value as in the first heating run (0.73) indicating that the S\(_{A1}\) phase are well defined and identical whether they are formed from the crystalline or from the S\(_B\) phase. This is also true for the S\(_{A1}\)-N transition and the nematic phase. In the isotropic phase, monomer-excimer conversion due to excimer dissociation and characterized by a temperature independent isoemissive point at 350 nm is observed as it was during the first heating run (Fig. 9).

4. Conclusion.

The study of the spectral distribution and intensity of the fluorescence measured as a function of temperature is a convenient method for obtaining phase diagrams of binary mesomorphic mixtures. The investigated system is composed of a fluorescent chromophore (9CB) which associates in neat phase to form excimers and a non fluorescent ester (5H5). In the mixture, the dimer association is disrupted by the presence of the non fluorescent compound: monomer and excimer fluorescence can be observed simultaneously. Ratios \( I_M/I_D \) ranging from 0 to \( \infty \)

Fig. 10. — Fluorescence spectra of a binary mixture 9CB/5H5 containing 15 weight % of 9CB during the second heating run. 25 °C : S\(_B\) phase (monomer fluorescence). 36 °C : S\(_{A1}\) phase. 46 °C : nematic phase. 79 °C : isotropic phase. Intensity in arbitrary units.

Fig. 11. — Fluorescence spectra of a binary mixture 9CB/5H5 containing 15 weight % of 9CB during the second heating run. Range h-i of figures 4B and 5B. Isoemissive point (temp.) : 369 nm. Intensity in arbitrary units.
can thus be obtained as a function of the composition, of the temperature and of the nature of the phase involved.

For a mixture of a given composition (15 weight % of 9CB in 5H5), continuous recording of the fluorescence intensity as a function of the temperature in the range of the monomer and of the excimer emission, shows two types of discontinuities at the phase transitions. The first type has to be interpreted as resulting from modifications of the refractive index on passing from a phase to another one. The second type is characteristic of monomer-excimer conversion and give information concerning the rigidity and the degree of order of the phase involved.

The advantages of the method can be summarized as follow: a few mg of a given mixture are sufficient to detect:

- phase transitions,
- molecular associations between the two components,
- the presence of monotropic transitions,
- the degree of order and the molecular mobility in the phase involved.

Acknowledgments.

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References