

SPECTROSCOPIC SENSOR AS A MINERAL OIL INDICATOR

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In this work a spectroscopic method to measure the degradation degree of paraffinic mineral oils is proposed. The behaviour of some molecules (indoles) in solution versus their surrounding environment (solvent polarity and viscosity) is the basis of the method. Experimental results obtained for VESTAN oil, confirming this theoretical scheme, are presented.

KEY WORDS: Fluorescence, Degradation oil, Viscosity, Polarity.

1. INTRODUCTION

The behaviour of some organic molecules versus their surrounding environment is well known. These organic molecules are characterized by a large change in their dipolar moment when they are excited. At high temperature, when the viscosity is low, fluorescence spectra are smoothed with a single broad envelope. However, if the temperature decreases (viscosity increases) the fluorescence spectra show a structured blue shifted profile. This behaviour can be understood as a friction mechanism preventing the complete dipole reorientation of the excited molecule before the emission.^{1,2,3,4,5} As a consequence, the emission is from a non-equilibrium state (Franck-Condon).

In non-polar environments there are not dipolar interaction between the solute and its surroundings, so that the fluorescence spectra do not change when the temperature varies. In every case, the spectra are similar to the low-temperature polar-environment fluorescence profiles.¹

Mineral oils have a strong thermal and chemical stability. All these, together with their excellent insulator properties allow their use as lubricants in several electric equipments. Before their utilization, they are paraffinic oils with very low polarity. Nevertheless, as a consequence of their use, an oil ageing takes place due to chemical processes and the effect of impurities entering from the surrounding environment. The oil oxidation and the breaking of their macromolecular chains are the main reasons of its retrodegradation. During the ageing of the oil, its optical constants are changed; in particular, the dielectric constant will be increased due to a polarity increase as a consequence of the macromolecular chains breaking.

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In this way, if we dissolve an appropriate organic molecule in a wear oil, and we illuminate with light of wavelength corresponding to its absorption bands, the fluorescence spectra profiles will show changes following the polarity environment and, therefore we'll get an indirect measure of the oil quality.

2. THEORETICAL CONSIDERATIONS

Due to the interactions with the surrounding environment, an organic molecule in solution changes its energy levels respect to these in vapour phase (Figure 1). If the main interaction is of dipole-dipole type, the shift of the energy levels is given by Ref. 6:

$$\Delta E = -\frac{2}{a^3} F(D, n) \vec{\mu}_i \cdot \vec{\mu}_j - \frac{1}{a^3} g(n) \vec{\mu}_i \cdot \vec{\mu}_i - \frac{4\pi\rho\alpha}{3a^3} \vec{\mu}_D \cdot \vec{\mu}_D + \mathcal{D} \quad (1)$$

where

- $\vec{\mu}_i$ dipolar moment of the solute molecule in the i th energy level,
- $\vec{\mu}_D$ dipolar moment of solvent molecules in their ground state,
- a Onsager's cavity radius,⁷
- α solute polarizability, and
- \mathcal{D} dispersion term.

The dielectric solvent function $f(D, n)$ is given by

$$f(D, n) = \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \quad (2)$$

and

$$g(n) = \frac{n^2-1}{n^2+2},$$

D being the static dielectric constant and n the refractive index.

In order to understand all the processes that can take place when we illuminate the solution, it is necessary to take into account the reaction fields from the solvent molecules surrounding the solute molecule. A fast reaction field is a result of solvent induced dipoles (second term in the right hand side of Eq. (1)), the other one, resulting from solvent permanent dipoles (first term in the right hand side of Eq. (1)), takes a time equal to the relaxation time τ_r to reach its equilibrium value. We can distinguish two different components in this relaxation time: $\tau_r = \tau_{r1} + \tau_{r2}$. A first one that take into account the solvent hydrodynamic friction due to the viscosity (Stokes-Einstein-Perrin equation), and another one due to the solute-solvent dielectric friction result from solute dipolar moment reorientation⁸ respectively:

$$\tau_{r1} = \frac{4\pi a^3}{kT} \eta \quad \tau_{r2} = \frac{4\pi\mu^2}{3VkT} \frac{D-1}{(2D+1)^2} \tau_D,$$

where η is the solvent viscosity, μ the solute dipolar moment, τ_D the solvent Debye relaxation time and V the Onsager's cavity volume.

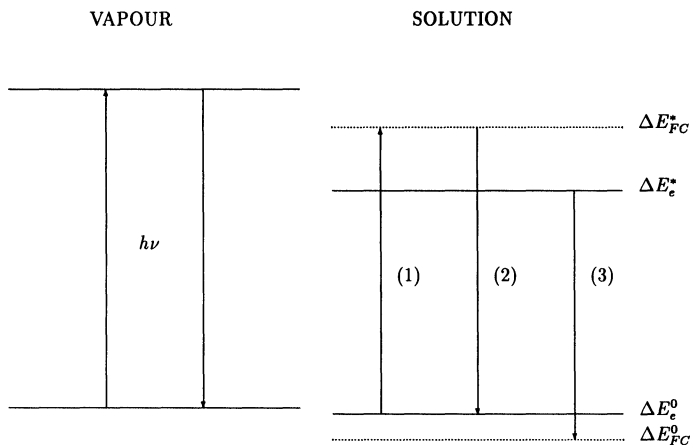


Figure 1 Energy levels of an organic molecule in solution and in vapour phase. (1) Absorption, (2) low temperature emission, (3) high temperature emission. ΔE_{FC}^* and ΔE_{FC}^0 are the interaction energies in the Franck-Condon states (non equilibrium) for excited and ground state respectively. In the same way, ΔE_e^* and ΔE_e^0 are the equilibrium interaction energies. The resonance energy of the organic molecule in vapour phase (no dipolar interactions) is done by $h\nu$.

Taking into account the scheme of levels in Figure 1, we can distinguish for an organic molecule in solution the processes 1, 2 and 3:

1. The solute molecule is excited from the equilibrium ground state to a Franck-Condon excited state. No orientation have occurred yet.
2. Practically all the solute molecules emit from a non-equilibrium state. Considering the lifetime τ of the excited state, we have $\tau_r \gg \tau$, that is, the low temperature limit (high viscosity).
3. Now $\tau_r \ll \tau$ and almost all the solute molecules emit from an equilibrium state, decaying to the Franck-Condon ground state (non-equilibrium). This is a result from a non-immediate reorientation processes (high temperature limit, low viscosity).

Whichever emission processes between 2 and 3 are also possible.

At toom temperatures usually the relaxation process is very fast and the emission average energy will be

$$E_e = E + \Delta E_e^* - \Delta E_{FC}^0, \quad (3)$$

that correspond to the gravity center (g.c.) of the fluorescence spectra.^{9,10} According with (1):

$$\Delta E_{FC}^0 = -\frac{2}{a^3} f(D, n) \vec{\mu}_0 \cdot \vec{\mu}_e - \frac{1}{a^3} g(n) \vec{\mu}_0 \cdot \vec{\mu}_0 - \frac{4\pi\rho\alpha}{3a^3} \vec{\mu}_D \cdot \vec{\mu}_D + \mathcal{D}$$

$\vec{\mu}_0$ and $\vec{\mu}_e$ being the solute dipolar moment of the ground and excited state, and

$$\Delta E_e^* = -\frac{2}{a^3} f(D, n) \vec{\mu}_e \cdot \vec{\mu}_e - \frac{1}{a^3} g(n) \vec{\mu}_e \cdot \vec{\mu}_e - \frac{4\pi\rho\alpha}{3a^3} \vec{\mu}_D \cdot \vec{\mu}_D + \mathcal{D}'.$$

Considering that the dispersion term $\mathcal{D} - \mathcal{D}'$ is negligible,⁶ we obtain from Eq. (3) the emission energy

$$E_e = E - \frac{2}{a^3} f(D, n) \mu_e (\mu_e - \mu_0 \cos \alpha) - \frac{1}{a^3} g(n) (\mu_e^2 - \mu_0^2) \quad (4)$$

where α is the angle between $\vec{\mu}_e$ and $\vec{\mu}_0$. For non-polar solvents $f(D, n) = 0$ and Eq. (4) becomes

$$E_e^{(np)} = E - \frac{1}{a^3} g(n) (\mu_e^2 - \mu_0^2),$$

so that the emission at room temperature is red-shifted with respect to vapour phase (we consider that $\mu_e > \mu_0$, as in our case). In polar solvents $f(D, n) > 0$ and usually also $\mu_e - \mu_0 \cos \alpha > 0$, then when the solvent polarity is increased the dielectric function is increased, the emission spectra is shifted to lower energies and the average emission energy is given by Eq. (4).

3. EXPERIMENTAL

In all cases the analysed samples correspond to a commercial mineral oil VESTAN with different wear degrees. The organic molecules used as solute was N-methylindole (NMI) from EGA-CHEMIE.

The measurements were carried out on a spectrofluorimeter made up with two monochromators H20 JOBIN YVON in continuous excitation. The emission monochromator exit slit is fitted with a detector housing containing a photomultiplier tube HAMAMATSU R928S. The signal is amplified by a lock-in amplifier ORTHOLOC-SC 9595 and recorded on a PC to perform the numerical treatment of obtained data.

Fluorescence spectra have been recorded by fixing the excitation monochromator at 290 nm and by scanning the emission monochromator from 291 nm to 360 nm. The excitation wavelength was carefully chosen to avoid oil absorption, in any case we got no emission from them.

We have made six solutions A, B, C, D, E and F of NMI in oil with an increase in wear degree from A to F respectively, A corresponding to fresh oil and F to the most degenerate oil. The concentrations were approximately 10^{-4} M l^{-1}

4. RESULTS AND DISCUSSION

Figure 2 shows fluorescence spectra obtained at room temperature for NMI in oils. The profile A correspond to the NMI solution in a fresh oil, a structured profile like that obtained from NMI in non-polar solvents.⁵ When the wear degree of the oil is increased, the fluorescence spectra is red-shifted. The spectrum B, corresponding to the wearest oil, is the most shifted profile, with a single broad envelope like NMI

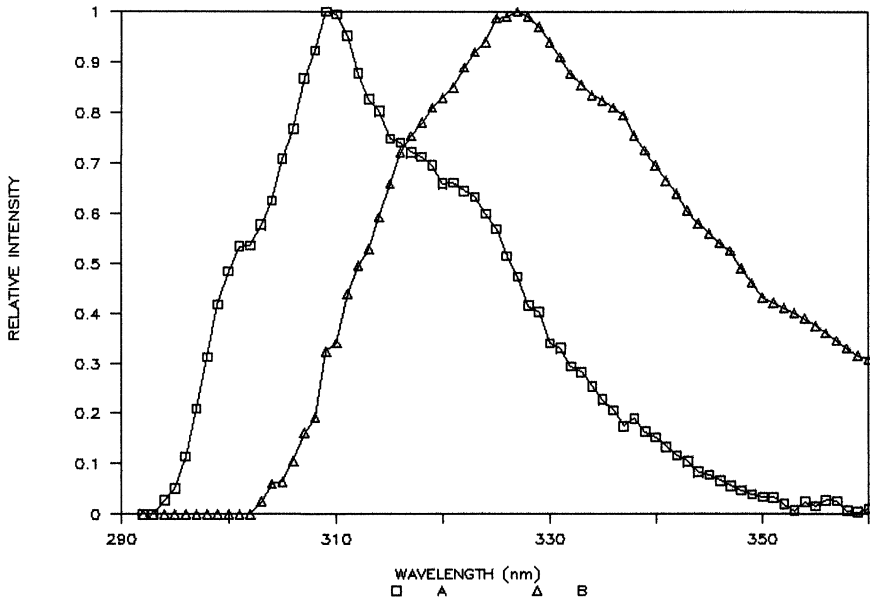


Figure 2 Fluorescence spectra of NMI solved in VESTAN at room temperature. Profile A correspond to the fresh oil (no degradation) and profile B to the wearest oil (maximum degradation).

fluorescence spectra in polar solvents. Intermediate spectra (Figure 3) show a mixed profile¹¹ resulting from the coexistence of two phases: the phase corresponding to fresh oil solution and the corresponding to wear oil (broken macromolecular chains, high polarity).

With the aid of a PC we obtained the mixed profiles of intermediate degradation oils as a sum of polar and non-polar contributions

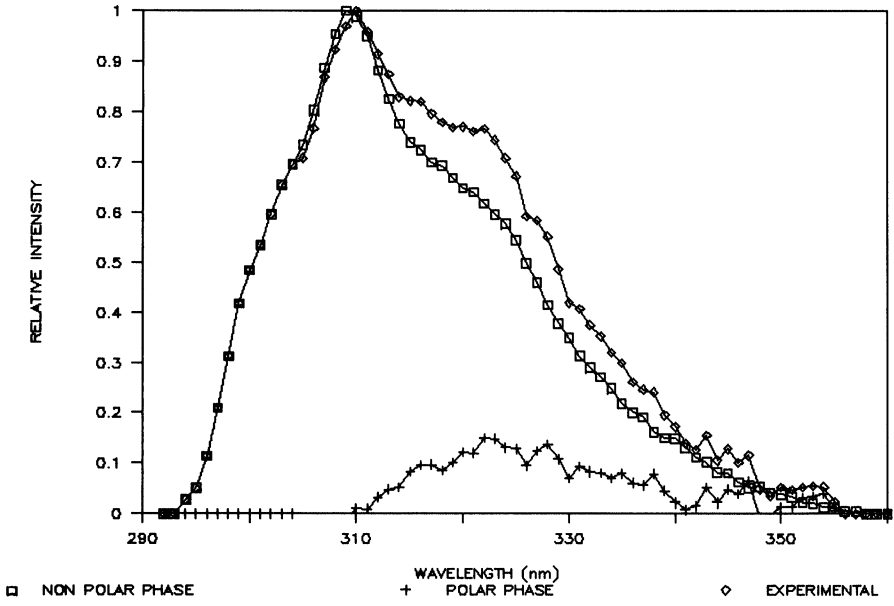
$$\varphi_f = x_{(np)}\varphi_f^{(np)} + x_{(p)}\varphi_f^{(p)}$$

where φ_f is the fluorescence mixed profile, $\varphi_f^{(np)}$ is the non polar contribution (spectrum A in Figure 2), $\varphi_f^{(p)}$ is the polar contribution (spectrum B in Figure 2) and $x_{(n)}$ and $x_{(np)}$ are related by $x_{(n)} + x_{(np)} = 1$. The results obtained with VESTAN oil can be seen in Table 1 and Figure 3.

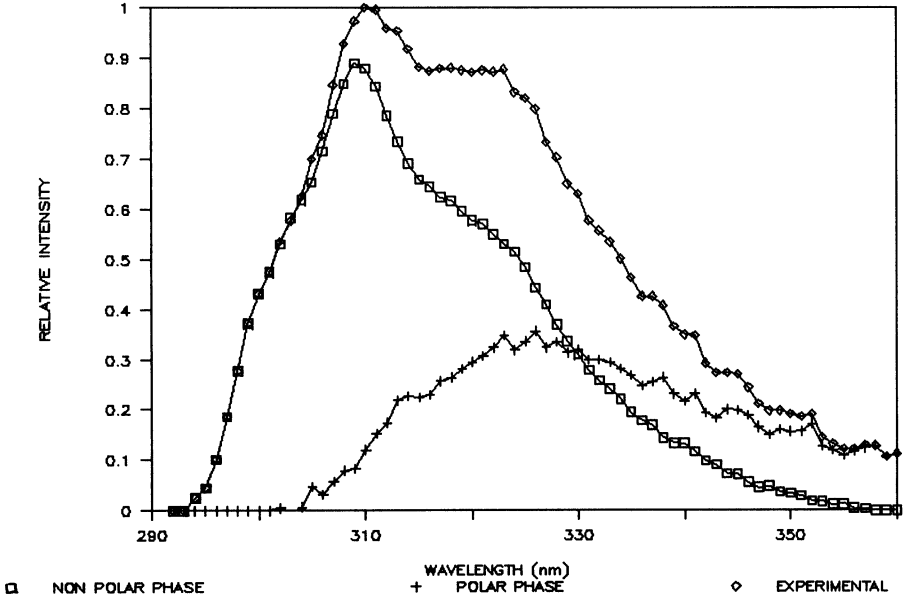
In order to particularize Eq. (4) to NMI fluorescence spectra in VESTAN, we have taken the values given in Ref. 12 for NMI dipolar moments. The fresh oil refractive index and dielectric constant are $n = 1.4680$ and $D = 2.8$ respectively. For the NMI fluorescence spectra in fresh oil, the gravity center is at 31645 cm^{-1} (Table 1), so that taking into account Eq. (4) we obtain for solution A, the average emission energy of NMI in vapour phase, a value of $6.36 \cdot 10^{-12} \text{ erg}$ that corresponds to a frequency of 32139 cm^{-1} .

Now we can write Eq. (4) for our particular case

$$v_e = 32,139 - 1,044g(n) - 2,089f_e(D, n) \quad (5)$$



(a)



(b)

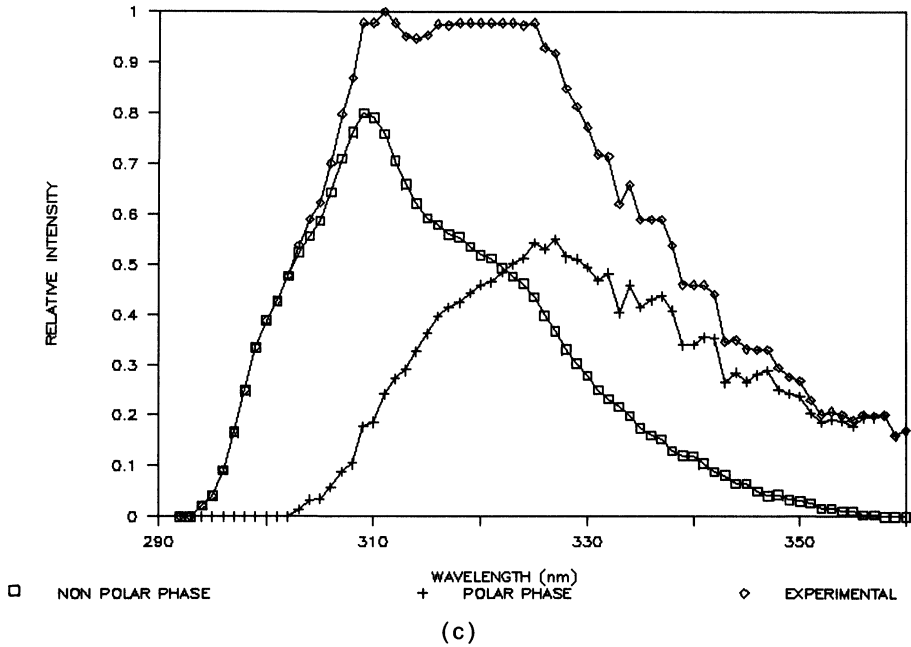


Figure 3 Mixed profiles of intermediate degradation oils as a sum of polar and non-polar contributions. The wear degree is increased from Figure 3a to Figure 3c.

Table 1 Results obtained for all the studied solutions

<i>Solution</i>	<i>g.c. (cm⁻¹)</i>	<i>x_(p)</i>	<i>x_(np)</i>
A	31,645	0.00	1.00
B	31,516	0.09	0.91
C	31,124	0.36	0.64
D	31,075	0.39	0.61
E	30,931	0.49	0.51
F	30,184	1.00	0.00

where we have expressed energy in frequency units (cm^{-1}) and g_e and f_e are the effective dielectric functions of the solvent

$$g_e(n) = x_{(np)}g(n_{(np)}) + x_{(p)}g(n_{(p)}),$$

$$f_e(D, n) = x_{(np)}f(D_{(np)}, n_{(np)}) + x_{(p)}f(D_{(p)}, n_{(p)}).$$

Applying Eq. (5) to the most degradate oil (spectrum B in Figure 2) we obtain a relation between their dielectric functions

$$g(n_{(p)}) = 1.87 - 2f(D_{(p)}, n_{(p)})$$

and according with the dielectric function definitions (Eq. (2))

$$\frac{n_{(p)}^2 - 1}{n_{(p)}^2 + 2} = 2 \frac{D_{(p)} - 1}{D_{(p)} + 2} - 1.87 \quad (6)$$

that give us a relation between the refractive index and the dielectric constant of the wearest oil (polar solvent).

Taking into account that $D_{(p)} > n_{(p)}^2$ and $f(D_{(p)}, n_{(p)}) > 0$ the possible solutions of Eq. (6) are constrained by

$$1 \leq n_{(p)} \leq 1.2034, \quad D_{(p)} > 44.15.$$

We can see that the oil optical constants change during the degradation process. The dielectric constant is strongly increased, as a result of the oil polarity increasing, while refractive index change less, although we can observe a small decrease in it.

5. CONCLUDING REMARKS

By means of spectroscopic methods we have carried out a complete characterization of mineral oil degradation processes. In the fluorescence spectra profile of our molecule-test will be showed the polarity state of the oil, and so its degradation. Likewise, opposite to Suppan's theory¹³ and resulting from the high oil viscosity at room temperature, it's expected that the diffusion of the big macromolecular chains will be negligible so that the $x_{(p)}$ constant will give us a measure of the rate of broken chains, and so a measure of the oil degradation state.

On the other hand, the mineral oils are also employed in medicine and pharmacy, so that it can be interesting for reasons of health to know the state of this oils before their utilization with medical and pharmaceutical purposes, as a quality control test. In this way, is interesting to know that our method is specially sensitivity to the little changes in polarity in the beginning of degradation process.

In a more general way, given the fluorescence spectra of a probe molecule in solution, knowing its emission energy in vapour phase and the solvent refractive index at room temperature, Eq. (4) give us an indirect method to measure its static dielectric constant.

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