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A solvatochromic dye-doped polymer for detection of polar additives in hydrocarbon blends

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We describe the preparation and characterization of a solvatochromic dye-doped polymer for the detection of polar additives in hydrocarbon blends. This polymer is prepared by inclusion of the strongly solvatochromic Reichardt's dye (RD) into poly(methyl methacrylate) (PMMA). The influence of various parameters on the detection of methanol, tert-butyl alcohol (TBA) and tert-butyl methylether (TBME) in hydrocarbon blends is analysed by u.v.-visible spectroscopy. RD–PMMA spin-coated films can detect repeatedly down to 0.1% (v/v) methanol and TBA and 1.0% (v/v) TBME, which makes them potential candidates of a solvatochromic-based fibre optic chemical sensor for *in situ* monitoring of octane improvers in gasoline.

(Keywords: solvatochromic dye; doping; hydrocarbon blends)

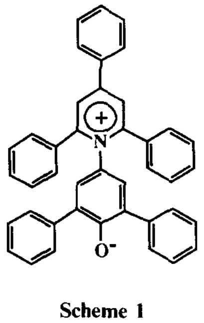
Introduction

For *in situ* monitoring of additives, such as octane improvers in gasolines, it is necessary to develop analytical systems operating in real time and in perfectly safe conditions. The combined use of optical fibres and chemical indicators has recently led to a new class of optical sensors called fibre optic chemical sensors (FOCS)[1]. In these devices, a chemical agent with potential optical properties (e.g. absorption, fluorescence) is immobilized at the tip of an optical fibre or used as its cladding. When a FOCS is introduced into a liquid or gaseous medium to be analysed (analyte), the chemical agent undergoes a reaction and generates an optically detectable modification which is characteristic of the chemical composition of the analyte. In an absorption-based FOCS, for example, absorption of an input light beam by the chemical agent is recorded after reflection of the beam on a mirror as an output absorption signal.

Since octane improvers are essentially oxygenated additives, they are generally more polar than the gasoline base, which is a complex mixture of non-polar hydrocarbons. This difference of polarity can easily be detected by using the well known solvatochromic effect, which consists of the pronounced shift of the longest wavelength absorption band of an organic dye consecutive to a slight variation of the polarity of the solvent. The influence of various parameters as well as potential applications of organic solvatochromism have been widely investigated and summarized by Reichardt[2].

We have thus been led to design a FOCS based on the solvatochromic effect. The first step consists of preparing a material with solvatochromic properties that can be deposited at the tip of an optical fibre without dissolving in saturated hydrocarbons. In this respect, dye-doped polymers are attractive because they can be easily tailored with infinite combinations by varying either the polymer matrix or the solvatochromic organic dye.

In this study, we selected Reichardt's dye (RD), a pyridinium-*N*-phenoxide betaine dye with a zwitterionic structure (see *Scheme 1*), as the solvatochromic chemical detector. Its long wavelength absorption band is hypsochromically shifted by 357 nm on going from a non-polar solvent such as diphenyl ether ($\lambda_{max} = 810$ nm) to water, which is highly polar ($\lambda_{max} = 453$ nm)[3,4]. RD solutions are red-coloured in methanol, violet in ethanol, blue in isoamyl alcohol, green in acetone and yellowish-green in ethyl acetate, thus covering the whole visible region and allowing an accurate visual estimate of the solvent polarity. The various optical properties of RD have been recently reviewed by Reichardt[5]. On the polymer side, we chose poly(methyl methacrylate) (PMMA) as the matrix because of its good optical transparency, mechanical strength and insolubility in saturated hydrocarbons. Hammack *et al.*[6] have already reported on the pressure-induced solvatochromism of the RD–PMMA system, while Paley *et al.*[7] have studied the characterization of



Scheme 1

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*To whom correspondence should be addressed solid polymers as solvent phases by preparing various dye-doped polymers including RD–PMMA.

In this communication, we report on the preparation of RD–PMMA dye-doped polymer films and their solvatochromic sensitivity towards small amounts of polar additives such as methanol, tert-butyl alcohol (TBA) and tert-butyl methylether (TBME) in hydrocarbon blends using u.v.-visible absorption spectroscopy.

Experimental

Materials preparation. Thin films of RD–PMMA dye-doped polymers are prepared according to the following procedure[8]. RD (Aldrich; 0.004 g; 7×10^{-6} mol) and PMMA ($MW=93\,000$, Aldrich; 0.110 g; 1.2×10^{-6} mol) are dissolved in 10 ml of hot dichloromethane (Rectapur). Thin films of RD–PMMA are then prepared by spin-coating (Set TP 6000; 20 s at 800 rev min^{-1}) onto glass slides (0.5 x 3.0 cm^2) previously cleaned in a sulfuric acid solution of chromium(III) oxide and rinsed with bi-distilled water. This technique affords homogeneous and transparent green films (thickness 100–200 μm) which are then dried at 80°C under vacuum for 30 min. The film samples are then allowed to cool down to room temperature under ambient laboratory air for 2 min before measurements, in order to avoid any thermochromic effect of the RD. As already reported by Paley *et al.*[7], the absorption spectra of RD–PMMA films are highly sensitive to atmospheric humidity owing to the adsorption of water molecules. Then, after cooling to room temperature, the RD–PMMA film is immediately immersed into the hydrocarbon blend to be analysed, so that no particular protection against atmospheric moisture is necessary.

The hydrocarbon mixture used in this study as the analyte is a naphtha blend provided by Shell Recherche SA (Grand Couronne, France). Precise amounts (0.0–2.0% v/v) of spectrophotometric grade methanol, TBA or TBME (Aldrich Chemical Co.) are added to this naphtha.

U.v.-visible spectroscopy. Since the purpose of this study is to prepare a material fitted to a solvatochromic FOCS device, we analysed the u.v.-visible properties of the RD–PMMA films in conditions close to those of a FOCS using an optical set-up purposely developed in our laboratory (*Figure 1*). This set-up is based on the use of optical fibres as the input and output signal transducers. Furthermore, a multichannel acquisition module allows real time absorption spectra to be recorded over the whole u.v.-visible range.

The analysing white light of an iodine lamp (ISA/Jobin-Yvon, 24 V, 70 W) is transmitted to the quartz optical cell (0.5 x 1.0 x 3.5 cm^3) by an input optical fibre, passes through the RD–PMMA film and is sent to the analyser via an output optical fibre. The optical cell is inserted in a home-built Teflon frame mounted on the top of a micrometric platform. Two apertures in the frame allow the optical fibres to be fixed; the glass slide supporting the film sample is held in the cell with the help of a screw. The monochromator is a Jobin-Yvon CP 200 with a focal length of 200 cm. It is fitted with a grating (200 grooves/mm). It forms an image of the fibre on a 2.5 cm photodiode array. The photodiode array detector is a Princeton Instrument non-intensified u.v.-visible detector fitted with a silicon diode array (1024 elements; sensitivity range 185–1100 nm; pixel dimension 25 μm x 2.5 mm). The multichannel analyser is a modular Jobin-Yvon 'Spectralink' analyser connected to a computer. It is driven by the 'enhanced PRISM' software provided by Jobin-Yvon. The analyser drives the detector and operates data processing. The minimum time required to record a 1024 pixels spectrum is 0.025 s, and the acquisition time used here is 1.0 s while the spectral resolution is 0.5 nm.

Results and discussion

Figure 2 shows the absorption spectra of an RD–PMMA film immersed in naphtha containing respectively 0.0 and 2.0% (v/v) of methanol. A strong hypsochromic shift ($\Delta\lambda_{max}=112$ nm) of the π–π^* transition band and an absorbance variation are simultaneously observed. As expected, this clearly shows that RD molecules embedded in a polymer matrix can be partially solvated by solvent molecules after diffusion through PMMA.

Figure 3 shows the dependence of the maximum absorption wavelength λ_{max} of an RD–PMMA film dipped into various naphtha blends as a function of the amount of methanol contained in the medium (0.0–2.0% v/v). The λ_{max} values plotted in *Figure 3* are recorded 4 min after introduction of the film into the naphtha, i.e. after complete stabilization of solvent diffusion into the polymer film. Since the RD–PMMA films absorb at $\lambda_{max}=654$ nm in MeOH-free naphtha, a strong blue-shift ($\Delta\lambda_{max}=57$ nm) appears on adding a quantity of methanol

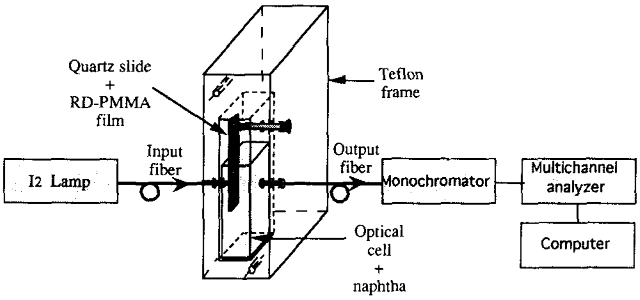


Figure 1 Experimental set-up for u.v.-visible absorption spectroscopy of RD–PMMA films immersed in naphtha blends containing polar additives. The optical cell is oversized for the sake of clarity

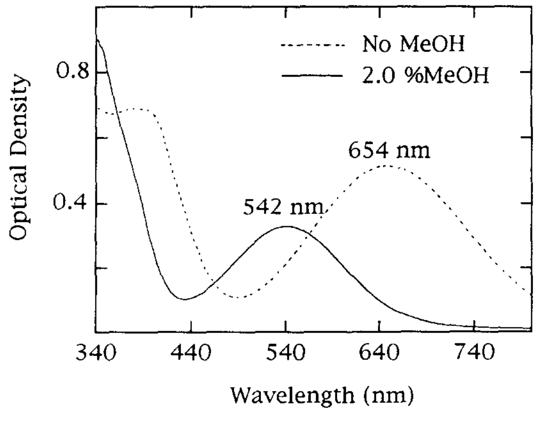


Figure 2 U.v.-visible absorption spectra of RD–PMMA film immersed in naphtha containing no methanol (---, $\lambda_{max}=654$ nm) and 2.0% (v/v) of methanol (— —, $\lambda_{max}=542$ nm)

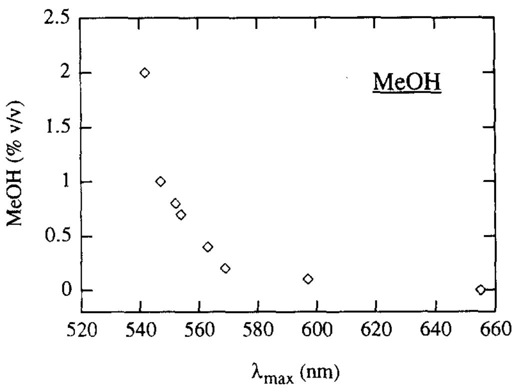


Figure 3 Maximum wavelength absorption of an RD–PMMA film as a function of the methanol volume content in the naphtha blend

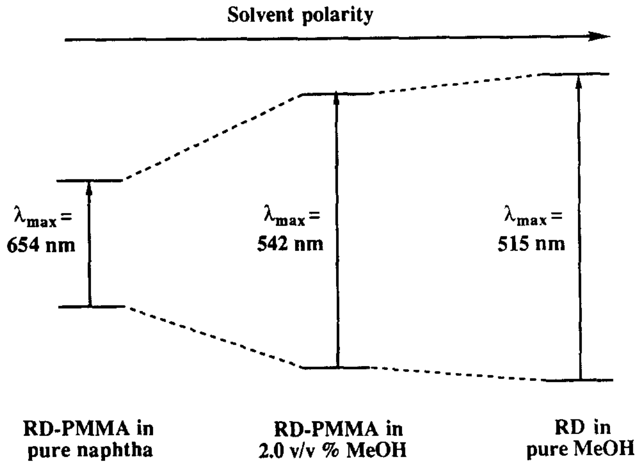
as small as 0.1% (v/v) ($\lambda_{max} = 597$ nm). Between 0.0 and 0.2% of methanol, the spectral shift is $\Delta\lambda_{max} = 85$ nm (final $\lambda_{max} = 569$ nm) and is only $\Delta\lambda_{max} = 107$ nm between 0.0 and 1.0% methanol.

These results clearly evidence the extreme solvatochromic sensitivity of the RD towards methanol even when immobilized in a solid-state polymeric matrix. The RD–PMMA dye-doped polymer appears then as a potential material for alcohol detection in naphtha blends. Above 1.0% (v/v) methanol, the absorption tends to stabilize at $\lambda_{max} = 545$ nm and then decreases slowly down to 542 nm for 5.0% methanol, which is the maximum miscibility of methanol in naphtha. It should be mentioned that the λ_{max} of the RD–PMMA system in pure methanol is $\lambda_{max} = 515$ nm, showing that the methanol detection limit is not yet reached for a 5.0% (v/v) content. *Scheme 2* illustrates the differential solvation of the electronic ground and excited states of RD in PMMA for various MeOH contents, i.e. for different medium polarity. Since MeOH is a Brønsted acid, solvatochromism results from the interaction of the phenoxide oxygen atom of RD with MeOH through hydrogen bonding. Since the positive charge of the pyridinium moiety is delocalized and shielded by steric effects due to the phenyl groups and to a lesser extent the PMMA chains, the charge transfer absorption of RD depends essentially on the hydrogen bond donor ability of MeOH (or other alcoholic additive). The RD–PMMA system is thus only efficient for small amounts of methanol and cannot be used to determine methanol contents larger than 2.0% (v/v).

Similar results are obtained with TBA. The initial absorption band at $\lambda_{max} = 654$ nm is hypsochromically shifted by $\Delta\lambda_{max} = 16$ nm after the addition of only 0.1% (v/v) TBA (*Figure 4*). Between a TBA-free solution and a solution containing 2.0% (v/v) TBA, the spectral shift is $\Delta\lambda_{max} = 99$ nm. As expected from the lower polarity of TBA as compared to methanol, the spectral shifts are systematically smaller. Furthermore, the non-polar TBME behaves similarly to TBA; a hypsochromic shift of $\Delta\lambda_{max} = 10$ nm is observed after the addition of 1.0% (v/v) of TBME and a shift of $\Delta\lambda_{max} = 31$ nm after addition of 10% (v/v) of TBME.

It should also be noted that no λ_{max} variation is observed when the RD–PMMA samples are dipped into hydrocarbon blends containing various amounts (0.0–20% v/v) of aromatic compounds such as benzene and toluene. Moreover, the presence of aromatic additives in the hydrocarbon blend induces a progressive degradation of the RD–PMMA films.

Figure 5 shows the time evolution of the absorbance at the initial λ_{max} of an RD–PMMA film (654 nm in air) dipped in various naphtha–methanol mixtures. For methanol contents higher than 0.4% (v/v), up to 2.0% (v/v), the absorbance first decreases steeply from OD = 0.5 ($t = 0$) down to OD < 0.2 in less than 30 s and then reaches



Scheme 2

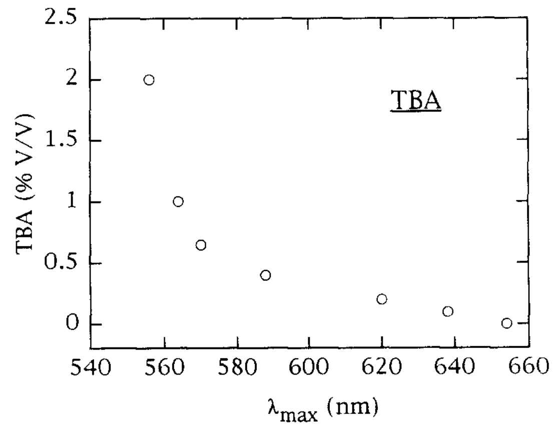


Figure 4 Maximum wavelength absorption of an RD–PMMA film as a function of the TBA volume content in the naphtha blend

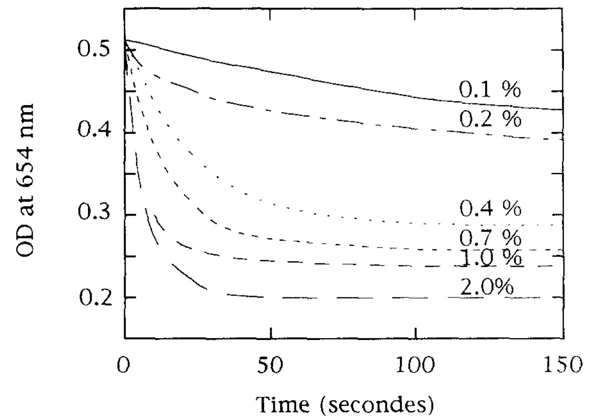


Figure 5 Time dependence of the absorbance at $\lambda_{max} = 654$ nm of an RD–PMMA film immersed in a hydrocarbon blend containing various amounts of methanol

a constant value within 100 s. For MeOH contents of 1.0 and 2.0% (v/v), a constant absorbance is even reached within 40 to 50 s. For every MeOH rate, the non-zero absorbance observed after stabilization of $\Delta\lambda_{max}$ is due to the partial overlap between the absorption spectrum of MeOH-free naphtha and that of the naphtha–MeOH mixtures. It is then clear that the higher the amount of methanol, the faster the response. It seems that the solvatochromism of these composite systems is essentially under the control of diffusion and that the influence of temperature, solvent viscosity and polymer porosity, as well as the additive concentration, determine the kinetics of the process.

After each absorbance measurement for a given additive amount, the RD–PMMA films are withdrawn from the cell and dried in an oven at 80°C. Reproducibility is systematically checked by placing the samples back into the optical cell. Note that it is important to let the sample cool down to room temperature before the measurements in order to avoid any thermochromic effect. Whatever the additive amount below 2.0% (v/v), the films exhibit exactly the same spectral and intensity characteristics over the first ten measurements. Each sample recovers its initial absorption ($\lambda_{max} = 654$ nm), showing that it is determined by the polarity of the PMMA matrix. This matrix effect can be observed using various polymers. In the less polar poly(vinyl chloride) (PVC), the maximum absorption of the RD dye is kept constant at $\lambda_{max} = 663$ nm from one measurement to the other. The λ_{max} variation for various methanol contents (0.0–2.0% v/v) is similar whatever the polymer matrix (PMMA, PVC or poly(ethylene oxide)).

Conclusion

Thin films of the RD–PMMA dye-doped polymer have a high solvatochromic sensitivity towards polar additives in hydrocarbon blends. Methanol or TBA quantities as small as 0.1% (v/v) can be detected within a few seconds by u.v.-visible absorption spectroscopy. Nevertheless, the RD–PMMA polymer is not sensitive to aromatic compounds such as toluene and thiophene, often found in large amounts in naphtha. These polymers have the required properties to design a fibre optical chemical sensor (FOCS) based on the solvatochromic effect. We will report soon on these new FOCS, which can be particularly useful for *in situ* and real-time monitoring of octane improvers in gasolines.

Acknowledgements

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