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Have Biofuel, Will Travel: A Colorful Experiment and a Different Approach To Teach the Undergraduate Laboratory

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S Supporting Information

ABSTRACT: The substitution of petroleum-based fuels with those from renewable sources has gained momentum worldwide. A UV–vis experiment for the quantitative analysis of biofuels (bioethanol or biodiesel) in (petroleum-based) diesel oil has been developed. Before the experiment, students were given a quiz on biofuels, and then they were asked to suggest a suitable UV–vis experiment for the quantification of biofuels in diesel oil. After discussing the results of the quiz, the experiment was conducted. This included the determination of λ_{max} of the medium-dependent, that is, solvatochromic, visible absorption band of the probe 2,6-bis[4-(*tert*-butyl)phenyl]-4-{2,4,6-tris[4-(*tert*-butyl)phenyl]pyridinium-1-yl}phenolate as a function of fuel composition. The students appreciated that the subject was linked to a daily situation and that they were asked to suggest the experiment. This experiment served to introduce the phenomena of solvation and solvatochromism.

KEYWORDS: Second-Year Undergraduate, Upper-Division Undergraduate, Analytical Chemistry, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Applications of Chemistry, Solutions/Solvents, UV–Vis Spectroscopy



The principles of green chemistry¹ have permeated our thinking; teaching chemistry is no exception.^{2–7} Renewable alternatives to petroleum-based fuels have gained momentum worldwide.^{8–10} Nowadays, alcohols and esters of fatty acids, the latter of which are produced by the transesterification of animal or vegetable triglycerides with short-chain alcohols, are almost always associated with biofuels. Carbohydrates are cited as the most prominent examples of renewable, biodegradable feed stocks.¹¹ Even before the term *biofuel* was coined, the gasoline sold in Brazil contained bioethanol (hereafter designed as “ethanol”). Mass-produced passenger cars have been running on hydrous ethanol for 32 years¹² (Figure 1). Since 2003, the cars sold in Brazil have been flexible-fuel vehicles; that is, they run on gasoline, ethanol, or any mixture of both. Since 2008, the petroleum-based diesel fuel contains biodiesel with a volume fraction of 2%;¹³ this will be increased to 5% in 2013.¹⁴ Ethanol-added diesel oil is being tested in some Brazilian metropolitan areas.¹⁵

An experiment on biofuels is included a spectroscopy course taught to chemistry-majors (fifth semester; 56 students), which includes a 4-h laboratory per week. Rather than giving a detailed “recipe” for this experiment, a different approach is used that is challenging to the students, interesting to do, and serves a purpose beyond the specific objectives of the experiment, for example, learning a practical skill. A week before the laboratory, a quiz is handed out in the classroom to evaluate the students’ knowledge of the history and industrial processing of biofuels. The students are asked to suggest a simple UV–vis spectroscopic experiment to determine the content of ethanol or biodiesel in diesel oil. Before doing the experiment, the student quiz answers

and suggested experiments are discussed in class, and the work that they are going to do is outlined.

A dye, 2,6-bis[4-(*tert*-butyl)phenyl]-4-{2,4,6-tris[4-(*tert*-butyl)phenyl]pyridinium-1-yl}phenolate (*t*-Bu₅RB) is added to various blends of biofuels. The visible absorption band, λ_{max} , of the medium-dependent, that is, solvatochromic, visible absorption band of *t*-Bu₅RB is used to determine the fuel composition. The laboratory is fun because of the range of vivid colors that solutions of the solvatochromic dye exhibit as a function of fuel composition. The experiment with a solvatochromic dye is also used to show how *solvatochromism* is relevant to understanding *solvation*.

■ PREPARATION BY THE STAFF BEFORE THE EXPERIMENT

Purification of the Starting Materials

The following treatments of the commercial products were carried out by the staff before the student experiment. “Anhydrous” ethanol was stirred with anhydrous K₂CO₃ and then filtered. Commercial diesel oil (500 mL; purchased from a local gas station) was washed three times with 50 mL each of an aqueous solution of NaCl (10%), aqueous HCl (1%), and finally with water. The fuel was stirred overnight with basic alumina (45 g) and then filtered to give a pale-yellow liquid. The biodiesel employed was methyl dodecanoate (purity >99.5%; Dhaymers Química Fina, São Paulo) and was used as received.

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Figure 1. The first prototype of a commercial vehicle that runs on hydrous ethanol, on exhibition at the Brazilian Aerospace Memorial in São José dos Campos, São Paulo.¹⁶

Synthesis of the Solvatochromic Dye

The solvatochromic dye, 2,6-bis[4-(*t*-butyl)phenyl]-4-{2,4,6-tris[4-(*t*-butyl)phenyl]pyridinium-1-yl}phenolate (*t*-Bu₅RB; Figure 2A)^{17–21} is not commercially available and had to be synthesized. The procedure included condensation of a 2,4,6-trisubstituted pyrylium salt with a 2,6-bisarylsubstituted 4-aminophenol and subsequent deprotonation of the *N*-(4-hydroxyphenyl)pyridinium salt formed by a base; see Scheme SI-1 in the Supporting Information.¹⁹

Preparation of *t*-Bu₅RB Samples for Student Use

Aliquots (0.2 mL of 1.0×10^{-3} M solution of *t*-Bu₅RB in purified ethanol) were pipetted into 2 mL volumetric flasks and the solvent was evaporated under reduced pressure. The flasks were stoppered and given to the students during the laboratory period.

STUDENT EXPERIMENT: SPECTROSCOPIC DETERMINATION OF THE FUEL COMPOSITION

Preparation of Fuel Samples

Eleven solutions of the dried ethanol (volume fraction 0–100%) in diesel oil and 10 solutions of biodiesel (volume fraction 4–100%) in diesel oil were directly prepared in the 2 mL volumetric flasks that contained the solid solvatochromic dye.

Determination of λ_{max} of the Dissolved Dye

The UV–vis spectra were recorded at 25 °C in the wavelength range of 400–900 nm with a scanning rate of 140 nm min^{−1} with a Beckman DU-70 or a Shimadzu UV-2550 spectrophotometer. The spectrophotometer was equipped with thermostatted compartments that hold four 1 cm path stoppered cells. The values of λ_{max} were calculated from the first derivative of the absorbance spectrum.

Calculation of the Solvent Polarity of the Dissolved Dye

The values of λ_{max} were used to calculate an empirical scale of solvent polarity that is based on the electronic transition energy, E_T , necessary to go from the ground state to the first excited state of the probe dye,

$$E_T(\text{probe}) (\text{kcal mol}^{-1}) = h\nu_{\text{max}} N_A = (2.8591 \times 10^{-3}) \nu_{\text{max}} (\text{cm}^{-1}) = 28591 / \lambda_{\text{max}} (\text{nm})$$

where h is Planck's constant, c the velocity of light, N_A Avogadro's number, ν_{max} the wavenumber, and λ_{max} the wavelength of the solvent-dependent visible absorption band. The use of the

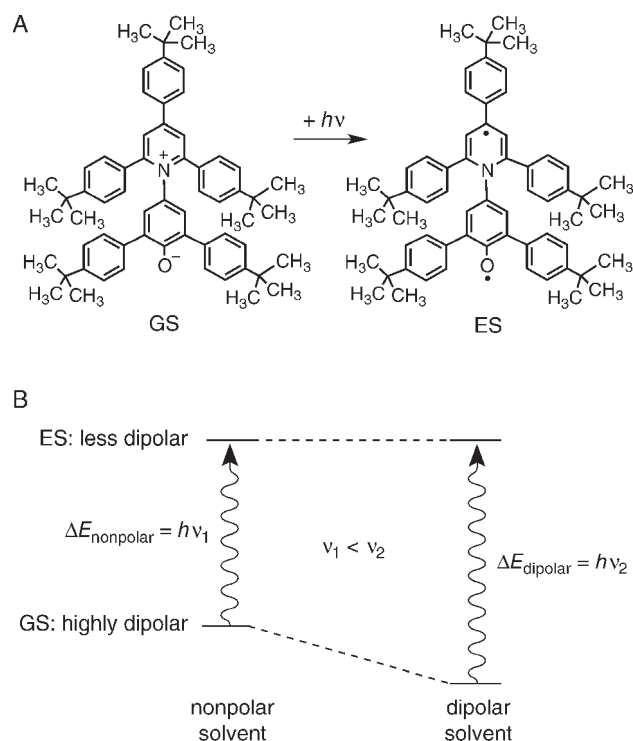


Figure 2. (A) The molecular structure of the solvatochromic indicator dye, *t*-Bu₅RB: a zwitterionic pyridinium-*N*-phenolate betaine dye with a highly dipolar electronic ground state (GS) and a much less dipolar first excited state (ES).^{17,19} (B) A schematic qualitative representation of the solvent influence on the differences ΔE between the energies of the GS and ES of *t*-Bu₅RB, dissolved in a nonpolar and a dipolar solvent, respectively.²¹

appropriate constants allows the calculation of the $E_T(\text{probe})$ in kcal mol^{−1}. Students plotted $E_T(\text{probe})$ versus the concentration of the added biofuel or biodiesel.

Treatment of the Generated Residues

The collected spent fuels were sent to the residue treatment unit for incineration.

HAZARDS

Although diesel fuel and biodiesel have low vapor pressure, their vapors should not be inhaled, as well as those of the other solvents employed such as ethanol, decalin, isooctane, and xylene, which are all flammable. The students should prepare all solutions in a fume hood. Filling the cuvettes and cleaning them should also be done in a fume cupboard. *t*-Bu₅RB may cause irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled.

RESULTS AND DISCUSSION

Comments on the Experimental Preparation

The presence of certain impurities in commercial fuels, in particular acids and peroxides, leads to the disappearance of the long-wavelength solvatochromic visible absorption band. In the presence of acidic impurities, *t*-Bu₅RB and other zwitterionic probes are (reversibly) protonated at the phenolic oxygen, leading to suppression of the intramolecular charge transfer, vide infra; oxidizing agents cause color bleach of the probe solution. Stirring with anhydrous potassium carbonate leads to removal of acidic impurities

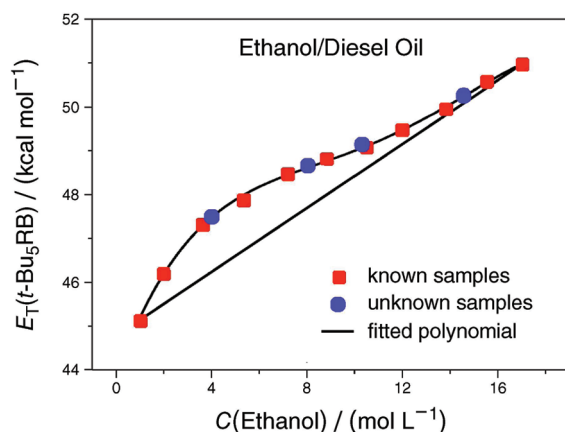


Figure 3. Dependence of $E_T(t\text{-Bu}_5\text{RB})$ on the composition of ethanol/diesel oil mixtures for known (red ■) and unknown samples (blue ●). The volume fraction of ethanol ranges from 5 to 100%.

and further drying of the alcohol. The indicated treatment of diesel oil decomposes any peroxides present.

Results of the Quiz

A quiz was given in two stages. Results of the first stage showed that all students were aware that some diesel oil employed in Brazil contained ethanol as additive, that biodiesel is being gradually introduced as additive to diesel oil, and that the terms B2 and B5 mean diesel oil with volume fractions of 2% and 5% of biodiesel, respectively. The methods suggested by the class (% of the class) for the industrial production of anhydrous ethanol included azeotropic distillation with benzene or toluene (10%); treatment with drying agents such as MgSO_4 , CaO , and H_2SO_4 (65%), or with activated molecular sieves (25%). Most of the students (75%) knew that biodiesel is produced by transesterification of fats and oils.

Before giving the second part of the quiz, the use of UV–vis spectroscopy for the quantitative analysis of fuels was discussed. It was indicated that this can be done either directly, by measuring the absorbance of the fuel, or by using an (unspecified) probe or indicator dye that is sensitive to fuel composition. Most of the students (58%) realized that quantitative analysis by measuring the absorbance of the fuel would not work. Although ethanol and biodiesel do not absorb in the visible region, diesel oil is usually colored; this color is irreproducible because it depends on the precursor crude oil, as well as its distillation conditions. The students suggested the use of a probe dye that is soluble in one component only, for example, ethanol or biodiesel. After constructing the Beer–Lambert law plots, the concentration of the additives in diesel oil can then be determined from the absorbance of the added dye.

The phenomenon of *solvatochromism* (dependence of solute color on solvent polarity) was introduced; an explanation of the dependence of this property on the composition of solvent mixtures was given. Subsequently, the solvatochromic indicator $t\text{-Bu}_5\text{RB}$ was introduced.¹⁹ Briefly, the reason for the observed negative solvatochromism of $t\text{-Bu}_5\text{RB}$ (a hypsochromic shift of the long-wavelength absorption band with increasing medium polarity) is that solvents stabilize the zwitterionic ground state much more than the diradical excited state (Figure 2A). The latter corresponds to a so-called Franck–Condon excited state: because the time scale of the electronic excitation (ca. 10^{-15} s) is much faster than that required for the solvent molecule to reorient to stabilize the

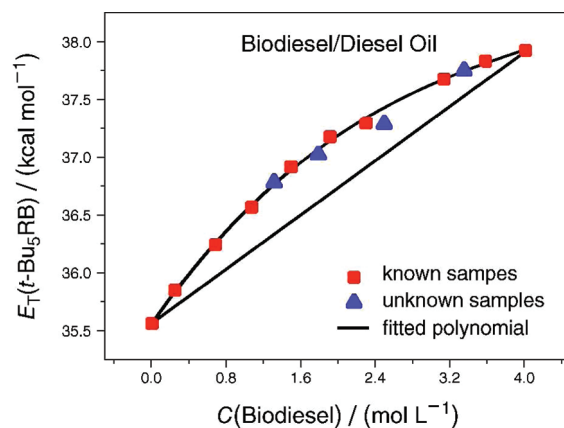


Figure 4. Dependence of $E_T(t\text{-Bu}_5\text{RB})$ on the composition of biodiesel/diesel oil mixtures for known (red ■) and unknown samples (blue ▲). The volume fraction of biodiesel ranges from 0 to 100%.

above-mentioned excited state, the solvent shell of the latter is the same as that of the ground state. The corresponding excitation energy $E_T(t\text{-Bu}_5\text{RB})$, given in kcal mol^{-1} ($E_T = 28591/\lambda_{\text{max}}$ in nm), is connected with the intramolecular charge-transfer from the phenolate to the pyridinium moiety. As shown in Figure 2B, the value of $E_T(t\text{-Bu}_5\text{RB})$ depends on the polarity of the surrounding medium, hence on its composition.^{18,21}

Performance of the Class

After the discussion, the laboratory work was started. The results obtained by the students, namely, the dependence of $E_T(t\text{-Bu}_5\text{RB})$ on the composition of known and unknown samples of ethanol/diesel oil and biodiesel/diesel oil mixtures, are shown in Figures 3 and 4, respectively. For both fuel mixtures, this dependence is not linear because of the *preferential solvation* of the probe dye by the more polar component of the fuel mixture (ethanol or biodiesel). This phenomenon is mainly due to nonspecific dipole–dipole and specific dye–solvent interactions, for example, hydrogen bonding between its phenolate oxygen and ethanol. It results in dye solvation shells whose composition is different (richer in ethanol or biodiesel) from that of the bulk solvent mixture.^{21,22} In Figure 3, the point of pure diesel oil is left out. Its $E_T(t\text{-Bu}_5\text{RB})$ value, $35.9 \text{ kcal mol}^{-1}$, is small, which makes curve fitting with a simple-power polynomial difficult. The reason for this “surge” in $E_T(t\text{-Bu}_5\text{RB})$ is the strong preferential solvation of the probe dye already at very low concentrations of (polar component) ethanol.²³

The students’ results, including the determination of the composition of the unknown samples, were excellent, in view of the fact that this was their first experience with a UV–vis spectrophotometer and with derivative spectra. After reporting their results, the approach that they suggested was discussed. Congo Red, an alternative probe dye, is soluble in ethanol, but not in diesel oil. One group of students was asked to construct a Beer–Lambert law plot; this was not possible because the dye precipitated on addition of diesel oil.

Student feedback via an evaluation sheet was highly positive. The students appreciated that the subject is linked to a daily situation, and they liked the different approach that we employed, namely, asking them to suggest the experiment. The vivid colors that solutions of this betaine dye show as a function of fuel composition added to the enjoyment of the laboratory (Figure 5).



Figure 5. The continuous color variation of solutions of *t*-Bu₃RB in going from pure diesel oil to pure ethanol as solvent. E refers to the volume fraction (%) of ethanol in diesel oil.



Figure 6. Dependence of the color of solutions of *t*-Bu₃RB on the composition of a model fuel, composed of equal volumes of decalin, isooctane, and xylenes. E refers to the % volume fraction of ethanol.

A DIFFERENT APPROACH TO TEACHING THE UNDERGRADUATE LABORATORY

In addition to learning an experimental skill (how to operate a UV–vis spectrophotometer) and something about theory (solvation), involving the students in planning the experiment is highly motivating, especially if the experiment is linked to a timely subject (biofuels). An important outcome of this experiment is that students became aware that solvation can be easily measured experimentally. Additionally, solvation in mixtures is not straightforward because the composition of the solvation shell of a solute may not be equal to that of the bulk mixture.

This experiment is versatile. Its simplicity, safety, and low cost make it appropriate for undergraduate students of diverse backgrounds such as chemistry, pharmacy, engineering, as well as for high school students. It is expedient because the time-consuming construction of a Beer–Lambert law plot is not necessary: the value of λ_{max} and not the dye absorbance, is required for the calculation of the fuel composition. Simpler equipment can be employed, for example, a colorimeter with a fiber optics absorbance accessory. This is possible because the difference between the measured visible absorption maxima is large ($\lambda_{\text{max}} = 796, 754$, and 561 nm for diesel oil, biodiesel, and ethanol, respectively).

The experimental part can be further simplified in at least two ways: substitution of *t*-Bu₃RB by a commercially available solvatochromic probe and use of a model fuel instead of diesel oil. The probe *t*-Bu₃RB was employed because the introduction of five *t*-butyl groups in the peripheral phenyl groups makes it lipophilic enough to dissolve in nonpolar solvents, for example, hydrocarbons.^{17,19,20} This renders the whole composition range from ethanol or biodiesel to diesel oil experimentally accessible. Other probe dyes can be employed to investigate at least certain fuel composition ranges, for example, the commercially available dye RB, that is, 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate;^{17,24} see a representative result in Figure SI-1. Although diesel oil was

used in the experiment, it is also possible to use any model fuel prepared from a mixture of hydrocarbons. This eliminates the labor involved in the purification of commercial fuel. The results obtained with *t*-Bu₃RB in a mixture composed of equal volumes of decalin, isooctane, and xylenes (mixture of isomers) are shown in Figure 6. The colors observed for this model fuel are similar to those for ethanol/diesel oil mixtures because of the strong preferential solvation of the probe dye by the more polar solvent ethanol.

ASSOCIATED CONTENT

Supporting Information

Demonstration of the continuous color change of solutions of *t*-Bu₃RB in going from ethanol/diesel fuel mixtures (E25 and E75) to pure ethanol (E100) in Figure SI; synthesis of *t*-Bu₃RB according to ref 19 in Scheme SI-1; CAS Registry Numbers of all chemicals used in Table SI-1; instructions for the instructor; protocol of the experiment; experimental details. This material is available via the Internet at <http://pubs.acs.org>.

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(17) The commercially available solvatochromic probe dye RB (abbreviation derived from Reichardt's Betaine), that is, *t*-Bu₅RB without the five peripheral *t*-butyl groups, has been used as standard dye for the quantitative determination of solvent polarity by means of so-called $E_T(30)$ values (in kcal mol⁻¹) or normalized dimensionless E_T^N values ($E_T^N = 0.0$ for TMS and 1.0 for water); see refs 18, 19, and 21.

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