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Resolution of absorption spectra of three azo dyes in monomeric state

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Abstract

A semi empirical method for the resolution of the absorption spectra of three ionic azo dyes (Acid Red 266, Congo Red and Benzopurpurine 4B) in monomeric state has been applied. The absorption spectra were measured in ethane-1,2-diol to ensure a monomeric state since in water as solvent aggregation phenomena lead to non-equidistant peak positions (measured in cm^{-1}) of the corresponding sub-bands. The spectra recorded were represented by a sum of 6 symmetrical Gaussian bands, the peak positions (ν_i) of which were related to the respective vibronic intervals ($\Delta\nu_{vib}$), as revealed by derivative spectroscopy to minimise an arbitrary choice of fitting parameters. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Despite the extensive use of azo dyes in the textile and paper industry [1], spectroscopic aspects such as the resolution of the corresponding absorption spectra have not found much interest up to now. In contrast to cyanine dyes, azo dyes do not exhibit a detailed vibronic fine structure. This is due to the nature of the chromophoric system, the azo group which is known as a "structure killer". Because of the fact that various electronic transitions occur, which become possible through rotations around the N–C-bond in direct proximity to the chromophor, a detailed vibronic fine structure is consequently blurred [2,3].

It is well known that at low temperatures the spectra become more structured due to the "freezing" of rotational motions [4,5]. However, specific experimental adjustments are necessary for recording absorption spectra at low temperatures. Those difficulties can be circumvented by using derivative spectroscopy to extract in principle the same piece of information just at room temperature. Of advantage is in this respect that by taking the derivatives of the corresponding absorption spectra at the same temperature, wavelength shifts and redistributions of the intensities of the individual sub-bands are excluded. Such effects are commonly observed when measurements at low temperatures are performed because changes in temperature affect both the dielectric constant of the solvent and the energy of the system [4].

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This work has been designed to analyse the absorption spectra of three ionic azo dyes in monomeric state in terms of a simple model based on the assumption of constant peak-to-peak separations, as suggested from the corresponding derivative spectra. In order to avoid a complication of the spectral analysis due to aggregation of the dyestuff molecules, which can occur in solvents such as water and lead to concentration-dependent wavelength shifts [6–8], ethane-1,2-diol was used. In the latter case, the peak positions of both absorption and derivative spectra were found to be independent of concentration, clearly proving a non-aggregating system. Three different azo dyes have been chosen to compare the results of the method applied.

2. Experimental

2.1. Materials

Acid Red 266 (AR) was a gift of Professor G.J.T. Tiddy (University of Salford). The purity was checked via elemental analysis and was found to be 97%. Benzopurpurine 4B (BP) and Congo Red (CR) were purchased from Sigma/Aldrich. The dye content of BP was about 60–65% only and further purification was, therefore, necessary. A detailed description of this procedure is reported elsewhere [9]. Finally, for BP a purity of >95% was found. CR was used as received since the dye content was certified as to be 97%. The spectra of BP and CR (measured in aqueous solution) were found to be in agreement with regard to the respective shape and the molar extinction coefficients tabulated in Ref. [10]. Ethane-1,2-diol (spectroscopic grade) was received from Fluka. Structural formulas of the dyes investigated are shown in Fig. 1.

2.2. Sample preparation

The respective dyes were first dispersed in ethane-1,2-diol and the dispersions were subsequently stirred and heated on a magnetic stirring hot plate. After several hours, the initial turbid dispersions turned into clear solutions. The solutions were allowed to cool down and the concentrations desired were adjusted by dilution. Rectangular cuvettes, type OS (Hellma) with 1 cm path length were used. Prior to each measurement, the cuvettes were prerinsed with the dyestuff solution to be measured. The reference was pure ethane-1,2-diol. Temperature was hold constant at 20 °C throughout all experiments.

2.3. UV/vis spectroscopy

Measurements were performed with an UV/vis/NIR double beam, double monochromator spectrophotometer (Perkin-Elmer). The spectral bandwidth was chosen as 1 nm, the data interval as 1 nm and the recording speed as 60 nm min^{-1}. The Perkin-Elmer software allowed generation of derivatives of various order, based on the method of Savitzky-Golay [11].

3. Results and discussion

3.1. The model

To resolve the spectra measured into the underlying vibrational sub-bands, the corresponding individual peak positions must be known. This can be a quite difficult task, especially in the case of azo dyes the spectra of which are lacking of a detailed vibrational fine structure, as can be seen in Fig. 2.

One method to treat such problems is the subsequent subtraction of “extracted” sub-bands from the remaining spectrum, as described by Perkampus [12]. However, the essential prerequisite for this procedure is that the longest wavelength band is not significantly overlapped by any of the other sub-bands. As it will be demonstrated in the following, this necessary condition for the dyes in the present investigation is not fulfilled (see Fig. 2). A different method to obtain a good guess of the peak positions of overlapping sub-bands, which are hidden under the spectrum recorded, is derivative spectroscopy. However, care has to be taken when applying this method. It is well known that with increasing order of the derivative the noise of the initial spectrum is amplified, giving rise to artificial peaks that might be misinterpreted

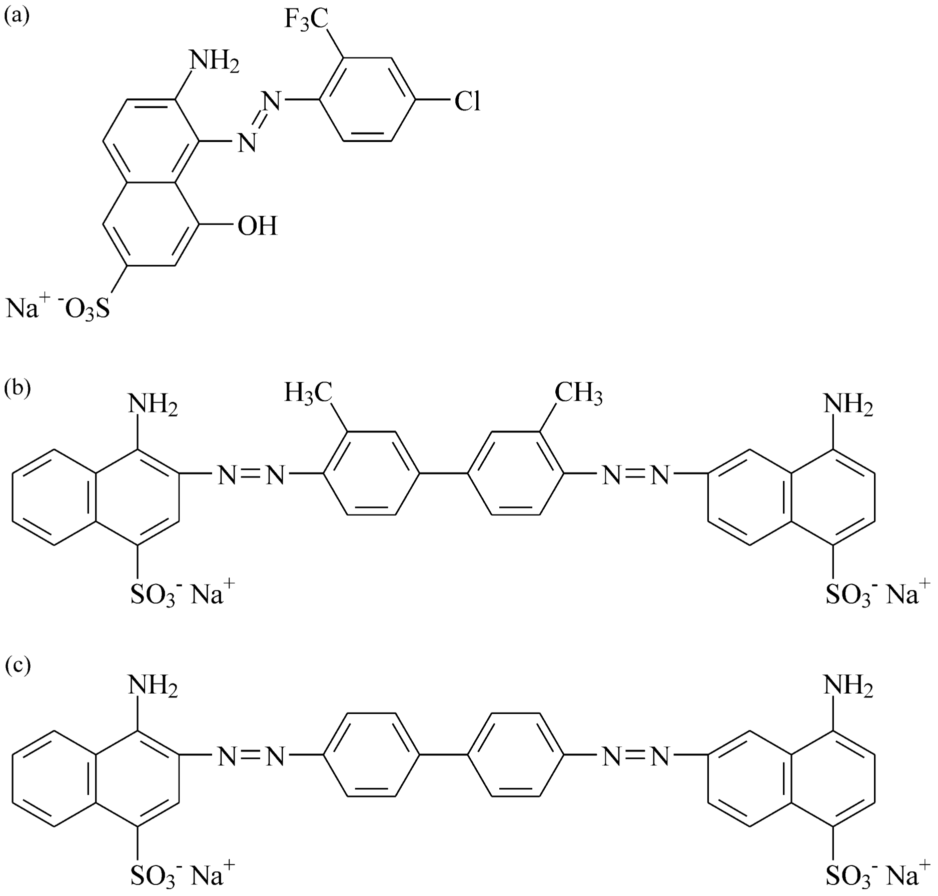

Fig. 1. Structural formulas for AR (a), BP (b) and CR (c).

as belonging to electronic transitions [13]. Unfortunately, in the present case for the azo dyes investigated, the 4th order of derivative had to be applied, as the 2nd one rendered a proper resolution of the sub-bands [14]. Fig. 3 shows that three individual peaks in each spectrum of the respective dyes could be resolved.

For each spectrum, the band spacing of three bands resolved (denoted as 0, 1 and 2 in Fig. 3) was found to be constant within experimental error. The order of magnitude of the peak-to-peak distance is typical of vibronic intervals for organic compounds ($\sim 1400\ \mathrm{cm}^{-1}$; Table 1) [15,16]. This finding strongly supports the idea that those peaks do not represent any artefact due to the derivation.

At the high-energy side of the respective spectra, even the derivatives could not reveal further sub-bands. The use of higher derivatives than that of 4th order were not considered for the aforementioned reasons. Nevertheless, the following approximate procedure appears to be physically more justified than trying to fit the short wavelength side by taking an arbitrary choice of peak positions in order to obtain the highest fit quality. Further band positions in the short wavelength regime ($i \geqslant 3$), denoted as ν_i, were, therefore, simply related to the same vibronic interval, $\Delta\nu_{\mathrm{vib}}$, which was certainly obtained from derivative spectroscopy:

$$\nu_i = \nu_0 + i\Delta\nu_{\mathrm{vib}},\ i = 0, 1, 2, \ldots 5 \tag{1}$$

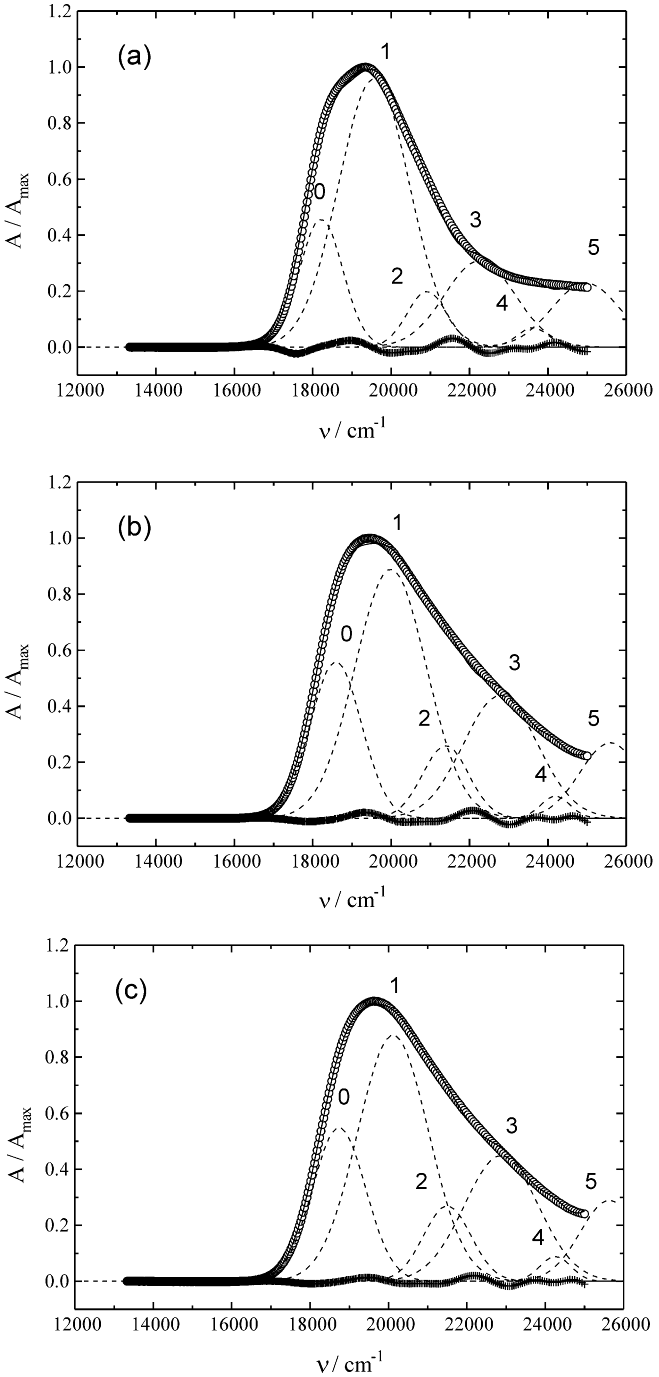

Fig. 2. Normalised absorption spectra (○) of AR (a), BP (b) and CR (c) recorded in ethane-1,2-diol at $T=20$ °C. Dyestuff concentration was 35×10^{-6} mol l^{-1} in each case. The solid line (—) represents the curve fitted according to Eqs. (1) and (2) and the dashed lines (- - - -) correspond to the individual sub-bands resolved. The crosses (+) show the deviations between measured and fitted spectra.

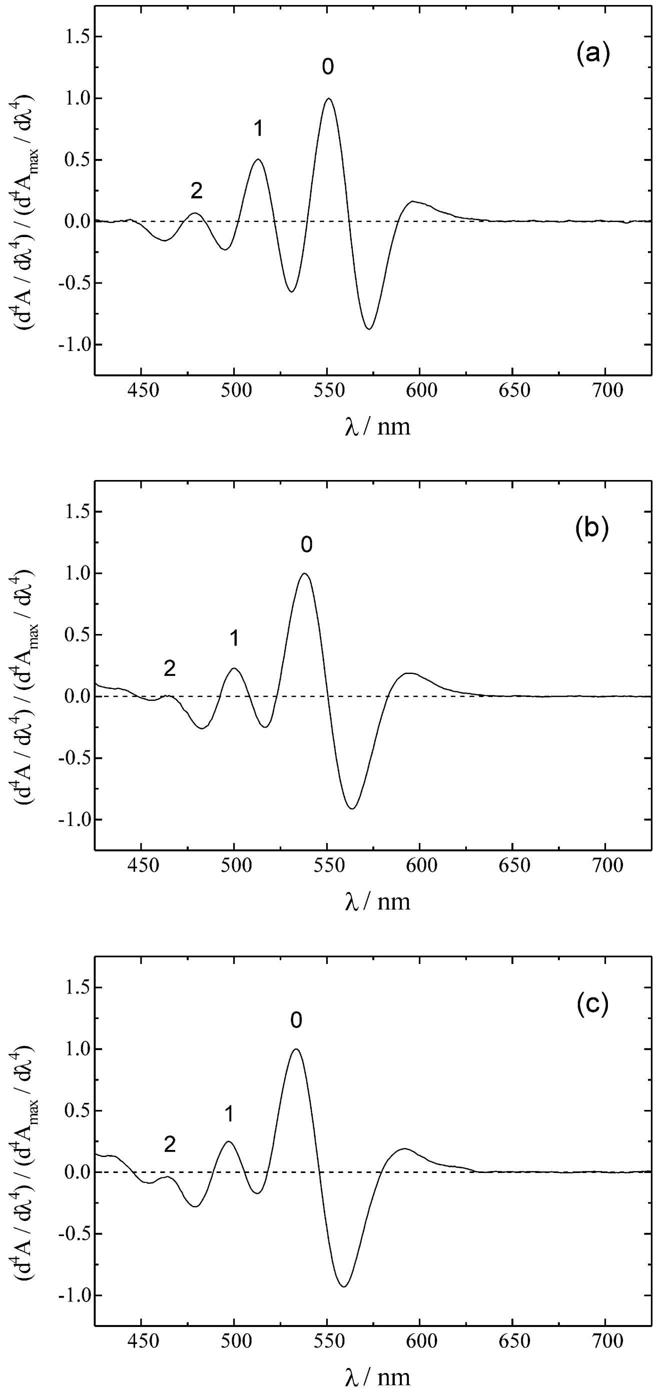

Fig. 3. Normalised derivative spectra of 4th order for AR (a), BP (b) and CR (c) recorded in ethane-1,2-diol at $T = 20$ °C. Dyestuff concentration was 35×10^{-6} mol l^{-1} in each case. Resolved peaks are denoted as 0, 1 and 2.

Table 1
Fit parameters obtained for the normalised absorption spectra of AR, BP and CR according to Eqs. (1) and (2)

Parameter	AR	BP	CR
A_0	0.46	0.56	0.55
A_1	0.96	0.89	0.88
A_2	0.20	0.26	0.27
A_3	0.31	0.44	0.45
A_4	0.07	0.08	0.09
A_5	0.23	0.27	0.29
$\Delta\nu_{0,1/2}/\mathrm{cm}^{-1}$	1290	1530	1590
$\Delta\nu_{1,1/2}/\mathrm{cm}^{-1}$	2130	2150	2130
$\Delta\nu_{2,1/2}/\mathrm{cm}^{-1}$	1190	1380	1420
$\Delta\nu_{3,1/2}/\mathrm{cm}^{-1}$	2110	2220	2210
$\Delta\nu_{4,1/2}/\mathrm{cm}^{-1}$	920	860	910
$\Delta\nu_{5,1/2}/\mathrm{cm}^{-1}$	2030	1820	1760
$\Delta\nu_{\mathrm{vib}}/\mathrm{cm}^{-1}$	1350	1400	1380
χ^2	1.3×10^{-4}	8.2×10^{-5}	4.0×10^{-5}

with ν_0 the band position corresponding to the smallest wavenumber (low-energy side). It should be noted that the numeration of the individual peaks is arbitrary and does not reflect a typical spectroscopic assignment of $0 \rightarrow i$ transitions. The respective smallest wavenumbers (ν_0) are 18,125 cm^{-1} for AR, 18,590 cm^{-1} for BP and 18,740 cm^{-1} for CR. The absorption curves were normalised to allow for a better comparison of the overall shape of the respective spectra. To represent the spectra measured, a sum of 6 symmetrical Gaussian bands was applied:

$$A(\nu)/A_{\max} = \sum_{i=0}^{5} A_{\mathrm{i}} \exp\left[-4\ln(2)(\nu-\nu_i)^2\Delta\nu_{1/2,i}^2\right] \tag{2}$$

Here A, $A_{\max}$ and A_{i} denote the absorbance at wavenumber, ν, at the maximum, $\nu_{\max}$, and at ν_{i}. The half widths (fwhm) of the individual bands are designated as $\Delta\nu_{1/2,i}$.

The number of peaks, 6, was found to give the best fitting results. The differences between the experimental values, $y_{i,\exp} \equiv A(\nu)/A_{\max}$, and the values calculated according to Eqs. (1) and (2), $y_{i,\mathrm{cal}}$, were minimised. The goodness of fit is expressed by the χ^2 value, which is defined below:

$$\chi^2 = \sum_{i}^{n}\left(Y_{i,\exp} - Y_{i,\mathrm{cal}}\right)^2/(n-p) \tag{3}$$

With n the total number of data points (350) and p the number of fitting parameters used (12). The spectra represented by Eqs. (1) and (2) are displayed in Fig. 2. In that figure are also shown the deviations between measured and fitted absorption curves. The largest deviations are around 3% for AR, which are within the overall accuracy of the absorption spectroscopic measurements (~3%), whereas CR shows best agreement, although still above the noise level (< 1%). In any case, each spectrum at the low energy side is well represented, whereas at the high energy side the vibrational fine structure appears to be exaggerated, which is due to the simplicity of the model applied. For the same reason of simplicity and to keep the number of fitting parameters as low as possible, no skewed bands were used, which may fit better the experimentally obtained spectra. However, in the case of different band profiles, the fit quality can be improved, the number of the respective sub-bands can be reduced, but the respective half widths will then increase correspondingly [17], which has to be justified in some way. The present, simple applied model gives quite reasonable values for the half widths, which range from ~900–2000 cm^{-1}. The fitting parameters obtained for all three dyes are listed in Table 1.

4. Conclusions

A semi empirical fitting procedure to resolve the absorption spectra of three azo dyes has been described. It has been shown that the spectra can be represented within an accuracy of $\leqslant 3\%$ by a simple sum of 6 symmetrical Gaussian bands, where the peak positions of the individual bands were related to the respective vibronic intervals, as obtained from derivative spectroscopy. Since the overall band shapes of azo dyes are quite similar, the procedure described appears to be suitable for a greater number of such compounds.

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