JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2005; **18:** 899–900
DOI: 10.1002/poc.961

Rapid Communication

New solvent scale applicable to microheterogeneous media

Stephen N. Batchelor[1]† and John Oakes[2]*

[1]Unilever Research, Quarry Road East, Bebington, Wirral CH63 3JW, UK
[2]John Oakes Associates, Farm Bungalow, Darnhall School Lane, Winsford, Cheshire CW7 1LH, UK

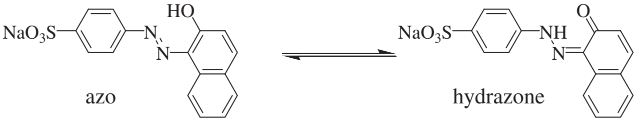
Received 18 March 2005; revised 19 April 2005; accepted 20 April 2005

ABSTRACT: A simple alternative solvent scale is suggested using phenylazonaphthol azo dyes which exhibit azo–hydrazone tautomerism, e.g. Orange II, enabling nanopolarities to be measured by UV–visible spectrophotometry. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: azo-hydrazone; tautomerism; UV–visible spectrophotometry; solvent scale; microheterogeneous; cotton; hydrophilic; hydrophobic

Solvent polarity is a key factor in many chemical reactions.[1] In quantifying solvent effects, the relative permittivity (dielectric constant, ε) of the bulk medium is not a good parameter as it does not always reflect the nanoscale solute–solvent interactions important in chemistry. To provide better solvent scales, a number of empirical parameters have been used, e.g. E_T^N and Z values, based on the solvent-induced shifts in the UV–visible absorption maxima of cationic dyes.[2–4] Although these scales are extremely useful for isotropic solutions, and may function in some materials,[5,6] in many nanostructured environments they can fail simply because the dye spectrum is subject to further, non-polarity-based effects in these situations.[7] For example, within the nanopores of cotton, most dye spectra exhibit small bathochromic band shifts, thought to be due to restricted rotation upon adsorption and adoption of a more planar structure.[7] In such situations, other polarity techniques can be used, such as ESR measurement of the nitrogen hyperfine coupling constant, $a_N(^{15}N)$, of nitroxide spin probes.[8] However, this requires specialist equipment and again fails for adsorbed species, particularly, when immobilization produces solid-state spectra.

A simple alternative solvent scale is suggested here using phenylazonaphthol azo dyes which exhibit azo–hydrazone tautomerism, e.g. Orange II:



The individual tautomers have distinct UV–visible spectra and the position of equilibrium is strongly solvent dependent,[4,9–12] with the the hydrazone tautomer predominating in highly polar media.[11–13] This is illustrated in Fig. 1 for Orange II.

As the polarity of the solvent decreases, the relative size of the shoulder at $\lambda = 430$ nm grows, reflecting an increase in the azo fraction. The azo/hydrazone fraction may be quantified simply by the relative absorption at the λ_{max} of hydrazone tautomer at 480–485 nm to the shoulder at $\lambda = 430$ nm and these values (ϕ) correlate well with the classical solvent parameter, E_T^N, in solution (Fig. 2), such that

$$E_T^N = 1.76 - 1.72\phi \quad R^2 = 0.86 \qquad (1)$$

Measurement of ϕ has a clear advantage that it does not depend critically on the λ_{max} of the azo dye, but is solvent polarity dependent. As a test of the system, the dye was adsorbed into cotton ($\varepsilon = 1.3$) and the UV–visible spectrum was measured by reflectance and is also shown in Fig. 1. The long-wavelength absorption band shows a large shift to higher wavelength, believed to be due to restricted rotation of the dye on adsorption within the cotton nanostructure. This makes measurement of polarity via λ_{max} impossible, but in all other respects the spectrum appears normal and a ϕ value can be easily obtained, which via Eqn (1) converts to an E_T^N of 1,

---

**Correspondence to:* J. Oakes, John Oakes Associates, Farm Bungalow, Darnhall School Lane, Winsford, Cheshire CW7 1LH, UK.
E-mail: John@OakesAssociates.Freeserve.co.uk
†*Correspondence to:* S. N. Batchelor, Unilever Research, Quarry Road East, Bebington, Wirral CH63 3JW, UK.
E-mail: Stephen.Batchelor@Unilever.com

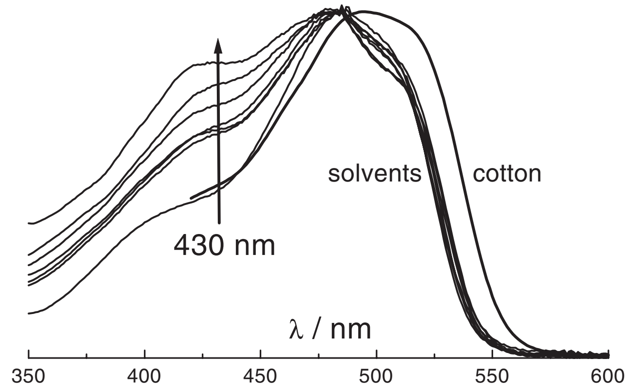


Figure 1. Normalized UV–visible spectra of Orange II in water, ethanol, propan-2-ol, propan-1-ol, acetonitrile, tetrahydofuran and acetone, from bottom to top. The normalized Kubelka–Munk spectrum of Orange II in non-mercerized cotton is indicated

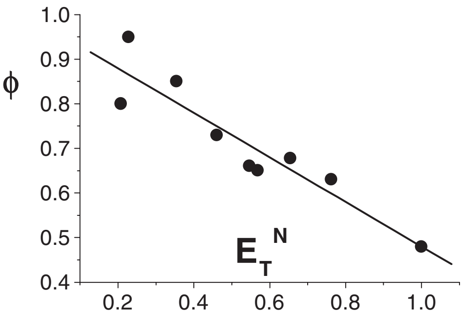


Figure 2. Linear correlation of azo–hydrazone tautomerism parameter ϕ with the normalized solvent parameter E_T^N.[1] Solvents used were water, methanol, ethanol, propan-2-ol, propan-1-ol, acetonitrile, tetrahydofuran, acetone and ethyl acetate

matching water. Previous ESR work on the polarity of the nanopores in cotton[8b,c] showed that species in the bulk of the pores have a polarity similar to that of water, but could not properly assess the polarity of species adsorbed on the walls of the pore. It is most likely that dyes are adsorbed on the walls, and the present results show that under normal humidities these areas are hydrophilic. Cotton under normal humidities contains ~8% of water by weight, all within the nanopores.[14] Hence it is reasonable that these areas are hydrophilic; however, it is notable that the cellulose chains of the amorphous nanopores have no effect in reducing the polarity experienced by the dye. Interestingly, a separate study has suggested the walls are hydrophobic,[15] but this result, based on the cleavage time of a photoexcited ketone, may well have been distorted by restricted rotation effects altering the lifetime.

A powerful feature of using solvent scales based on phenylazonaphthol dyes is that related dye derivatives can be selected to characterize fully the polarity of polysaccharide chains,[7] those of other fabric types,[7] e.g. nylon and polyester, and the microheterogeneous regions of inorganic and biological materials, such as zeolites and proteins.

REFERENCES

1. Reichardt C. *Solvent and Solvent Effects in Organic Chemistry* (3rd edn). Wiley-VCH: Weinheim, 2003.
2. Kosower EM. *J. Am. Chem. Soc.* 1958; **80**: 3253–3260.
3. Reichardt C. In *Molecular Interactions*, vol. 3, Ratajczak H, Orville-Thomas WJ (eds). Wiley: Chichester, 1982; Chapt. 5, 241–282.
4. Zollinger H. *Color Chemistry* (3rd edn). Wiley-VCH: Weinheim, 2003.
5. Reichardt C. *Pure Appl. Chem.* 2004; **76**: 1903–1919.
6. Spange S, Vilsmeier E, Fischer K, Reuter A, Prause S, Zimmermann Y, Schmidt Ch. *Macromol. Rapid Commun.* 2000; **21**: 643–659.
7. Oakes J, Batchelor SN, Dixon S. *Color Technol.* accepted.
8. (a) Knauer BR, Napier JJJ. *J Am Chem Soc*. 1976; **98**: 4395–4400; (b) Batchelor SN. *J. Phys. Chem. B* 1999; **103**: 6700–6703; (c) Scheuermann R, Roduner E, Batchelor SN. *J. Phys. Chem. B* 2001; **105**: 11474–11479.
9. Mustroph H. *Z. Chem.* 1987; **27**: 281–289.
10. Nishimura N, Danjo K, Sueishi Y, Yamamoto S. *Aust. J. Chem.* 1988; **41**: 863–872.
11. Oakes J, Dixon S. *Rev. Prog. Color* 2004; **30**: 110–128.
12. Abbott LC, Batchelor SN, Gilbert BC, Oakes J, Whitwood AC, Lindsay Smith JR, Moore JN. *J. Phys. Chem. A* 2005; **109**: 2894–2905.
13. Oakes J, Gratton P. *Color Technol.* 2003; **119**: 91–99.
14. Krässig HA. In *Cellulose*. Gordon Breach: Amsterdam, 1993.
15. Batchelor SN, Shushin AI. *Appl. Magn. Reson.* 2002; **22**: 47–60.