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Short Communication

Dimroth's $E_T(30)$ as parameters of solvent polarity: a caveat

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In 1963 Dimroth *et al.* [1] pointed out that the electronic transition energies E_T (now popularly known as $E_T(30)$ parameters) defined by

$$E_T \text{ (kcal mol}^{-1}) = hc\bar{\nu}N$$
$$= 2.859 \times 10^{-3}\bar{\nu} \text{ (cm}^{-1}) \tag{1}$$

can be used as empirical parameters of solvent polarity. In eqn. (1), h, c and N stand for Planck's constant, the velocity of light and Avogadro's number respectively, and $\bar{\nu}$ represents either $\bar{\nu}_a$ (the frequency of the absorption maximum) or $\bar{\nu}_e$ (the frequency of the emission maximum). Extensive lists of $E_T(30)$ parameters of solvents are available [2]. These parameters were obtained by using a solvatochromic dye, pyridiniophenolate (P), as a standard and by determining its $\bar{\nu}_a$ in a series of solvent media. Today, utility of $E_T(30)$ parameters to interpret the environmental effects of solvents on the photophysical properties of dyes is a popular practice [3 - 5].

It is the purpose of this note to caution against the use of listed values of $E_T(30)$ parameters. In cases involving dyes other than P, it cannot be assumed that $\bar{\nu}_a$ (or $\bar{\nu}_e$) is independent of the chemical nature of the dye molecules. Given this, any use of $E_T(30)$ parameters to establish correlations for other dyes becomes questionable. To demonstrate this, let us consider two dyes P and Q which in their excited states, P* and Q*, behave differently with respect to their interactions with the surrounding medium, *e.g.* a polar solvent. We further require that P* strongly interacts (*e.g.* via electrostatic interactions) with the solvent while Q* does not. This allows the identification of P with dyes such as 2,6-diphenyl-4,2-(2,4,6-triphenyl-1-pyridinio-phenolate) which has been used to derive extensive tables of $E_T(30)$ parameters and of Q with molecules such as 3-(α-naphthyl)benzo[*b*]thiophen whose emission maxima in a number of solvents have been correlated by Lablache-Combier *et al.* [3] to the $E_T(30)$ parameters. Let us now consider another dye, R, which in its excited state behaves as P*. An example of such a dye is *N,N*-dimethyl-6-[(4-methylphenyl)amino]-2-naphthalenesulfona-mide. Emission maxima $\bar{\nu}$ of P, Q and R in a number of polar solvents

TABLE 1

Transition energies and the frequencies corresponding to the emission maxima of P, Q and R in different solvents

Solvent	$\bar{\nu}_P \times 10^{-4}$ [a] (cm^{-1})	$\bar{\nu}_Q \times 10^{-4}$ [b] (cm^{-1})	$\bar{\nu}_R \times 10^{-4}$ [c] (cm^{-1})	$E_T(30)$ (kcal mol^{-1})
1,2,3-propanetriol	1.994	2.721	—	57.0
1,2-ethanediol	1.969	2.701	—	56.3
Methanol	1.941	2.755	1.931	55.5
Ethanol	1.815	2.755	2.022	51.9
1-propanol	1.773	2.801	2.050	50.7
1-butanol	1.756	2.799	2.081	50.2
1-pentanol	1.773	2.774	2.090	50.7
2-propanol	1.700	2.809	—	48.6
Cyclohexanol	1.641	2.728	—	46.9
2-pentanol	1.626	2.745	—	46.5
1-hexanol	—	—	2.134	48.8
1-octanol	—	—	2.169	48.3
1-decanol	—	—	2.193	47.6
1-dodecanol	—	—	2.214	46.7

[a] From ref. 2.
[b] From ref. 3.
[c] From ref. 6.

together with $E_T(30)$ solvent polarity parameters are given in Table 1 and a plot of $\bar{\nu}$ versus $E_T(30)$ is given in Fig. 1. The absolute values of the slope $|m|$ of the $\bar{\nu}$ versus $E_T(30)$ plot are 3.5×10^2 cm^{-1} mol kcal^{-1}, 0.00 cm^{-1} mol kcal^{-1} and 3.3×10^2 cm^{-1} mol kcal^{-1} for P, Q and R respectively.

Clearly, should one wish to extend the utility of $E_T(30)$ parameters of dye P to another dye Z, then the criterion of this applicability is
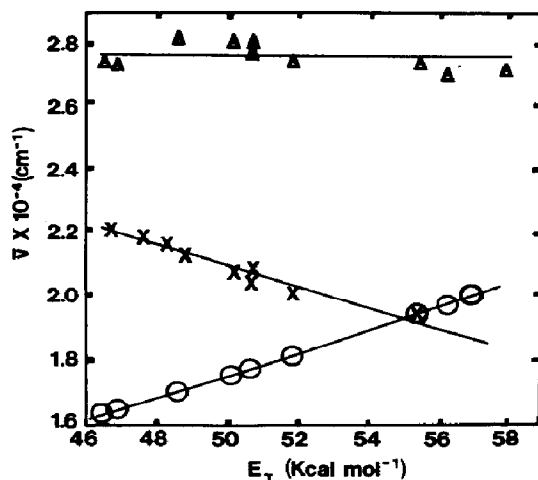

Fig. 1. Shifts in emission maxima of P (○), Q (△) and R (×) plotted against the $E_T(30)$ solvent parameters.

$$|m_{\mathrm{P}}| = |m_{\mathrm{Z}}|$$

It is now worth noting that for $Z \equiv Q$, $|m_{\mathrm{P}}| \neq |m_{\mathrm{Q}}|$. However, for $Z \equiv R$, the equality $|m_{\mathrm{P}}| = |m_{\mathrm{R}}|$ firmly holds.

From the foregoing, we conclude that $E_{\mathrm{T}}(30)$ parameters have their meanings only for dyes which in their excited states interact with the solvent medium as P^* does and that the utility of $E_{\mathrm{T}}(30)$ parameters cannot be extended to other dyes of different chemical nature.

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