

Short Communication

About Dimroth's $E_T(30)$ solvent parameter

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An article was published recently in relation to the misuse of Dimroth's $E_T(30)$ parameter of solvent polarity in the interpretation of emission spectral data [1]. This parameter was originally defined for the absorption maximum of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (P) [2] and a recent publication by Reichardt and Harbusch-Görnert [3] in which the $E_T(30)$ solvent polarity scale was enlarged does not consider emission at all. However, the reported $\bar{\nu}_p$ values [1] actually correspond to transition energies of absorption maxima. Moreover, in the literature there are several correlations between $E_T(30)$ and the frequencies of emission maxima for other substances [4]. The example of the dyes P, Q (3-(α -naphthyl)benzo[*b*]-thiophen) and R (*N,N*-dimethyl-6-[(4-methylphenyl)amino]-2-naphthalene-sulfonamide) is unfortunate because the emission of P* must be accompanied by a great increase in its dipole moment [5], whereas the emission of Q* [6] and R* [7] from their charge transfer excited states gives the corresponding singlet ground states which are certainly much less polar than the former states. The criterion of applicability of the $E_T(30)$ parameter would be such that the absolute slope $|m|$ of the $\bar{\nu}$ versus $E_T(30)$ plot for a dye X must be consistent with the equality $|m_X| = |m_P|$ [1]. One must reject this proposition for the following reasons.

(1) The fulfilment of the condition $|m_P| = |m_R|$ is coincidental because the line corresponding to P refers to absorption solvent shifts which are not necessarily correlated in any simple way with the emission solvent shifts [8].

(2) If we consider the emission frequency of the dye Q as a function of $E_T(30)$ in alcoholic solvents then the behaviour is indeed very irregular [1]. Moreover, Lablache-Combier *et al.* [6] found that the slope of the $(\bar{\nu}_a - \bar{\nu}_e)$ versus $E_T(30)$ line is small but not zero. It was claimed that the absorption maximum of Q has no solvent dependence; if this is so the slopes of the plots of $(\bar{\nu}_a - \bar{\nu}_e)$ and $\bar{\nu}_e$ versus $E_T(30)$ must be equal. As a matter of fact, the least-squares regression line corresponding to Q in the plot of $\bar{\nu}_e$ versus $E_T(30)$ [1] has a slope of $-42.5 \pm 30.3 \text{ cm}^{-1} \text{ mol kcal}^{-1}$, but the variables $\bar{\nu}_e$ and $E_T(30)$ are hardly correlated at all ($r = -0.443$, $n = 10$; for 1-pentanol

the correct E_T value of 49.1 kcal mol⁻¹ was used instead of 50.7 kcal mol⁻¹). Therefore, the dye Q must also be rejected as a true example of dependence between $\bar{\nu}_e$ and $E_T(30)$.

(3) It is clear that both $\bar{\nu}_a$ and $\bar{\nu}_e$ depend on the electronic nature of the dye [1], but for two closely related dyes one can hardly expect to find exactly the same relationship between $\bar{\nu}_e$ and $E_T(30)$ because the variation of $\bar{\nu}_e$ with environment depends in a complex way on the overall dynamics of the solute-solvent system [9].

Of course, in many cases the $E_T(30)$ parameter may prove inapplicable, but there is statistical evidence, from numerous correlations of $E_T(30)$ with spectroscopic data [4, 10], of the general reliability of the $E_T(30)$ solvent scale as a measure of solute-solvent interactions of solute molecules (not necessarily dyes) in their ground states or even their excited states.

To take just one case from another related field, chemical kinetics data have also been correlated with E_T [11]. It is obvious that the absorption process of the P dye from the ground state to the Franck-Condon excited state is difficult to relate to a chemical reaction in which the transition state is assumed to be in equilibrium with the reactants and therefore with the solvent. Nevertheless, this last point is very controversial [12].

We conclude that a solvent parameter such as $E_T(30)$ can be rigorously used to interpret a phenomenon when the latter is directly related to the physicochemical model process which defines the parameter, *i.e.* the existence of a good correlation is helpful because of the possible underlying relationship; clearly one can reject an interpretation which is entirely based on this correlation alone.

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