ELSEVIER

Thermochimica Acta 328 (1999) 155–159

thermochimica acta

Calorimetric evidence of aggregation of the $E_T(30)$ dye in alcoholic solutions

Clodoaldo Machado[a,*], Maria da Graça Nascimento[b], Marcos Caroli Rezende[c], Anthony E. Beezer[d]

[a]*Departamento de Química, Universidade Regional de Blumenau, FURB, Blumenau CEP 89010971, Brazil*
[b]*Departamento de Química, Universidade Federal de Santa Catarina, UFSC, Florianópolis CEP 88040900, Brazil*
[c]*Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, Correo 33, Chile*
[d]*Chemical Laboratory, University of Kent, Canterbury CT2 7NH, UK*

Accepted 2 October 1998

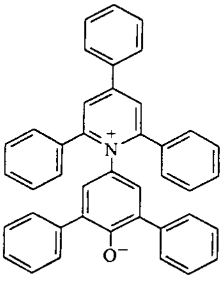
Abstract

This paper deals with the thermodynamic aspects of solvatochromic and halochromic systems. Enthalpic measurements of dilution of solutions of the $E_T(30)$ dye in various alcohols and in the presence of increasing concentrations of sodium iodide were carried out by means of calorimetric techniques. Contrary to observations based on purely spectroscopic methods, these calorimetric measurements showed evidences of dye aggregation in solution. In addition, the results confirmed the existence of previously described dye–cation associations in the organic media.

Keywords: Solvatochromism; Halochromism; Dyes; Calorimetry

1. Introduction

In their search for ways of measuring the polarity of solvents, chemists have resorted, among others, to kinetic [1] and spectroscopic techniques [2–7]. Several solvatochromic dyes have been employed to build polarity scales. One of the most widely used compounds among them is Reichardt's pyridiniophenolate (1); the basis of the $E_T(30)$ polarity scale [5–7].



1

The high sensitivity of its charge-transfer band in the visible to environmental changes has allowed the measurement of the polarity of various media, such as pure solvents [5–7], binary solvent mixtures [8–13] and electrolyte solutions [14–16]. The spectroscopic changes observed in the latter media were taken as a measure of the halochromic behaviour of dye (1) and of related systems [17–19], and were accounted for in terms of dye–salt associations in solution [20,21].

Despite the considerable interest in the behaviour and uses of solvatochromic dyes in solution, the thermodynamic aspects of these systems remain still largely unexplored. Such studies, carried out through the use of calorimetric techniques, might shed light on phenomena which have been interpreted solely through spectroscopic observations. As an example, dye aggregation in solution has been detected sometimes through spectral changes, in which the aggregates tend to absorb at different wavelengths from the monomeric dye [22,23]. This, however, is not general.

---

*Corresponding author.

PII: S0040-6031(98)00636-4

Solutions of the $E_T(30)$ dye, for example, tend to follow Beer's law for various dilutions; an indication that the dye does not aggregate in such media. Calorimetric measurements of dilution enthalpies in organic solutions of the $E_T(30)$ dye should provide an independent way of verifying this assumption.

Calorimeters have been used before for measuring solute–solvent interactions as a means of establishing polarity scales: Gutmann proposed the donor number (DN), based on the enthalpy of interaction of $SbCl_5$ with the solvent [24]. More recently, the acidity of organic solvents was measured making use of the same technique [25]. The good correlation generally observed between thermodynamic properties and intermolecular forces in solution [26] gave further support to our idea of applying a calorimetric technique to the study of solvatochromic and halochromic systems.

In the present paper we report the use of a microcalorimeter to obtain enthalpies of dilution of the widely employed $E_T(30)$ dye in a series of aliphatic alcohols and in the presence of increasing amounts of added sodium iodide. The results are discussed in terms of dye–cation (halochromism) and dye–solvent interactions (solvatochromism), investigating the possibility of associations in solution.

2. Experimental

A Hewlett Packard 8452A spectrophotometer was used to obtain the UV–Vis spectra.

Calorimetric measurements were performed with a TAM thermometric microcalorimeter, equipped with stainless steel ampoules and an LKB 2277-401/402 titration unit.

Solvents, of HPLC grade, and the $E_T(30)$ dye, were purchased from Aldrich. Sodium iodide (Fisons) was dried under vacuum before use.

All calorimetric experiments were performed isothermally at 298.15 K. The calorimeter was calibrated using the electrical substitution method before each batch of experiments was performed. Two hours equilibration was allowed between loading the ampoules and starting data collection.

For the $E_T(30)$ dilution measurements, two experiments were carried out, the first one by successive additions of a concentrated solution of the dye to the solvent, and the second by adding the pure solvent to a solution of the dye. In the first experiment, 10 μl of a 10^{-3} mol dm^{-3} solution of the dye were successively added to an initial volume of 100 μl of the solvent. In the second experiment, 10 μl of the solvent were successively added to an initial volume of 100 μl of 5×10^{-4} mol dm^{-3} solution of the $E_T(30)$ dye. These volumes were chosen so as to achieve final concentrations in the same range as those commonly used in spectroscopic studies. The collected data of power versus time were converted into ASC II files and analysed with the help of Origin 3.0 software (Microcal, Amherst, MI, USA).

For the calorimetric measurements of dye–cation association, 10 μl of a 1.0 mol dm^{-3} alcoholic solution of sodium iodide were successively injected into 100 μl of an $E_T(30)$ solution in the same solvent, with an initial concentration of 5.0×10^{-4} mol dm^{-3}.

3. Results and discussion

The enthalpies of dilution of the $E_T(30)$ dye were measured in a series of primary alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol) and in two secondary alcohols (2-propanol and 2-butanol). The enthalpies of sodium iodide–$E_T(30)$ association were evaluated in three different media, ethanol, 1-propanol and 1-butanol.

In order to obtain these enthalpies, five different experiments were performed, as shown below.

	Successive 10 μl injections of	*Into 100 μl of*
1	Pure solvent	Pure solvent
2	$E_T(30)$ dye solution	Pure solvent
3	Pure solvent	$E_T(30)$ dye solution
4	NaI solution	Pure solvent
5	NaI solution	$E_T(30)$ dye solution

Subtraction of the heats of the blank experiment 1 from the heats of experiments 2 or 3 gave the enthalpies of dilution of the $E_T(30)$ dye in all solvents, $H_2 - H_1$ and $H_3 - H_1$, which are shown as a function of the dye concentration in Figs. 1 and 2, respectively.

In order to obtain the dye–salt association enthalpy, the heats of NaI (experiment 4) and of $E_T(30)$ dilution (experiment 3), besides the blank heats of experiment

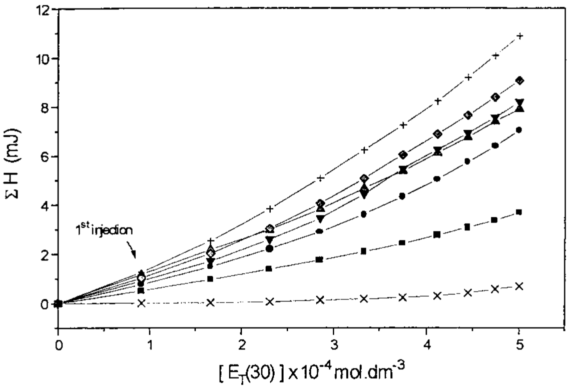


Fig. 1. Enthalpies of dilution of the $E_T(30)$ dye in primary alcohols. Measurements were performed by injecting a concentrated solution of the dye (1.0×10^{-3} mol dm^{-3}) into the pure solvent: × ethanol; ■ 1-propanol; ● 1-butanol; ▲ 1-pentanol; ▼ 1-hexanol; ◆ 1-heptanol; + 1-octanol.

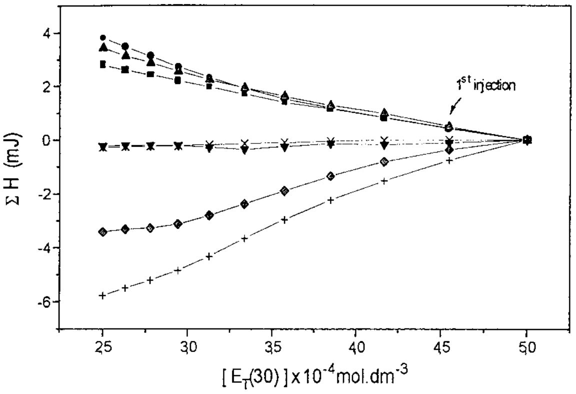


Fig. 2. Enthalpies of dilution of the $E_T(30)$ dye in primary alcohols. Measurements were performed by adding small volumes of the solvent to a solution of the dye with an initial concentration of 5.0×10^{-4} mol dm^{-3}. × ethanol; ■ 1-propanol; ● 1-butanol; ▲ 1-pentanol; ▼ 1-hexanol; ◆ 1-heptanol; + 1-octanol.

1, had to be subtracted from the composite heats of experiment 5. These dye–salt association enthalpies in different alcohols were then obtained as $H_5 - (H_4 + H_3 + H_1)$, and are shown in Fig. 3 as a function of the salt concentration.

The $E_T(30)$ dye molecule is a zwitterion with a very high dipole moment, increasingly solvated in more polar media. Such solvation arises from attractive dipole–dipole interactions and, in an alcoholic medium, from hydrogen bonding with the solvent, and these are all exothermic processes.

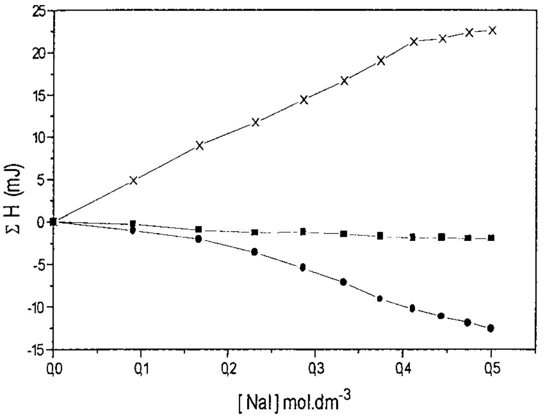


Fig. 3. Enthalpies of $E_T(30)$/NaI interaction in × ethanol, ■ 1-propanol and ● 1-butanol as a function of the concentration of added sodium iodide. The initial dye concentration was 5.0×10^{-4} mol dm^{-3}.

Addition of successive amounts of the monomeric dye to an alcohol, with more solvent molecules available for solvation, should lead to modest exothermic processes. The resulting negative enthalpies would be expected to increase in absolute value with the increasing polarity of the solvent. The observed trends of Fig. 1 are at variance with these expectations.

With the exception of ethanol, in all other alcohols endothermic processes were observed, with enthalpies increasing with decreasing polarity of the solvent. Clearly this implies a bond-breaking process should be operating here, a fact which is difficult to reconcile with the assumption that the dye existed as monomeric species in the more concentrated (10^{-3} mol dm^{-3}), injected samples. On the contrary, dye aggregation should increase with the decrease in polarity of the medium, leading to greater endothermic bond-breaking in less polar solvents, as the dye is two to ten-fold diluted. This interpretation is in agreement with the trends of Fig. 1, which, therefore, suggests $E_T(30)$ aggregation in most alcohols in this range of concentrations. However, the enthalpy of dilution is the balance of the following processes: dye–dye, dye–solvent and solvent–solvent interactions. The sign of the overall enthalpy, positive as reported here, will depend on the relative magnitudes of these interactions. Thus endothermicity is not a necessary condition for indicating aggregation although it is highly suggestive of such a phenomenon. However, the deviations shown for the dilution processes as displayed in Fig. 1 are confirmatory evidence for aggregation since the data indicate that the final state of the dilution process depends upon the dye concentration. Aggregation could be weak since the enthalpies are small and could possibly be the result of overlap of dye solvation shells because of charge effects – this could account for the larger effects being observed for lower dielectric constant solvents.

In the alternative dilution experiment, the data for which is shown in Fig. 2, increasing amounts of the solvent were gradually added to a solution of the dye. Dilution processes were increasingly endothermic with increase in the alcohol chain length, as observed in Fig. 1. However, beyond 1-butanol, the reverse trend was observed, the dilution enthalpies becoming smaller and eventually even negative for the larger alcohols (1-heptanol and 1-octanol). This reversal in solvent behaviour points to an interplay of opposing effects. In the experiment of Fig. 1, a sudden ten-fold dilution of the aggregated dye made the heat of bond-breaking the major enthalpic contribution to the overall process. In the gradual dilution of Fig. 2, the aggregate-bond-breaking process competes with the exothermic dilution of the aggregate by the added solvent. We may write for the total observed enthalpy $H_{\mathrm{obs}} = H_{\mathrm{diss.agg.}} + H_{\mathrm{dil.agg.}}$, where $H_{\mathrm{diss.agg.}}$ is the positive enthalpy of aggregate dissociation and $H_{\mathrm{dil.agg.}}$ is the negative enthalpy of aggregate dilution. The term $H_{\mathrm{diss.agg.}}$ depends on the size and number of aggregates in solution, and of the dissociating power of the solvent. The former increases with the decreasing polarity of the solvent, while the dissociating power of the medium becomes smaller in less polar alcohols. The change observed for 1-pentanol is a consequence that, for larger alcohols, there is an increasing tendency of the new solvating molecules to dilute the aggregates, instead of breaking them.

The enthalpies of dilution in 1-hexanol were close to zero. This indicates that in this solvent the opposing enthalpic contributions nearly cancel each other. The small values of enthalpy in ethanol reflect the fact that in this polar solvent there is little dye aggregation.

The trends of Fig. 2 were confirmed in a comparison between two secondary alcohols, 2-propanol and 2-butanol. In the former, the enthalpy values were close to zero, while in 2-butanol there was a small ($\Sigma H = -1.5$ mJ after ten injections) exothermic process. Secondary alcohols are less polar than primary alcohols with the same number of carbons, it is thus reasonable that the behaviour in 2-propanol ($\mathrm{E_T}(30) = 48.4$ kcal mol^{-1}: here the assignment of the polarity scale measure is that of Reichardt [5–7]) differed from 1-propanol ($\mathrm{E_T}(30) = 50.7$ kcal mol^{-1}), approaching that in 1-hexanol ($\mathrm{E_T}(30) = 48.8$ kcal mol^{-1}). In the less polar 2-butanol ($\mathrm{E_T}(30) = 47.1$ kcal mol^{-1}), the small negative enthalpy is an indication that aggregate dilution is slightly favoured over dissociation upon addition of the solvent.

The above suggestions of dye aggregation in alcoholic $\mathrm{E_T}(30)$ solutions depart from the hitherto accepted view that this compound does not form aggregates in organic media. We had in fact investigated the spectral behaviour of dilute solutions of this dye in methanol and chloroform, in concentration ranges that yielded absorbance readings in the UV region not larger than 1.0 for the most intense absorption (concentrations smaller than 2.5×10^{-5} mol dm^{-3}). The good linearity of the plots of A versus dye concentration (graphs not shown) confirmed the view that, in this range of concentration, the Lambert–Beer law was obeyed and the dye did not aggregate. However, the investigated concentrations were much smaller than those commonly utilised in solvatochromic measurements. Our calorimetric results, obtained with these more concentrated solutions, may, therefore, be reconciled with the existing spectroscopic evidence. In addition, preliminary measurements of diffusion coefficients of the $\mathrm{E_T}(30)$ dye in alcohols [27], support the present contention that this dye forms aggregates in these media.

We were also interested in measuring the enthalpies of dye–salt association in various alcoholic $\mathrm{E_T}(30)$ solutions containing sodium iodide. Direct association between the electrolyte cation and the phenoxide fragment of the $\mathrm{E_T}(30)$ and related dyes has been held responsible for their halochromism [14–21].

Fig. 3 depicts the enthalpies of $\mathrm{E_T}(30)$–NaI association in three primary alcohols, as a function of the concentration of the added electrolyte. This is an endothermic process in ethanol, in agreement with the fact that, in this polar solvent, the dye is strongly solvated by hydrogen bonding with the solvent. Formation of the dye–cation pair requires breaking these bonds in an enthalpically unfavourable process. As the solvent becomes less polar, dye–solvent interactions through hydrogen-bonding become weaker, and the exothermic dye–cation association enthalpies cancel (as in 1-propanol) or even take over the former effect, as can be seen for 1-butanol. These trends are in full agreement with previous interpretations of the halochromic behaviour of the $E_T(30)$ and related dyes, based on spectroscopic evidence. The enthalpies of interaction are again small and are, for example, on the order of 0.5 kJ mol^{-1} in ethanol.

In conclusion, the results presented in this paper point to the existence of aggregated species in various alcoholic solutions of the $E_T(30)$ dye, in concentrations greater than 2×10^{-4} mol dm^{-3}. Because of the different range of studied concentrations, this conclusion may be reconciled with seemingly conflicting spectroscopic evidence that this dye does not aggregate in solution. The calorimetric measurements of the enthalpy of dye–salt interaction in $E_T(30)$/NaI alcoholic solutions were in agreement with previous interpretations of the halochromic behaviour of this and related systems [17–19].

Acknowledgements

C.M. thanks the Brazilian CNPq and CAPES research foundation for financial support.

References

[1] E. Grunwald, S. Winstein, J. Am. Chem. Soc. 70 (1948) 846–854.
[2] E.M. Kosower, J. Am. Chem. Soc. 80 (1958) 3253–3260.
[3] E.M. Kosower, J. Am. Chem. Soc. 80 (1958) 3261–3267.
[4] E.M. Kosower, J. Am. Chem. Soc. 80 (1958) 3267–3270.
[5] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 2nd ed., Chap. 7, Weinheim, 1988.
[6] C. Reichardt, Chem. Rev. 94 (1994) 2319–2358.
[7] C. Reichardt, G. Schaefer, Liebigs Ann. (1995) 1579–1582.
[8] C.B. Ramirez, N. Carrasco, M.C. Rezende, J. Chem. Soc., Faraday Trans. 91 (1995) 3839–3842.
[9] M. Rosés, C. Ràfols, J. Ortega, E. Bosch, J. Chem. Soc., Perkin Trans. 2 (1995) 1607–1615.
[10] J. Ortega, C. Ràfols, E. Bosch, M. Rosés, J. Chem. Soc., Perkin Trans. 2 (1996) 1497–1503.
[11] P.C. Liu, S. Hoz, E. Buncel, Gazz. Chim. Ital. 126 (1996) 31–35.
[12] L.P. Novaki, O.A. El Seoud, Ber. Bunsenges. Phys. Chem. 101 (1997) 105–113.
[13] V.G. Machado, C. Machado, M.G. Nascimento, M.C. Rezende, J. Phys. Org. Chem. 10 (1997) 731–736.
[14] M.C. Rezende, C. Zucco, D. Zanette, Tetrahedron 41 (1985) 87–92.
[15] C. Reichardt, S. Asharin-Fard, G. Schaefer, Chem. Ber. 126 (1993) 143–147.
[16] C.-H. Wunderlich, G. Bergerhoff, Chem. Ber. 127 (1994) 1185–1190.
[17] V.G. Machado, M. Aillon, M.C. Rezende, J. Chem. Soc., Faraday Trans. 88 (1992) 201–204.
[18] S.P. Zanotto, M. Scremin, C. Machado, M.C. Rezende, J. Phys. Org. Chem. 6 (1993) 637–641.
[19] C. Machado, M.G. Nascimento, M.C. Rezende, J. Chem. Soc., Perkin Trans. 2 (1994) 2539–2544.
[20] R.J. Lavallee, M.B. Zimmt, J. Phys. Chem. 98 (1994) 4254–4260.
[21] D.A. Binder, M.M. Kreevoy, J. Phys. Chem. 98 (1994) 10008–10016.
[22] M. Niedbalska, I. Gruda, Can. J. Chem. 68 (1990) 691–695.
[23] H. Sato, A. Matsuzaki, S. Nishio, M. Yoshimi, K. Yamamoto, H. Tomioka, Chem. Lett. (1996) 715–716.
[24] V. Gutmann, E. Wychera, Inorg. Nucl. Chem. Lett. 2 (1966) 257.
[25] J. Catalán, A. Couto, J. Gomez, J.L. Saiz, J. Laynez, J. Chem. Soc., Perkin Trans. 2 (1992) 1181–1185.
[26] M.S. Westell, M.S. Searle, D.J. Wales, D.H. Williams, J. Am. Chem. Soc. 117 (1995) 5013–5015.
[27] C. Machado, A.E. Beezer, M.G. Nascimento, M.C. Rezende, unpublished results.