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Influence of Fluorine-containing Substituents on the Energy of Intermolecular Interactions and the Heat of Evaporation of Disperse Azo Dyes

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SUMMARY

The heats of evaporation of some fluorine-containing disperse azo dyes have been determined by electronic absorption spectroscopy. The introduction of fluorine or fluorine-containing substituents into azo dye molecules decreases the energy of intermolecular interactions and correspondingly the heat of evaporation of dyes by 10–40 kJ mol^{-1} as compared with dyes without fluorine. Such dyes may therefore be recommended for gas-phase methods of dyeing and printing. The energy of orientation–induction interactions is the main contribution to the heat of evaporation.

1. INTRODUCTION

The influence of fluorine-containing substituents on colour and other characteristics of disperse azo dyes has been studied systematically.[1–3] A number of the dyes possess high fastness to light and wet treatment on polyester but in some cases sublimation fastness is low. The latter is especially important for dyes for gas-phase methods of dyeing and printing. The dyes for transfer printing should be readily sublimed at 150–220 °C while having good affinity for the substrate. In this connection

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the heats of evaporation of some fluorine-containing azo dyes have been determined by spectral methods.

Based on the spectral characteristics obtained in different media the contributions of disperse and orientation–induction forces to a general energy of intermolecular interaction have been calculated. This energy determines the heat of evaporation. The method has been used for investigating certain disperse dyes of the anthraquinone and azobenzene types.[4–6]

2. THEORY

The gas-phase dyeing process depends upon dye sublimation with subsequent adsorption in the polymer. These processes proceed by both universal and specific intramolecular interactions. Spectral methods provide one approach to the determination of the energy and character of intramolecular interactions.

According to the theory of universal intermolecular interactions (this theory has been worked out by Bakhshiev[7] on the basis of the Onsager–Böttcher theory) the general expression for the shift of the molecular electronic band absorption ($\Delta\nu$) at a vapour–solution phase transition is as follows.

$$hc\,\Delta\nu = \frac{2n^2+1}{n^2+2}\left[C_1\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+C_2\frac{n^2+1}{n^2+2}\right] + C_3\frac{n^2-1}{n^2+2}+C_4\frac{n^2-1}{2n^2+1} \tag{1}$$

In eqn. (1), h is Planck's constant, n is the refractive index, ε is the solvent dielectric permeability and

$$C_1 = \frac{2\mu_g(\mu_g-\mu_e\cos\varphi)}{a^3} \tag{1a}$$

$$C_2 = \frac{\mu_g^2-\mu_e^2}{a^3} \tag{1b}$$

$$C_3 = \frac{3}{2}\left(\frac{\alpha_g-\alpha_e}{a^3}\right)\cdot\frac{II_1}{I+I_1} \tag{1c}$$

$$C_4 = \frac{e^2hF}{m8\pi^2\tilde{\nu}_e a^3} \tag{1d}$$

in which a is the radius of the Onsager hole; α_g and α_e are the polarisabilities of the solute molecules in ground and excited states; I and I_1 are the ionisation potentials of the solute and solvent respectively; μ_g and μ_e are the dipole moments of the solute molecules in the ground and excited states; φ is the angle between the vectors of the dipole moments in the ground and excited states; e, m are the electron charge and mass; f is the oscillator force; $\tilde{\nu}_e$ is the frequency of the only electron transition; F is the Faraday constant.

In order to make comparisons with experimental results eqn (1) is modified:

$$hc\,\Delta\nu = C_1\left[\frac{2n^2+1}{2n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+P_1\frac{n^2-1}{n^2+2}\right] \qquad (2)$$

in which

$$P_1 = \frac{C_2 + C_3 + C_4}{C_1}$$

This equation permits the estimation of the terms for the general energy of intermolecular interactions: the dispersion energy as a function of refractive index and the orientational–inductive energy as a function of dielectric permeability and refractive index.

Dispersion and orientational–inductive interactions (calculated by eqns (1) and (2)) include the ground and excited states of the molecule. Therefore another characteristic of the orientational–inductive interactions was measured and calculated—structural parameter μ^2/a^3 (μ = dipole moment, a = molecule radius). This parameter is measured by the shift of the band absorption in a two-component solvent and it depends on the concentration of the solvating component.[8] In this case this parameter is characterised only by the ground molecule state.

3. RESULTS AND DISCUSSION

Disperse azo dyes with fluorine-containing substituents in the side chain of the coupling component (R_2, compounds **4–7**) and in the *p*-position of the diazo component (R_1, compounds **8–13**) were selected for the investigation. Azo dyes without fluorine (compounds **1–3**) were also used for comparison of physicochemical properties. The main experimental results are shown in Table 1.

TABLE 1

Energy of Intermolecular Interactions (ΔE) and Heat of Evaporation (ΔH_{evap}) of Azo Dyes R_1–C$_6$H$_4$–N=N–C$_6$H$_4$–R_2

Compound	R_1	R_2	ΔE ($kJ\ mol^{-1}$)			μ^2/a^3 ($kJ\ mol^{-1}$)	ΔH_{evap} ($kJ\ mol^{-1}$)
			General	*Disperse*	*Orientation-induction*		
1	—	$N(C_2H_5)_2$	48·0	30·6	17·4	5·3	106·4
2	NO_2	NH_2	78·0	36·0	42·0	10·5	127·6
3	NO_2	$N(C_2H_4OH)(C_2H_5)$	87·8	42·0	45·8	—	136·8
4	NO_2	$N(CH_3)(CH_2CF_2CF_2H)$	56·4	31·2	25·2	6·7	100·8
5	NO_2	$N(C_2H_5)(CH_2CF_2CF_2H)$	57·6	33·6	24·0	7·1	103·0
6	NO_2	$N(C_2H_5)(CH_2(CF_2CF_2)_2H)$	60·0	34·8	25·2	8·4	112·6
7	NO_2	$N(C_2H_4OH)(CH_2CF_2CF_2H)$	70·8	36·0	34·8	12·6	124·4
8	F	$N(CH_3)_2$	44·4	31·2	13·2	1·3	91·2
9	OCF_3	$N(CH_3)_2$	49·9	31·2	18·0	2·5	96·8
10	SCF_3	$N(CH_3)_2$	55·2	31·2	24·0	5·0	100·8
11	CF_3	$N(CH_3)_2$	51·6	33·6	18·0	2·1	95·8
12	SO_2F	$N(CH_3)_2$	57·6	34·8	22·8	4·2	105·6
13	SO_2CF_3	$N(CH_3)_2$	66·0	36·0	30·0	8·8	—

The heats of evaporation (ΔH_{evap}) of the azo dyes were determined at 160–250 °C. In this temperature range a linear dependence is observed between the logarithm of the dye concentration in the gas phase and the inverse value of the absolute temperature (Fig. 1) testifying to the ideality of the dye vapours. At lower temperatures equilibria are observed when the spectrum of the 'cold' form is similar to that of the crystal spectrum.

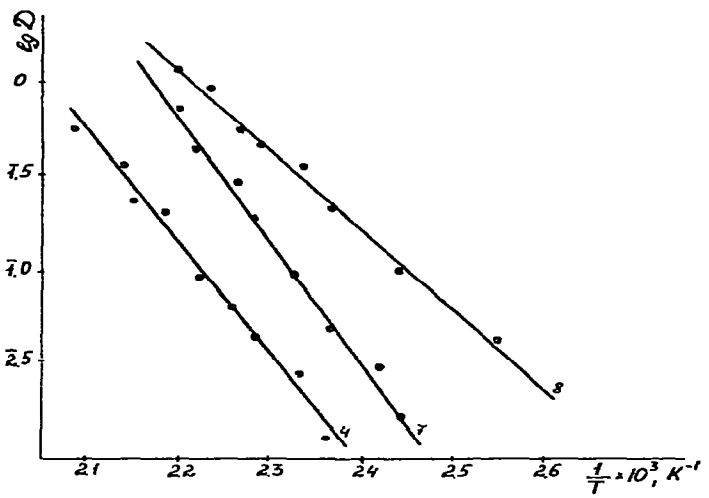

Fig. 1. Dependence of the logarithm of the dye concentration in the gas phase (lg D) on the inverse value of the absolute temperature ($1/T$). The numbers on the curves correspond to the compounds in Table 1.

For example, in the case of compound **6** the spectrum of the 'cold' form (up to 165 °C) is characterised by a band with $\lambda_{max} = 439$ nm, similar to λ_{max} of the crystal (Fig. 2). With a temperature rise a transformation is observed characterised by $\lambda_{max} = 369$ nm, by a decrease of the half-width by 1500 cm^{-1} and by an approximately two-fold increase of extinction coefficient. This equilibrium is reversible and it may be interpreted as a dye transformation from aggregate to monomer in the gas phase. Similar equilibria are also observed for other azo dyes.

The heats of evaporation of the fluorine derivatives of the first group are lower by 20–40 kJ mol^{-1} as compared with nitroaminoderivatives compounds **2**, **3** and **4**–**7**). The same is observed for the fluorine derivatives of the second group. When comparing compounds **8**–**12** with the azobenzene dialkylamino derivative (compound **1**) it becomes clear

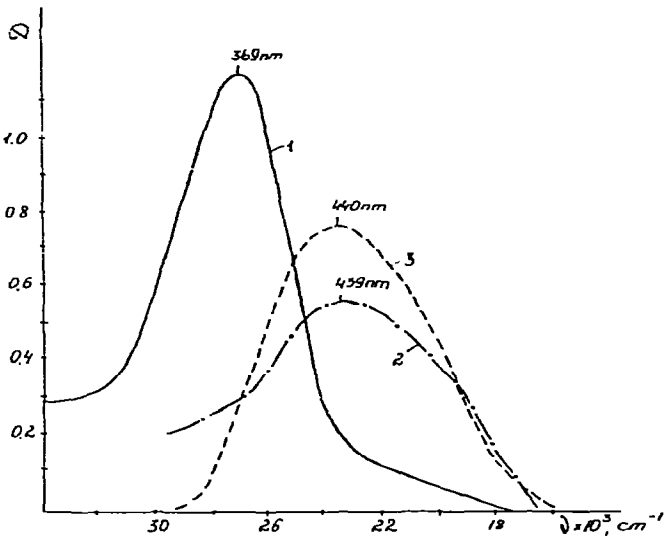

Fig. 2. Electronic absorption spectrum of compound **6** in the gas and crystalline phases. 1, Vapour at 200 °C; 2, vapour at 165 °C; 3, crystal.

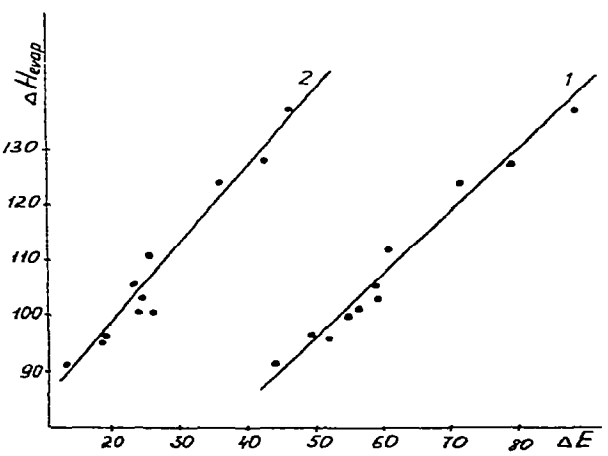

Fig. 3. Dependence of heat of evaporation ($\Delta H_{evap.}$) on the energy of intermolecular interactions (in kJ mol^{-1}). 1, General energy; 2, energy of orientation–induction interactions.

that introduction of fluorine or fluorine-containing substituents to the ring of the coupling component lowers the heat of evaporation ($\Delta H_{evap.}$). The latter increases with the volume and polarity of the substituents for the groups examined in the series of fluorine-containing azo dyes.

It is clear from Table 1 and Fig. 3 that analogous changes of $\Delta H_{evap.}$ and spectral energy parameters of the intermolecular interactions (the general energy, $\Delta E_{gen.}$, and contributions to it of disperse, $\Delta E_{disp.}$ and orientation–induction forces, $\Delta E_{or.-ind.}$) are based on the Bakshiev equation.[7] A decrease in the general energy of intermolecular interactions as compared with dyes without fluorine is noted for all fluorine derivatives examined. A decrease of $\Delta E_{gen.}$ is mainly associated with changes in orientation–induction interactions. The contribution of disperse interactions to the variability of $\Delta E_{gen.}$ lies within 5 kJ mol^{-1} while changes due to orientation–induction interactions are 10–12 kJ mol^{-1}.

The magnitude of $\Delta E_{or.-ind.}$ is determined[6] by the value of a structural parameter of the orientation–induction interactions of molecules, μ^2/a^3 (where μ is dipole moment and a^3 is molecule volume). The values of μ^2/a^3 have also been determined by this method.[7] The correlation between the heat of evaporation and the value of the orientation–induction interactions structural parameter is shown in Fig. 4. The linear character of such a dependence permits the use of the value of the structural parameter of orientation–induction molecules interactions for the estimation of the heat of evaporation of new derivatives of this class of dyes.

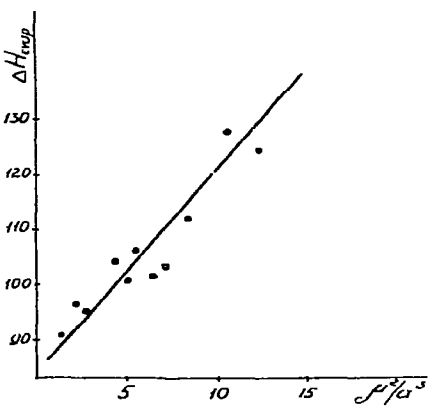

Fig. 4. Dependence of heat of evaporation ($\Delta H_{evap.}$) on the structural parameter of orientation–induction interaction of molecules (μ^2/a^3) (in kJ mol^{-1}).

4. EXPERIMENTAL

Electronic absorption spectra of the azo dyes were measured using a Specord UV-VIS spectrophotometer in the range <200–700 nm. Crystal spectra were determined in KCl tablets which were prepared in the following way. A known weight of the dye ($\sim 10^{-5}$–10^{-4} g) was dispersed with 0·8 g of purified dried KCl in an Ardenne vibrator GM 9459 (DDR), then the mixture was subjected to a pressure of 200 kg cm^{-2}. The prepared tablet was clear. Vapour spectra were measured in a special vacuum quartz cuvette with optical length 5 cm and electroheating to 400 °C. Hexane, carbon tetrachloride, ethyl acetate, ethanol and dimethylformamide were used as solvents.

The spectral energy of intermolecular interactions ($\Delta E = hc\,\Delta\nu$) was determined on the basis of dependence $\Delta\nu = \nu_{\text{vapour}} - \nu_{\text{medium}}$ from medium properties [$f(\varepsilon, n^2)$] (ε = dielectric permeability, n = refractive index). The contributions of the dispersion and orientational–inductive interactions to the general energy of intermolecular interactions were calculated by Bakhshiev's equation.[7]

5. CONCLUSION

It has been established by the investigation that the introduction of fluorine or fluorine-containing substituents to azo dye molecules leads to an energy decrease in intermolecular interactions and correspondingly to a decrease in the heat of evaporation of the dyes by 10–40 kJ mol^{-1} as compared with dyes without fluorine.

The energy of orientation–induction interactions is the main contribution to the general energy of intermolecular interactions and consequently to the heat of evaporation.

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