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A Study of the Self-Association of Simple Azo Dyes using the Potentiometric Method

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ABSTRACT

The thermodynamic aspects of the self-association of three monoazo dyes, viz. C.I. Acid Red 88, C.I. Acid Orange 7 and C.I. Acid Orange 8, in aqueous solution have been studied by means of a potentiometric method. An ion-selective membrane electrode, selective to a dye anion, has been constructed. This electrode permits a direct determination of the dye monomer concentration.

Measurements of e.m.f. versus dye concentration were carried out and the results show that the e.m.f. response is not linear over the whole measured concentration range. Because of dye association at higher concentrations the measured e.m.f. values start to deviate from the theoretical linear relationship. From these deviations the dye monomer concentration at a given total dye concentration was determined. Using an appropriate stepwise association model the dimerization constants and concentrations of the dimers and higher multimers were calculated. It is concluded that C.I. Acid Red 88 aggregates more readily than C.I. Acid Orange 7. C.I. Acid Orange 8, the structure of which includes a charged sulphonic acid group in the central part of the molecule, does not aggregate in the measured concentration range. The effects of temperature and added salt on the association of C.I. Acid Red 88 have also been investigated. From the results, it can be seen that the association of C.I. Acid Red 88 decreases with increasing *temperature, and strongly increases with increasing salt concentration. Thermodynamic functions of dimerization of C.I. Acid Red 88 in aqueous solutions at different temperatures were also determined. It appears that the dimerization of C.I. Acid Red 88 in aqueous solution is governed mainly by dispersive interactions between the dye molecules.*

1 INTRODUCTION

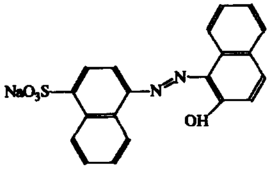
Although the association behaviour of ionic dyes in aqueous solution has been widely examined using a variety of methods,[1–15] neither the nature of the association equilibria nor the interactions involved at association are well established. The major hindrance is the lack of an appropriate investigative method, which would directly give the amount of dye present in solution as monomer.

In recent years ion-selective electrodes based on plasticized PVC, and sensitive to monomers of drugs, surfactants, dyes and many other substances[16–25] have been constructed, which permit the determination of the monomer concentration of such substances in aqueous solutions. In this present work, the self-association equilibria of some acid azo dyes have been studied using the above mentioned electrodes containing a surfactant–dye complex in plasticized PVC membrane.

2 EXPERIMENTAL

2.1 Materials

Three monobasic azo dyes: C.I. Acid Red 88 (C.I. 15620, A), C.I. Acid Orange 7 (C.I. 15510, B) and C.I. Acid Orange 8 (C) were synthesized from reagent grade chemicals.[26] Careful purification of the dyes was extremely important in order to obtain reproducible results. The dyes were recrystallized three times from an ethanol : water (1 : 1) mixture, redissolved in water, converted to the sodium form by ion exchange and further recrystallized from a mixture of acetone and water (1 : 1). The dyes were finally recrystallized several times from an *N*,*N*′-dimethylformamide and benzene (1 : 3) mixture.



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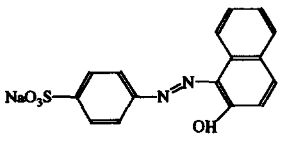

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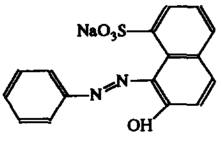

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N-cetylpyridinium bromide (CPBr) (Kemika, Zagreb, Croatia) was rigorously purified by repeated recrystallization from acetone. Poly(vinyl chloride) (PVC) (Solvic, Belgium) was purified by extraction from methanol. Other reagents used were of analytical grade and were used without further purification. All dye solutions were prepared in triple distilled water. The dye solution concentrations were determined by titration using the same dye selective membrane electrode as in the potentiometric measurements.

2.2 Method of investigation

The dye–surfactant electrode was prepared according to the procedure described by Cutler *et al.*[17] for the preparation of surfactant-selective polymeric membrane electrodes. The electrode membrane consisted of 0·35 g PVC, 1·15 g dioctylphthalate and 0·005 g dye anion : cetylpyridinium cation carrier complex.

The organization of the membrane electrode cell may be represented as follows:

Hg | Hg_2Cl_2 | KCl(satd.) ||
| test solution | polymer membrane | internal solution ||
$Na^+ D^-$ + $CPBr^+ D^-$ $Na^+ D^-$
× mol dm^{-3} $1 \cdot 10^{-4}$ mol dm^{-3}
| KCl(satd.) | Hg_2Cl_2 | Hg

where D^- is the dye anion. The electrode was tested against the reference calomel electrode (Model HEK 0301, Iskra, Slovenia) via an ammonium nitrate salt bridge. Since the aggregation of dyes is extremely sensitive to the presence of neutral electrolytes, a small glass tube with a pinhole was placed in the test and reference electrode solutions to prevent contamination of dye solutions by salt bridges.[27] The membrane electrode cell is shown schematically in Fig. 1.

After the electrode assembly had been equilibrated, the dye solution was added to the same test solution in discrete steps, and the resulting potential difference was measured with a Model PHM 26 Radiometer pH meter. In all experiments the temperature was controlled within ±0·1°C by circulation of thermostatted water through a double wall glass cell. The sample solution was continuously stirred using a magnetic stirrer. Response times of the electrodes were in the range of half a minute to a few minutes, depending on the temperature and composition of the test solution.

Measurements of the dependence of the e.m.f. of the cell on the log of dye concentration (log *m*) were carried out in the concentration range 10^{-6}–10^{-3} mol kg^{-1} for dyes C.I. Acid Orange 7 and C.I. Acid Orange 8 in

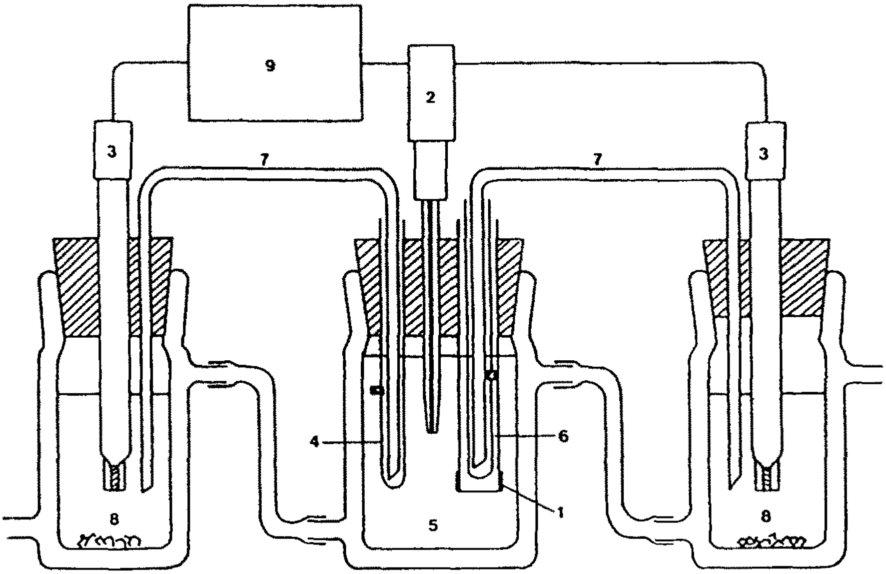

Fig. 1. Schematic diagram of the membrane electrode cell. 1, PVC membrane electrode; 2, Micrometer burette; 3, Reference calomel electrode; 4, Small glass tube with a pinhole; 5, Test solution; 6, Reference solution; 7, Ammonium nitrate salt bridge; 8, Saturated KCl solution; and 9, pH meter.

aqueous solutions at 25°C and for C.I. Acid Red 88 in aqueous solution at 15, 20, 25, 30, 35, 40 and 45°C and also in the presence of different fixed amounts of added NaCl at 25°C ($5{\cdot}10^{-5}$, $1{\cdot}10^{-4}$, $1{\cdot}10^{-3}$ and $1{\cdot}10^{-2}$ mol kg^{-1}).

3 RESULTS AND DISCUSSION

Plots of measured e.m.f. (E) versus the logarithm of the total molar dye concentration ($\log m_T$) at 25°C for the three dyes studied are given in Fig. 2; a dye is assumed to be in a monomeric form in a very dilute solution and the curve E vs $\log m_T$ is consequently a straight line. In this concentration range the concentration of the monomeric form (m_1) is equal to the total dye concentration (m_T). The slope of the linear plot is $-47{\cdot}8$ mV/decade for C.I. Acid Red 88, $-51{\cdot}2$ mV/decade for C.I. Acid Orange 7 and $-72{\cdot}2$ mV/decade for C.I. Acid Orange 8. With increasing concentration, the dyes C.I. Acid Red 88 and C.I. Acid Orange 7 start to aggregate and consequently the concentration of the monomeric form becomes lower than the total dye concentration. Because the dye electrode is sensitive only to the free dye anions, the measured e.m.f. changes accompanying the increased dye concentration become smaller than they would be in cases where all dye molecules in the solution are present in the monomeric form. In other words, the experimental curve starts deviating from linearity. From the

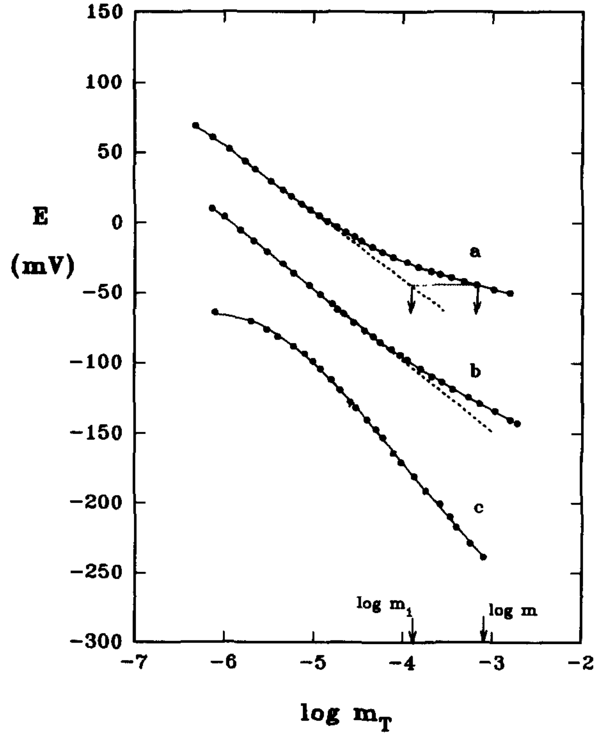

Fig. 2. Plots of e.m.f. (E) of the cell vs the log of the molal concentration (log m_T) of dyes C.I. Acid Red 88, C.I. Acid Orange 7 and C.I. Acid Orange 8 in aqueous solution at 25°C. a, C.I. Acid Red 88; b, C.I. Acid Orange 7; c, C.I. Acid Orange 8.

observed deviations, the concentrations of the monomeric form (m_1), and of aggregates were determined (Fig. 2). The observed curvature at the lowest concentration range can be attributed to the limit of detection.[28]

The fraction of the dye monomeric form, denoted by α, can be expressed as:[8,9]

$$\alpha = \frac{m_1}{m_T} \tag{1}$$

where m_1 represents the concentration of the monomeric dye form at a given stoichiometric total molal dye concentration (m_T) obtained from the straight linear plot which would be obtained if the electrode responded ideally and no aggregation occurred (Fig. 2(a)).

In Fig. 3, the obtained values α for C.I. Acid Red 88 and C.I. Acid Orange 7 are plotted against total dye concentration m_T. It can be seen that C.I. Acid Red 88, with two naphthalene rings, aggregates more readily than C.I. Acid Orange 7 which has lower molecular weight. Using ^{19}F NMR spectroscopy and electronic absorption, the same behaviour of similar acid dyes has been observed.[10,11]

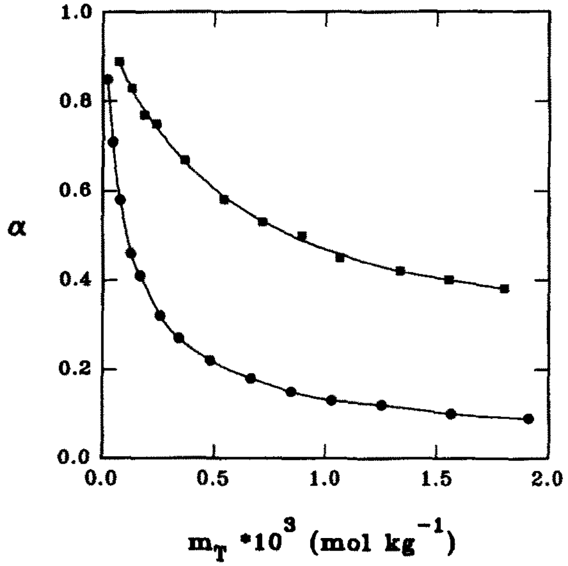

Fig. 3. Plots of the fraction of dye monomeric form α vs total dye concentration (m_T) of C.I. Acid Red 88 and C.I. Acid Orange 7 in aqueous solution at 25°C. -■-■-, C.I. Acid Orange 7 and -●-●-, C.I. Acid Red 88.

The third dye, C.I. Acid Orange 8, behaves in a quite different manner. Up to the electrode limit of detection, the dependence of E on log m_T is linear in the whole measured concentration range (Fig. 2(c)). The reason for such behaviour lies in the structure of this dye; the charged sulphonic group is located in the central part of the molecule thus preventing a closer approach of two or more dye anions. This finding confirms the general assumption that the deviation from ideal behaviour of dyes in aqueous solutions is caused mainly by dye anion aggregation.

In addition, the effect of different temperatures and added NaCl on the association of the C.I. Acid Red 88 has been studied. Figures 4 and 5 show plots of measured E vs log m_T for C.I. Acid Red 88 at seven different temperatures and in the presence of different amounts of added NaCl.

Robinson *et al.*[4] have described the process of dye association in aqueous solution as a set of multiple equilibria of the type:

$$\begin{aligned} &D_1^{-1} + D_1^{-1} \overset{K_{12}}{\longleftrightarrow} D_2^{-2} \\ &D_1^{-1} + D_2^{-2} \overset{K_{23}}{\longleftrightarrow} D_3^{-3} \\ &\cdots \\ &D_1^{-1} + D_n^{-n} \overset{K_{n,n+1}}{\longleftrightarrow} D_{n+1}^{-n-1} \end{aligned} \tag{2}$$

where D_1^{-1}, D_2^{-2}, . . ., D_{n+1}^{-n-1} represent a monomer, dimer, . . ., a multimer with $n + 1$ monomer units and of $-n$–1 charge.

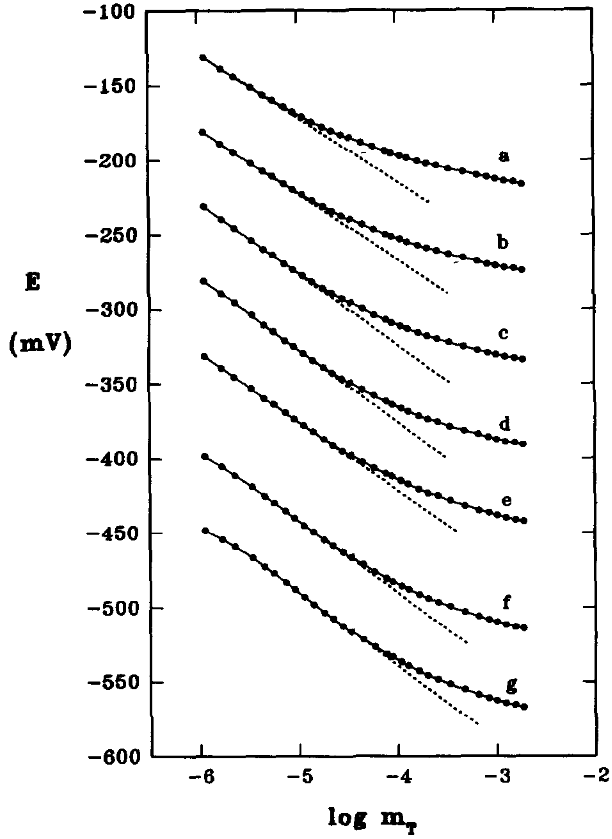

Fig. 4. Plots of e.m.f. (E) of the cell vs the log of C.I. Acid Red 88 dye concentration (log m_T) in the temperature range 15–45°C. a, 15°C; b, 20°C; c, 25°C; d, 30°C; e, 35°C; f, 40°C; g, 45°C.

The association constant $K_{n,n+1}$ is related to the dimerization constant K_{12} by the following expression:[4]

$$K_{n,n+1} = \frac{m_{n+1}}{m_n m_1} = K_{12} \exp\left\{-q \sum_{2}^{\infty} \frac{1}{n}\right\} \tag{3}$$

where m_n and m_{n+1} are the molal concentrations of multimers, q is equal to $N_A e_0^2/\sigma a RT$, N_A is the Avogadro number, e_0 is the electron charge, a is the distance of closest approach between dye anions in the stack, and σ is the screening factor, which is equal to the effective dielectric constant experienced by the stack. As σ increases, the repulsive effect of charges in the stacks correspondingly diminishes. A value of σ can vary between 1 and ∞ and a value of q between 0 and ∞.

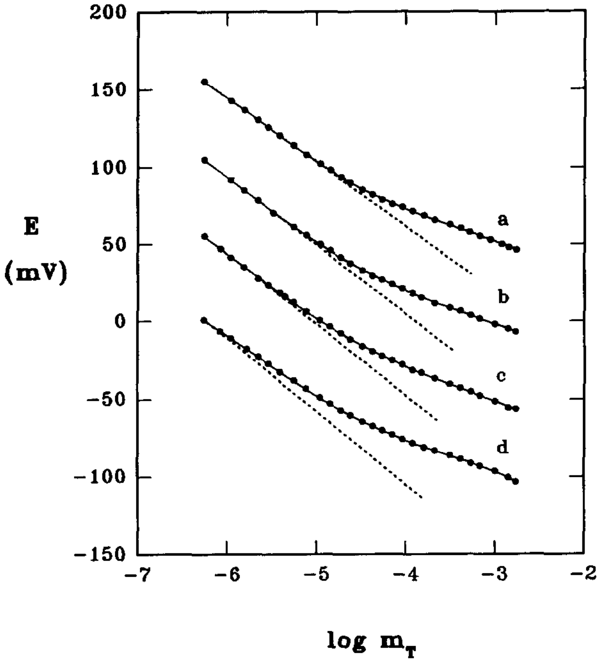

Fig. 5. Plots of e.m.f. (E) of the cell vs the log of C.I. Acid Red 88 dye concentration (log m_T) at 25°C in the presence of different fixed amounts of added NaCl. a, 5 . 10^{-5} mol kg^{-1} NaCl; b, 1 . 10^{-4} mol kg^{-1} NaCl; c, 1 . 10^{-3} mol kg^{-1} NaCl; d, 1 . 10^{-2} mol kg^{-1} NaCl.

The total dye concentration m_T in terms of monomer species is:[1]

$$m_T = m_1 + 2m_2 + 3m_3 + \cdots + nm_n = \sum_1^n nm_n \tag{4}$$

Combining eqns (3) and (4) we obtain the expression:

$$m_T = m_1 + 2K_{12}m_1^2 + 3K_{12}^2m_1^3 \exp(-(q/2)) + 4K_{12}^3m_1^4 \exp(-4(q/3)) + \cdots \tag{5}$$

or

$$m_T = m_1 + \sum_{l=2}^{n} lK_{12}^{l-1}m_1^l \left\{\exp\left[-q\sum_{j=1}^{l-2}\sum_{k=2}^{j+1}\frac{1}{k}\right]\right\} \tag{6}$$

From eqn (3), in which the association constants are related to q, it can be seen that when the $K_{12} \geq K_{n,n+1}$, this leads to a positive value of q. This is opposite to the observation where the stepwise trimerization constant K_{23} was found to be greater than K_{12}.[29] According to Robinson, Löffler and Schwarz,[4] strong electrostatic repulsion can be expected when $q \gg 1$ and K_{12} has much higher value as the equilibrium constant of higher oligomers. Medium electrostatic repulsion occurs when $q \cong 1$, and the equilibrium constants slowly decrease as the degree of aggregation n

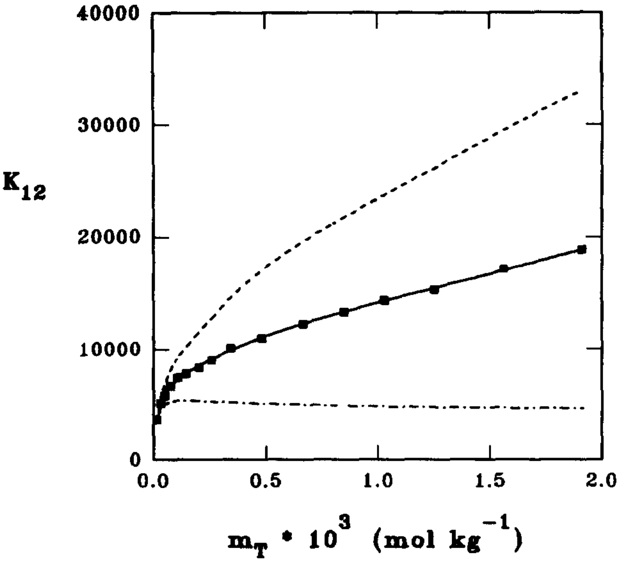

Fig. 6. Plots of calculated dimerization constants K_∞, K_0, K'_{12} vs C.I. Acid Red 88 dye concentration (m_T) at 25°C. – – – –, K_∞ vs m_T; -■-■-, K'_{12} vs m_T; – · – · –, K_0 vs m_T.

increases. On the other hand, weak electrostatic repulsion is observed when $q \ll 1$ and consequently $K_{12} = K_{n,n+1}$; this latter behaviour corresponds to the isodesmic model of ion association.[4]

From values of m_1, m_T, K_{12} and q it is possible to calculate the oligomer distribution of the dye and consequently the average degree of dye aggregation N'_n at given concentration m_T as follows:[3]

$$N'_n = \frac{\sum nm_n}{\sum m_n} \tag{7}$$

To obtain the concentrations of dimers (m_2), trimers (m_3) and higher multimers (m_n) which are used in the summation term, it is necessary to know the values of K_{12} and q at a given stoichiometric dye concentration (m_T). Using the experimentally obtained $m_T(m_1)$ data, we have calculated the dimerization constants K_∞ at $q = \infty$ and K_0 at $q = 0$, and from these values the mean value of K'_{12} at a given dye concentration m_T and the corresponding value of $q(K'_{12})$. In Figs 6 and 7 the calculated plots of K_∞, K_0, K'_{12} and q against C.I. Acid Red 88 dye concentration m_T at 25°C are shown. It is apparent that the values of K_∞, K_0 and consequently K'_{12} give the same value of K_{12} when $m_T \to 0$ and that the calculated values of $q(K'_{12})$ are slightly higher than unity at lower concentrations. This corresponds to nearly medium long-range electrostatic interactions.[4] From values of K'_{12} and $q(K'_{12})$ we have calculated the concentrations m_2, m_3, m_n and the average degree of dye aggregation N'_n. The summation was carried out up to

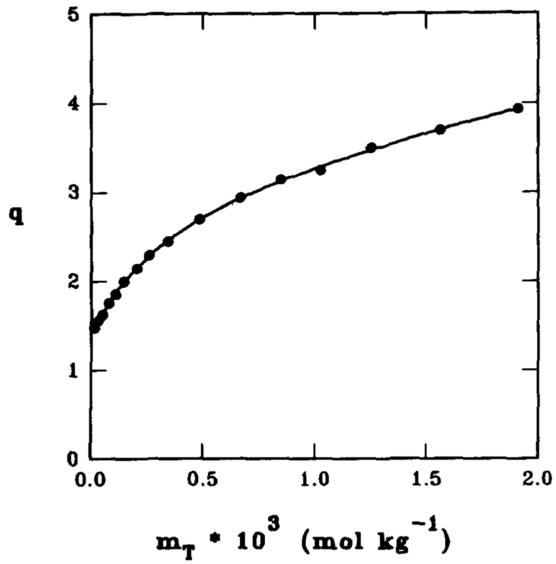

Fig. 7. A plot of calculated value of q vs C.I. Acid Red 88 dye concentration (m_T) at 25°C.

$n = 8$ because higher terms were negligibly small. Figure 8 shows plots of the average degree of aggregation N_n' of C.I. Acid Red 88 versus concentration (m_T) at seven different temperatures.

At very low concentrations, one may assume that the stacking of the dye molecules is so low that aggregation beyond the dimer stage may be neglected. The actual value of the dimerization constant (K_{12}) can then

TABLE 1
Dimerization Constants K_{12} for C.I. Acid Red 88 and C.I. Acid Orange 7 at Different Temperatures and Different Concentrations of NaCl

T (°C)	*NaCl (mol kg^{-1})*	K_{12}
(A) C.I. Acid Red 88		
15	0	3748 ± 486
20	0	2879 ± 241
25	0	2414 ± 228
25	$5 . 10^{-5}$	3655 ± 159
25	$1 . 10^{-4}$	4744 ± 547
25	$1 . 10^{-3}$	12550 ± 253
30	0	1045 ± 331
35	0	997 ± 239
40	0	758 ± 96
45	0	415 ± 81
(B) C.I. Acid Orange 7		
25	0	980

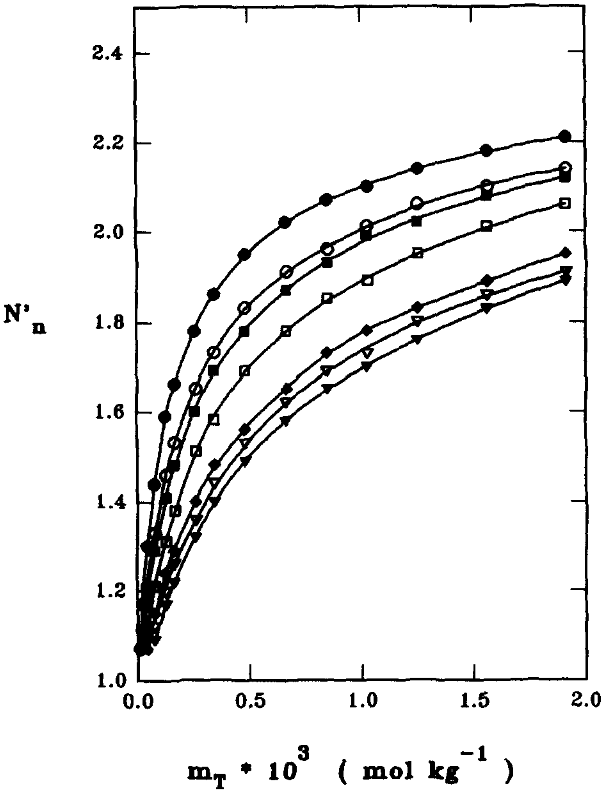

Fig. 8. Plots of the average degree of dye aggregation N_n' vs concentration (m_T) of C.I. Acid Red 88 at seven different temperatures. -●-●-, at 15°C; -○-○-, at 20°C; -■-■-, at 25°C; -□-□-, at 30°C; -◆-◆-, at 35°C; -▽-▽-, at 40°C; -▼-▼-, at 45°C.

be obtained from experimental m_T and m_1 data by the graphical method. Equation (5) can be rewritten in the form:[29,30]

$$F=\frac{m_T-m_1}{m_1^2}=2K_{12}+3K_{12}^2m_1\exp(-(q/2))+4K_{12}^3m_1^3\exp(-4(q/3))+\cdots \quad (8)$$

From eqn (8) it follows that

$$\lim_{m_1\to 0} F = 2K_{12}$$

which means that if the values of F are plotted against the monomer concentration (m_1) the intercept on the ordinate gives $2K_{12}$.

Figure 9 shows plots of values of F vs m_1 for C.I. Acid Orange 7 at 25°C and for C.I. Acid Red 88 at different temperatures and Fig. 10 plots of F vs m_1 for C.I. Acid Red 88 in the presence of different amounts of added NaCl at 25°C. From the figures it is evident that the F vs m_1 plots are linear at low temperatures over a substantial range. The corresponding K_{12} values were calculated and are collated in Table 1.

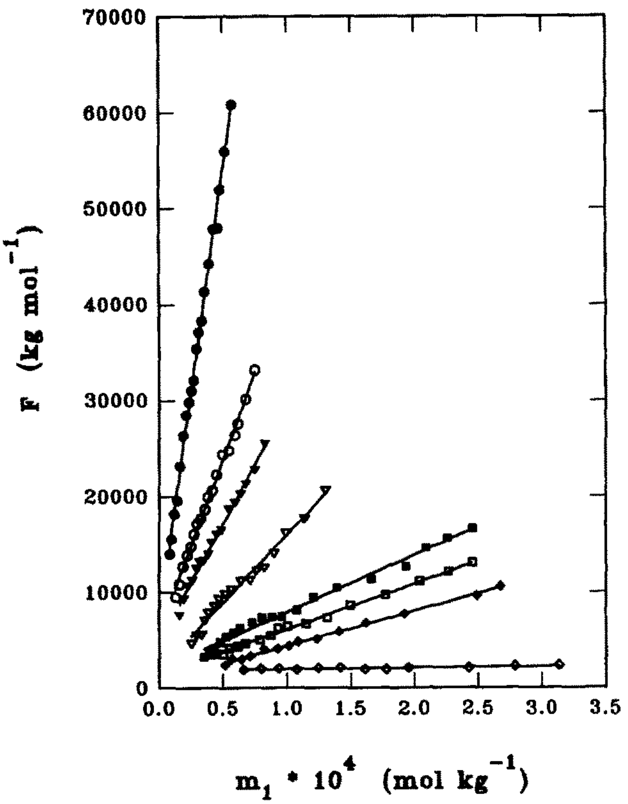

Fig. 9. Plots of the function F vs monomer concentration (m_1) for C.I. Acid Red 88 at different temperatures and for C.I. Acid Orange 7 at 25°C. -●-●-, C.I. Acid Red 88 at 15°C; -○-○-, C.I. Acid Red 88 at 20°C; -▼-▼-, C.I. Acid Red 88 at 25°C; -▽-▽-, C.I. Acid Red 88 at 30°C; -■-■-, C.I. Acid Red 88 at 35°C; -□-□-, C.I. Acid Red 88 at 40°C; -◆-◆-, C.I. Acid Red 88 at 45°C; -◇-◇-, C.I. Acid Orange 7 at 25°C.

It can be seen from Table 1 that values of the dimerization constant (K_{12}) sharply increase with concentration of added salt, which means that aggregation of dye increases with increasing concentration of simple electrolyte.

Inspection of the K_{12} values determined for C.I. Acid Red 88 in pure aqueous solutions at seven different temperatures shows that K_{12} decreases with increasing temperature meaning that at higher temperatures the aggregation process becomes less pronounced.

For C.I. Acid Red 88 Hamada *et al.*[15] obtained a K_{12} value of 2900 at 27°C (determined by means of visible absorption spectroscopy). The value is in good agreement with our value of 2400 obtained at 25°C (Table 1(A)). Using a liquid membrane electrode and a simple isodesmic model of dye aggregation, Kale, Cussler and Evans[7] obtained $K_{12} = 1030$ (1080) for C.I. Acid Orange 7 at 25°C. Applying our method to their data, we calculated $K_{12} = 953$. Both results are in good agreement with ours

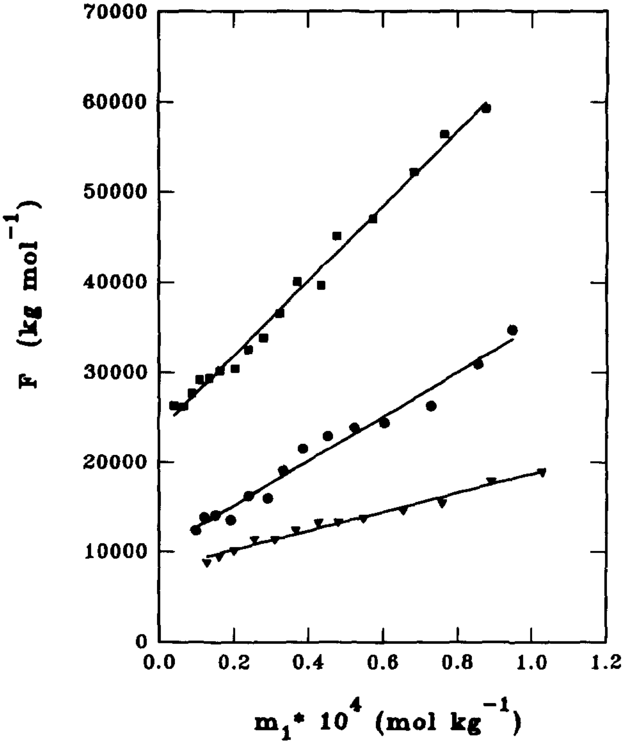

Fig. 10. Plots of the function F vs monomer concentration (m_1) for C.I. Acid Red 88 in the presence of different fixed amounts of added NaCl. -■-■-, 1 . 10^{-3} mol kg^{-1} NaCl; -●-●-, 1 . 10^{-4} mol kg^{-1} NaCl; -▼-▼-, 5 . 10^{-5} mol kg^{-1} NaCl.

(Table 1(B)). On the other hand our value is somewhat higher than the value of K_{12} = 705 obtained by Reeves *et al.*[31] from spectroscopic and NMR measurements, and lower than the value of 1320 obtained by visible spectroscopy[32] and the value of 1400 calculated from solubility data.[33,29]

Thermodynamic aspects of self-association of the dye C.I. Acid Red 88 were studied for the process of dimerization, that is the equilibrium system of dimer formation from two monomers with an equilibrium constant K_{12}.

From the values obtained for K_{12} at different temperatures (Table 1), the standard free enthalpy change (ΔG^0_D), the standard enthalpy change (ΔH^0_D) and the standard entropy change (ΔS^0_D) for the dimer formation can be calculated as follows:[34]

$$\Delta G^0_D = -RT \ln K_{12} \tag{9}$$

$$\Delta H^0_D = \frac{\partial(\Delta G^0_D/T)}{\partial(1/T)} \tag{10}$$

$$\Delta S^0_D = \frac{\Delta H^0_D - \Delta G^0_D}{T} \tag{11}$$

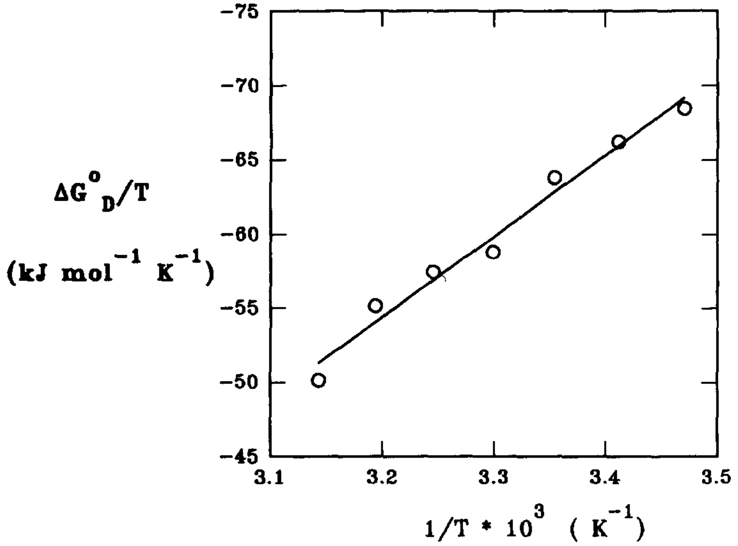

Fig. 11. Plot of $\Delta G^0_D/T$ vs $1/T$ for C.I. Acid Red 88.

From eqn 10 it can be seen that if $\Delta G^0_D/T$ is plotted against $1/T$, the slope of the curve at any temperature is equal to ΔH^0_D at this temperature. As shown in Fig. 11, the relationship between $\Delta G^0_D/T$ and $1/T$ is practically linear, indicating ΔH^0_D is constant for the reaction over the experimental temperature range. The value of ΔH^0_D calculated from the slope is $-55{\cdot}2 \pm 5{\cdot}2$ kJ/mol.

ΔH^0_D is called the heat of dimerization and represents the change in enthalpy on dimer formation. Because $\Delta H^0{}_D < 0$, this reaction is exothermic (the equilibrium constant K_{12} decreases as temperature is raised). The values of ΔG^0_D, ΔH^0_D and ΔS^0_D are given in Table 2.

For the dimerization process, where two monomer (D_1^{1-}), are combined in one dimer (D_2^{2-}),

$$D_1^{-1} + D_1^{-1} \longrightarrow D_2^{-2}$$

the free enthalpy of dimerization, ΔG_D, can be expressed as:[34]

$$\Delta G_D = \mu_2^0 - 2\mu_1^0 + RT \ln \frac{\gamma_2}{\gamma_1^2} + RT \ln \frac{m_2}{m_1^2} \qquad (12)$$

where μ_1^0 and μ_2^0 are the standard chemical potentials of monomers and dimers, γ_1 and γ_2 are the molal activity coefficients of monomers and dimers, respectively.

TABLE 2
Thermodynamic Functions of Dimerization of C.I. Acid Red 88 in Aqueous Solution at Different Temperatures

T (°C)	ΔG^0_D (kJ/mol)	ΔH^0_D (kJ/mol)	ΔS^0_D (J/molK)	ΔG^0_{el} (kJ/mol)	ΔG^0_{atr} (kJ/mol)	ΔG^0_{mix} (kJ/mol)	ΔH^0_{el} (kJ/mol)	ΔH^0_{atr} (kJ/mol)	ΔS^0_{atr} (J/molK)
15	−19·7	−55·2	−123·2	3·6	−32·9	9·6	−1·2	−54·0	−73·3
20	−19·4	−55·2	−122·1	3·7	−32·9	9·8	−1·3	−53·9	−71·9
25	−19·3	−55·2	−120·4	3·7	−33·0	10·0	−1·4	−53·8	−69·9
30	−17·5	−55·2	−124·3	3·8	−31·4	10·1	−1·5	−53·7	−73·5
35	−17·7	−55·2	−121·8	3·8	−31·8	10·3	−1·6	−53·6	−70·7
40	−17·3	−55·2	−121·2	3·9	−31·6	10·5	−1·7	−53·5	−69·8
45	−15·9	−55·2	−123·4	4·0	−30·5	10·6	−1·8	−53·4	−71·8

At low concentrations the term containing activity coefficients may be neglected and eqn (12) becomes:

$$\Delta G_D = \Delta G^0_D + RT \ln \frac{m_2}{m_1^2} \tag{13}$$

where $\Delta G^0{}_D$ is the standard free enthalpy of dimerization.

ΔG_D can be expressed in a similar way in terms of mole fractions of monomers X_1 and dimers X_2 and the correspoonding activity coefficients, f_1 and f_2, expressed on the mole fraction basis:

$$\Delta G_D = (\mu_2^0)' - 2(\mu_1^0)' + RT \ln \frac{f_2}{f_1^2} + RT \ln \frac{X_2}{X_1^2} \tag{14}$$

where $(\mu_1^0)'$ and $(\mu_2^0)'$ are the standard chemical potentials on the mole fractions scale of monomers and dimers, respectively. At low concentrations, again the term containing activity coefficients is neglected and eqn (14) takes the form:

$$\Delta G_D = \Delta G^0_u + RT \ln \frac{X_2}{X_1^2} \tag{15}$$

where ΔG^0_u is the standard unitary free enthalpy of dimerization.

A very dilute solution, in which only the dimerization process takes place, contains n_1 moles of monomers, n_2 moles of dimers and n_w moles of water. Because the sum $(n_1 + n_2)$ is much less than n_w, the mole fractions X_1 and X_2 can be expressed as:

$$\lim_{n_1 \to 0} X_1 = \frac{n_1}{n_w}; \ldots \lim_{n_2 \to 0} X_2 = \frac{n_2}{n_w} \tag{16}$$

Since the molality of a component is defined as the amount of the component per unit mass of the solvent (1 kg water), the molal concentrations m_1 and m_2 can be written instead of n_1 and n_2 in eqn (16); n_w is then equal to $100/M_w = 55{\cdot}6$ and is written as $1/M_0$. Equation (16) becomes:

$$\lim_{m_1 \to 0} X_1 = m_1 M_0; \ldots \lim_{m_2 \to 0} X_2 = m_2 M_0 \tag{17}$$

According to this equation, the expression of the free enthalpy change ΔG_D in eqn (15) can be written as:

$$\Delta G_D = \Delta G_u^0 + RT \ln \frac{m_2}{m_1^2} - RT \ln M_0 \tag{18}$$

From eqn (13) and (18) it follows:

$$\Delta G_D^0 = \Delta G_u^0 - RT \ln M_0 \tag{19}$$

where

$$\Delta G_{mix}^0 = - RT \ln M_0 \tag{20}$$

and ΔG_{mix}^0 is the standard free enthalpy of mixing which represents the contribution from the random mixing of the dye molecules with water, when dye monomers transform to dimer. Differentiation of the standard free enthalpy of dimerization with respect to temperature gives the standard entropy change of dimerization:[35,36]

$$\Delta S_D^0 = \Delta S_u^0 + R \ln M_0 \tag{21}$$

In eqn (21), ΔS_u^0 is unitary or contact entropy, which represents the contribution to the entropy due to the dye–solvent interaction. The term $R \ln M_0$, is called the cratic contribution to the entropy and is equal to $-33{\cdot}4$ J mol^{-1} K^{-1}.

The change of standard free enthalpy of dimerization ΔG_D^0 can be represented by three contributions:[4]

$$\Delta G_D^0 = \Delta G_{el}^0 + \Delta G_{atr}^0 + \Delta G_{mix}^0 \tag{22}$$

ΔG_{el}^0 is the electrostatic contribution resulting from long range electrostatic interactions. On the other hand, ΔG_{atr}^0 incorporates all contributions resulting from attractive noncoulombic hydrophobic and dispersive interactions.

Assuming that the ionic strength is very low, that there is no electrolyte added to the solution and that only the electrostatic ion–ion interactions are important, ΔG_{el}^0 may be expressed as:[37]

$$\Delta G_{el}^0 = \frac{\mathrm{N_A} e_0^2}{a\sigma} = qRT \tag{23}$$

In eqn (23), $\mathrm{N_A}$ is Avogadro's constant, e_0 is the electronic charge, a is the average separation between charges in the dimer and σ is a screening factor.

The values of ΔG^0_{atr} and ΔG^0_{el} are calculated from eqn (20), (22) and (23).

By applying the Gibbs–Helmholtz equation[34] to eqn (20) and (22) one obtains $\Delta H^0_{mix} = 0$ and

$$\Delta H^0_{atr} = \Delta H^0_D - \Delta H^0_{el} \tag{24}$$

where ΔH^0_{el} is equal to $\Delta G^0_{el} - T\Delta S^0_{el}$.

ΔS^0_{el} can be evaluated from the following equation:[38]

$$\Delta S^0_{el} = -\frac{d(\Delta G_{el})}{dT} = \Delta G^0_{el}\frac{d\ln(\varepsilon)}{dT} \tag{25}$$

where $d\ln\varepsilon/dT$ is equal to $-4{\cdot}6\,.\,10^{-3}\ K^{-1}$.[38–40]

According to eqn (11), the standard entropy of attraction is:

$$\Delta S^0_{atr} = \frac{(\Delta H^0_{atr} - \Delta G^0_{atr})}{T} \tag{26}$$

All thermodynamic functions calculated from the equations described above are compiled in Table 2.

The standard free enthalpy change of dimerization, ΔG^0_D, which is in direct correlation with the dimerization constant, K_{12}, (eqn (9)) is an indication of the tendency of dimer formation. The process of dye dimerization is favoured with the decrease in free enthalpy. Comparing the value of ΔG^0_D for C.I. Acid Orange 7, which is equal to −17·1 kJ/mol, to the value of −19·3 kJ/mol for C.I. Acid Red 88 at 25°C, we can conclude that C.I. Acid Red 88 aggregates more readily than C.I. Acid Orange 7 at the same conditions (Fig. 3).

Table 1 shows that the value of ΔG^0_D for C.I. Acid Red 88 is negative at all seven studied temperatures. It is more negative at 15°C than at 45°C, indicating that dimerization decreases with increasing temperature. It should be mentioned that the opposite behaviour has been observed with the association processes of the hydrophobic species (hydrocarbons) in aqueous solutions, where an increase in temperature tends to drive the equilibrium towards 'hydrophobic bonding' rather than towards dissociation.[41,42]

The value of ΔG^0_D consists of three contributions ΔG^0_{el}, ΔG^0_{atr} and ΔG^0_{mix} (eqn (22)). From Table 2 it can be seen that the coulombic term ΔG^0_{el} for dimer formation, which includes the electrostatic interactions, is positive at all studied temperatures and has a value of 3·6–4·0 kJ/mol. It means that this electrostatic contribution to ΔG^0_D opposes the dimer formation. ΔG^0_{atr} and ΔG^0_{mix} are contributions to the overall standard free enthalpy change of dimerization due to the short range stacking interactions and solute–solvent interactions, respectively. $\Delta G^0_{\mathrm{atr}}$, which includes all contributions resulting from attractive noncoulombic hydrophobic and dispersive interactions has a negative value of $-30{\cdot}5$–$-33{\cdot}0$ kJ/mol and represents the main contribution to the negative value of ΔG^0_{D}. The $\Delta G^0_{\mathrm{mix}}$ for converting two monomer species into dimer species has a positive value of 9·6–10·6 kJ/mol at all studied temperatures.

Our data show that for the C.I. Acid Red 88 the studied entropy of dimerization, ΔS^0_{D}, is negative. This negative value may be interpreted in terms of two opposing contributions. The first would be the one that favours the dimerization and thus gives a positive contribution to ΔS^0_{D}. This contribution can be ascribed to the disruption of the hydrophobically structured water around the monomers that occurs when monomers associate into dimers.[43–46] The second contribution, which opposes the dimerization and thus gives a negative contribution to ΔS^0_{D}, arises from the loss of the rotational and translational entropy that accompanies the process of dimerization. This second contribution obviously prevails since the observed ΔS^0_{D} value is negative.

Inspection of data in Table 2 shows that for C.I. Acid Red 88 the ΔH^0_{D} value is highly exothermic and strongly governed by the hydrophobic and dispersive interactions ($\Delta H^0_{\mathrm{D}} \approx \Delta H^0_{\mathrm{atr}}$). The contribution due to hydrophobic interactions, which results from the disruption of the hydrophobically structured water around the monomers when they combine into a dimer, is undoubtedly endothermic. On the other hand dye molecules that are highly polarizable aromatic systems are known to interact between themselves much more intensively than with water.[38] Such strong dispersive interactions should, therefore, lead to a large negative value of $\Delta H^0_{\mathrm{atr}}$. For C.I. Acid Red 88, our results show that endothermic breakdown of the structured water around the monomers that accompanies their dimerization has little effect on the ΔH^0_{D} (Table 2). The main contribution to the enthalpy of dimerization obviously comes from the dispersive interactions.

In conclusion, the dimerization of C.I. Acid Red 88 in aqueous solutions appears to be governed mainly by the dispersive interactions between the dye molecules.

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