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Thermochromic Character of Dyes

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SUMMARY

Dyes whose acid and base forms are differently coloured from each other have the possibility of showing thermochromism based on the temperature dependence of the acid–base equilibrium. To clarify such character of the dyes, the temperature dependence of the acid–base equilibrium and the colour change have been investigated using 1-hydroxyanthraquinones and phthaleins. 1-*Hydroxyanthraquinones in solution of sodium acetate showed such a colour change, i.e. yellow at lower temperature and orange at higher temperature. This colour change was due to the larger temperature dependence of their acidity than that of the basicity of the medium. In solution of triethylamine, on the other hand, the reverse colour change was observed because the temperature dependence of their acidity is smaller than that of the basicity of the medium. Similar thermochromic character of the phthaleins was also investigated.*

1 INTRODUCTION

The thermochromic transitions can be roughly classified into two types as follows: (1) the thermochromism caused by structural change of a compound, as represented by spiropirane;[1] (2) the thermochromism due to solvatochromism caused by the temperature change of the polar character

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of the medium.[2] If a dye is present in an acid–base equilibrium, and its acid form is differently coloured from its basic form, the dye will show thermochromism due to temperature dependence of the equilibrium constant.

$$\mathrm{AH} \underset{\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} \mathrm{A^-} \tag{1}$$

In such thermochromism, the essential factors are the temperature dependences of both the acidity of AH and the basicity of the medium. When the decrease in the basicity of the medium with a rise in temperature is less than the increase in the acidity of AH, or when the basicity of the medium with increase of temperature is unchanged or increases, the degree of dissociation of AH becomes greater. When the decrease in the basicity of the medium with a rise in temperature is larger than the increase in the acidity of AH, the degree of dissociation of AH becomes smaller (Fig. 1).

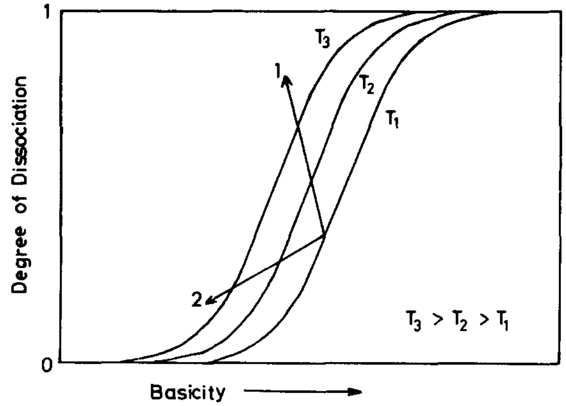


Fig. 1. Relationship between the basicity of medium and the degree of dissociation of acid; T = temperature. 1. The case when the decrease in the basicity of the medium with rise in temperature is less than the increase in the acidity of the acid, or when the basicity of the medium with increase of temperature is unchanged or increases. 2. The case when the decrease in the basicity of the medium with rise in temperature is larger than the increase in the acidity of the acid.

Thus the selection of medium can bring about reverse colour changes with the same dye. Although many thermochromic compounds, and the mechanism of the thermochromic transitions, have been reported,[1,3,4] thermochromism caused by the temperature dependence of the acid–base equilibrium has not been described. We have investigated the thermochromism of 1-hydroxyanthraquinones and of some phthalein pH indicators as examples of the above mentioned thermochromic dyes.

2 RESULTS AND DISCUSSION

2.1 Thermochromism in solution of sodium acetate

The pH of aqueous sodium acetate is expressed as follows, neglecting the terms of activity coefficients;

$$\mathrm{pH} = \tfrac{1}{2}(\mathrm{p}K_\mathrm{w} + \mathrm{p}K_\mathrm{a}^\mathrm{ac} + \log C) \tag{2}$$

where K_w, K_a^ac, and C are the ionic product of water, the dissociation constant of acetic acid and the analytical concentration of sodium acetate, respectively. Therefore the enthalpy change of pH, ΔH, is

$$\Delta H = \tfrac{1}{2}(\Delta H_\mathrm{w} + \Delta H_\mathrm{a}) \tag{3}$$

when ΔH_w and ΔH_a express the enthalpy of $\mathrm{p}K_\mathrm{w}$ and $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$, respectively. The ΔH was evaluated as 26·5 kJ mol^{-1}, and in the case of methanol solution, the enthalpy of pH($-\log[\mathrm{CH_3OH_2^+}]$) was estimated to be 20·5 kJ mol^{-1}, similar to that in aqueous solution. (The value of ΔH_w, 54·5 kJ mol^{-1} and that of ΔH_a, $-1·5$ kJ mol^{-1}, were obtained from the linear plot of $\mathrm{p}K_\mathrm{w}$[5] and $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$[5] vs $1/T$ in the temperature range from 20°C to 50°C. In the case of methanol solution the corresponding values were estimated to be 41·9 kJ mol^{-1} and $-0·96$ kJ mol^{-1} from the similar plot by use of the ionic product of methanol at 5° intervals between 15°C and 45°C[6] and the $\mathrm{p}K_\mathrm{a}^\mathrm{ac}$ in methanol at 18°C, 25°C and 37°C.[7])

Figure 2 shows the spectral change of sodium 1-hydroxyanthraquinone-2-sulfonate (**1**) in aqueous sodium acetate with rise of temperature, where the absorption maxima are observed near 400 nm and 500 nm. A reversible colour change of the solution between yellow (lower temperature) and orange (higher temperature) was observed. Both the pH of aqueous sodium acetate and the $\mathrm{p}K_\mathrm{a}$ of **1** decreases with increase in temperature. However, the degree of dissociation of **1** increases, because the enthalpy of the $\mathrm{p}K_\mathrm{a}$ (Table 1) is larger than that of the pH. Consequently, a bathochromic colour change of **1** is observed. In methanolic sodium acetate, compound **1**, 1-hydroxyanthraquinone (**2**), 1-hydroxy-2-bromoanthraquinone (**3**), 1-hydroxy-2,4-dibromoanthraquinone (**4**), and 1-hydroxy-2-methylanthraquinone (**5**) also showed a bathochromic colour change since the enthalpy of the $\mathrm{p}K_\mathrm{a}$ values of these compounds in methanol (Table 1) is lower than that of the pH($-\log[\mathrm{CH_3OH_2^+}]$) of the methanolic sodium acetate.

On the basis of the above consideration, pH indicators would be expected to show a similar thermochromism. The colour change of the pH indicators shown in Table 2 was examined in methanolic sodium acetate. Since the ΔH value of Bromothymol Blue (BTB) is less than that of the 1-hydroxyanthraquinones as shown in Table 1, the temperature dependence

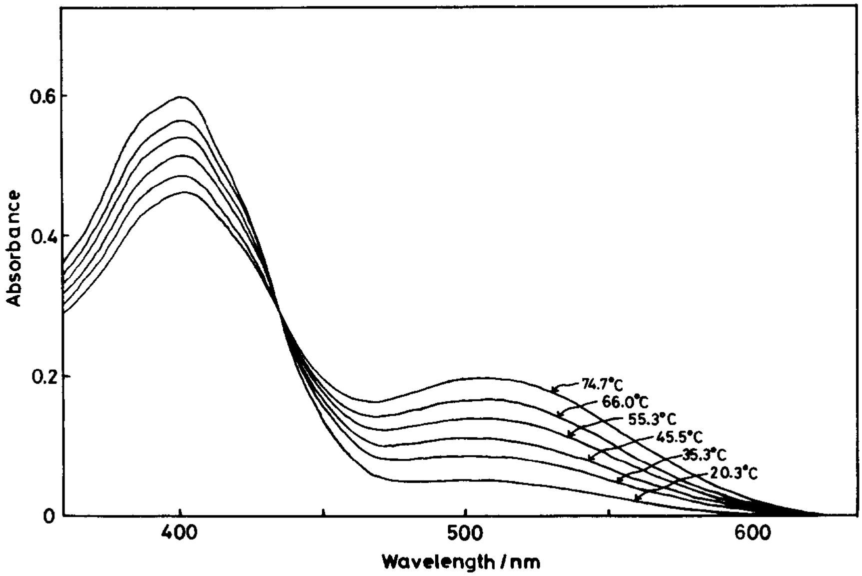
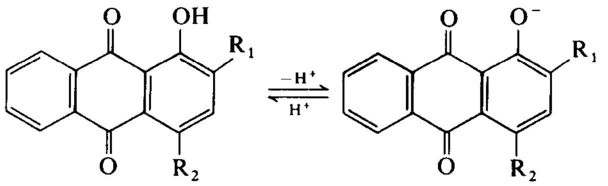


Fig. 2. Absorption spectrum of **1** in aqueous sodium acetate. $[\mathbf{1}] = 1{\cdot}00 \times 10^{-4}$ mol dm^{-3}, $[CH_3COONa] = 0{\cdot}301$ mol dm^{-3}.

TABLE 1

Thermodynamic Quantities for the Acid Ionization of 1-Hydroxyanthraquinones and Bromothymol Blue[a]



Compound	*Solvent*	*ΔH* (*kJ mol^{-1}*)	*ΔS* (*J K^{-1} mol^{-1}*)	*pK$_a$ (25°C)*
1 $R_1 = SO_3Na$	H_2O	34	−65	9·3
$R_2 = H$	MeOH	37	−125	13·0
2 $R_1 = R_2 = H$	MeOH	35	−154	14·2
3 $R_1 = Br$ $R_2 = H$	MeOH	34	−130	12·7
4 $R_1 = R_2 = Br$	MeOH	33	−123	12·3
5 $R_1 = CH_3$ $R_2 = H$	MeOH	40	−152	15·1
Bromothymol	MeOH	19	−176	12·5

[a] The plots of pK_a vs $1/T$ were linear in the range of about 10–60°C, where the pK_a values had been measured. The enthalpies and entropies of ionization were calculated from the slopes and intercepts of the straight lines, respectively.

TABLE 2

Colour Changes of Indicators in Methanol[a]

Indicator	*In methanolic sodium acetate* 20°C	60°C	*In methanolic triethylamine* 20°C	60°C
Bromothymol Blue	Yellowish green	Green	Blue	Green
Phenol Red	Orange	Reddish orange	Red	Orange
Cresol Red	Orange	Dark orange	Red	Yellowish orange
Thymolphthalein	Yellowish green	Yellowish green	Blue	Green[b]
Phenolphthalein	Pale pink	Pink	Pink	Pale pink[b]

[a] The hues of solution are dependent on the concentrations of indicator and base. The colour changes listed here are only examples.

[b] A small amount of water was added to make the indicator dissociate.

of the degree of dissociation of BTB is not as large as with the 1-hydroxyanthraquinones. The faint colour change of the solution of the other pH indicators is also considered to be caused by the lower ΔH value.

By comparing the enthalpy of the ionization of dyes with that of pH, the lowest values of ΔH of ionization of the dyes which show a bathochromic shift with increase in temperature is estimated to be about 26 kJ mol^{-1} in aqueous sodium acetate and about 20 kJ mol^{-1} in methanolic sodium acetate, respectively.

2.2 Thermochromism in solution of triethylamine

In a medium which has a large decrease in basicity with rise of temperature the degree of dissociation of the dyes should be depressed.

The pH of aqueous amine is expressed by eqn (2), where K_a^{ac} must be replaced by the dissociation constant of the conjugate acid of the amine, $K_a^{H^+}$. The enthalpy of pH was evaluated as 47·6 kJ mol^{-1} by use of the enthalpy of p$K_a^{H^+}$ of the triethylammonium ion obtained from the linear plot of p$K_a^{H^+}$ vs $1/T$ over the temperature range from 20°C to 45°C.[8]

Since the enthalpy of pH of aqueous triethylamine, 47·6 kJ mol^{-1}, is larger than that of compound **1**, the degree of dissociation of **1** is lowered with temperature rise in aqueous triethylamine. The aqueous solution of **1** was observed to change colour from orange to yellow in the presence of triethylamine with increase in temperature. Since the small decrease in the pK_a of the dye is favourable in this case, a small ΔH is preferable. The upper limit of ΔH of ionization of dyes showing a hypsochromic shift in aqueous triethylamine is estimated to be about 47 kJ mol^{-1} on the basis of the enthalpy of pH of aqueous triethylamine. The methanolic solutions of the 1-hydroxyanthraquinones (**1**–**5**) also changed colour in the presence of

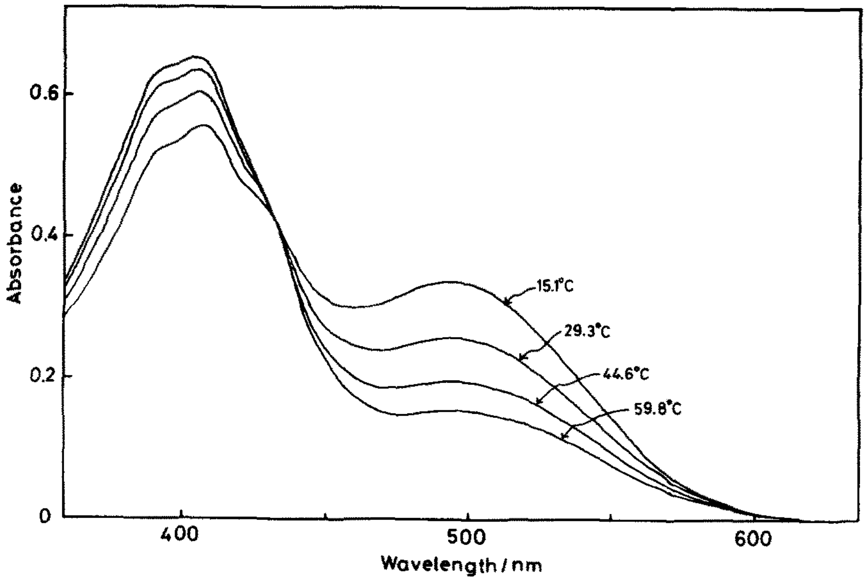


Fig. 3. Absorption spectrum of **3** in methanolic triethylamine. [**3**] = $1{\cdot}27 \times 10^{-4}$ mol dm^{-3}, [NEt$_3$] = $7{\cdot}19 \times 10^{-3}$ mol dm^{-3}.

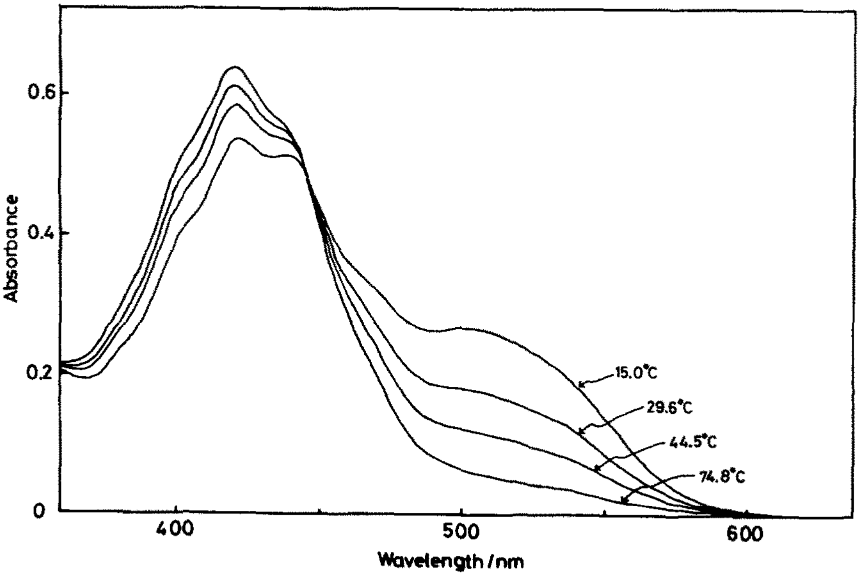


Fig. 4. Absorption spectrum of **4** in toluene solution of triethylamine. [**4**] = $1{\cdot}03 \times 10^{-4}$ mol dm^{-3}, [NEt$_3$] = $2{\cdot}2$ mol dm^{-3}.

triethylamine, similar to those of aqueous solution of **1**. The spectral change of **3** is shown in Fig. 3 as an example.

The spectral change of **4** in toluene was recorded in the presence of triethylamine (Fig. 4). A reversible colour change between orange (lower temperature) and yellow (higher temperature) was observed. The equilibrium constant of complex formation between AH and NEt_3 (eqn (4)) in toluene indicates that increase in temperature displaces the equilibrium to the left, thus resulting in a colour change (Table 3).

$$AH + NEt_3 \rightleftharpoons [A^- \cdots HN^+Et_3] \qquad (4)$$

The colour change of the methanolic solution of the pH indicators was also examined in the presence of triethylamine (Table 3). Reversible colour changes were observed similar to those found with the 1-hydroxyanthraquinones. Some of the pH indicators in toluene showed the reversible colour change in the presence of triethylamine. Bromocresol Green (BCG) displayed a remarkable spectral change (Fig. 5), the colour changing from purple at lower temperature to dark yellow at higher temperature. The solution of Bromophenol Blue also showed a reversible colour change from purple at lower temperature to light reddish yellow at higher temperature. As shown in Table 3, the equilibrium constant of the complex formation between BCG and triethylamine (eqn 4) indicates that increase in temperature displaces the equilibrium of the left, thus causing a similar

TABLE 3
Equilibrium Constants of Complex Formation of Compound **4** and Bromocresol Green with Triethylamine[a]

4		*Bromocresol Green*	
T (°C)	*K (dm^3 mol^{-1})*	*T (°C)*	*K (dm^3 mol^{-1})*
30·2	0·312	25·1	785
45·0	0·214	35·2	340
62·0	0·117	45·5	209
74·8	0·083	54·7	111
		64·8	71·6
		75·2	49·8

[a] The thermodynamic quantities for the complex formation obtained from the linear plot pK vs $1/T$ are as follows: $\Delta H = -26{\cdot}7\,kJ\,mol^{-1}$, $\Delta S = 97{\cdot}3\,J\,K^{-1}$ for **4**; $\Delta H = -47{\cdot}5\,kJ\,mol^{-1}$, $\Delta S = 105\,J\,K^{-1}\,mol^{-1}$ for Bromocresol Green.

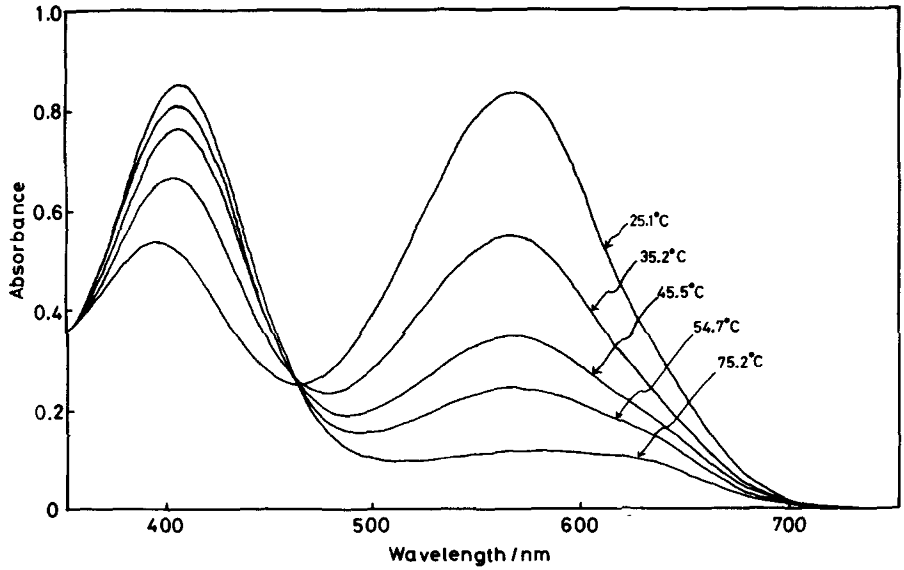


Fig. 5. Absorption spectrum of Bromocresol Green in toluene solution of triethylamine. [Bromocresol Green] = $5{\cdot}15 \times 10^{-5}$ mol dm^{-3}, [NEt_3] = $2{\cdot}04 \times 10^{-3}$ mol dm^{-3}.

colour change to that observed in compound **4**. The larger value of $-\Delta H$, 48 kJ mol^{-1} of the complex formation of BCG resulted in the remarkable spectral change of the solution, as shown in Fig. 5.

3 EXPERIMENTAL

3.1 Materials and solvents

Sodium 1-hydroxyanthraquinone-2-sulfonate (**1**) was obtained by the sulfonation of 1-hydroxyanthraquinone (**2**) in 20% oleum and subsequent salting out.[9] Compound **2** was prepared by the diazotization of 1-amino-anthraquinone followed by the decomposition in aqueous sulfuric acid.[10] 1-Hydroxy-2-bromoanthraquinone (**3**) and 1-hydroxy-2,4-dibromoanthraquinone (**4**) were synthesized by the bromination of **2** in acetic acid.[11,12] 1-Hydroxy-2-methylanthraquinone (**5**) was obtained by the photomethylation of **2**.[13] These compounds were purified by repeated recrystallization from appropriate solvents. The indicators, sodium acetate, triethylamine, and the other materials were of analytical grade and were used without further purification. Methanol was dried with magnesium and freed from basic impurities by distillation from sulfanilic acid. Toluene was purified by distillation using a Widmer fractionating column.

3.2 Measurements of absorption spectra and pH

Absorption spectra were recorded on a Shimadz Model UV-210 A spectrophotometer using glass cells maintained at constant temperature by a water-circulating device. Measurements of pH were made with a Denki Kagaku Keiki Model HG-3 pH-meter.

3.3 Determinations of pK_a and equilibrium constant of complex formation

The pK_a values of compound **1** in water were determined from the measurement of the absorption spectra in universal buffer mixtures[14] at an ionic strength of 0·3. The pK_a values of compounds **2** and **5** were also obtained from their spectra in methanolic sodium methoxide[15] and the values for the other compounds were estimated by the conventional indicator method using spectrophotometric measurements.

The equilibrium constants of the complex formation between compound **3** and triethylamine were estimated from Benesi–Hildebrant plots, and those of BCG were directly evaluated using the molar extinction coefficient of the complex at 562 nm.

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