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Thermochromism of Dyes on Silica Gel

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ABSTRACT

1-Hydroxyanthraquinone derivatives and some pH indicators showed thermochromism on silica gel, based on the shift in the acid-base equilibrium. In a lower temperature range, the degree of acid dissociation of the dyes increased with a rise in temperature, mainly based on the increase in the basic sites on silica gel resulting from the decreasing amount of water adhering on it. In a higher temperature range, on the other hand, the acid dissociation of the dyes with a rise in temperature was promoted by the increase in acidity of the dyes. © 1998 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

Many types of thermochromic organic compounds including organic complexes of metal ions are known, and the mechanisms of their thermochromic

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transitions have been reported [1–4]. The thermochromic transitions can be fundamentally classified into the following two categories:

1. thermochromism caused by structural changes in the compounds typically, exemplified by spiropyrans [1];
2. thermochromism due to a temperature change in the characteristics of the medium such as solvatochromism induced by a change in polarity of a solvent [5].

We have previously reported the thermochromism of some 1-hydroxyanthraquinones and some phthalein pH indicators in solutions of sodium acetate and of triethylamine [6]. Regarding the changes between the acid and basic forms of the dyes as structural changes, this thermochromism can be considered as a case of a combination of (1) and (2). We have demonstrated that the color change can be predicted to some extent, based on the thermodynamic parameters of the ionization of dyes and additives. A study has recently been reported on the quantitative prediction of temperature-dependent spectral changes of pH indicators [7]. We have found that hydroxyanthraquinone derivatives and some pH indicators exhibited thermochromism on silica gel with a color change which is considered to be based on the shift in the acid-base equilibrium. In this paper, we report the thermochromism of the dyes on silica gel from a mechanistic viewpoint of the thermochromic transition.

RESULTS AND DISCUSSION

Thermochromism of the dyes on silica gel

1-Hydroxyanthraquinone (**1**) and its derivatives 2-methyl (**2**), 2-bromo (**3**), 2,4-dibromo (**4**), and 4-nitroanthraquinone (**5**) changed their color from yellow∼orange to orange∼red on silica gel with a rise in temperature. Methyl Red (MR) and Neutral Red (NR) also showed a color change from red to yellowish orange on silica gel with increase in temperature. These color changes were reversible, and the colors at higher temperature reverted to the original color with decrease in temperature.

The 1-hydroxyanthraquinones showed a similar spectral change on silica gel with a change in temperature. For example, compound **5** showed a spectral change with rise in temperature, as shown in Fig. 1. The absorption near 470 nm increased, and that near 390 nm decreased, with an isosbestic point at 423 nm. The spectral change was reversible and the spectrum reverted to the original one with a drop in temperature. Dyes MR and NR also showed a

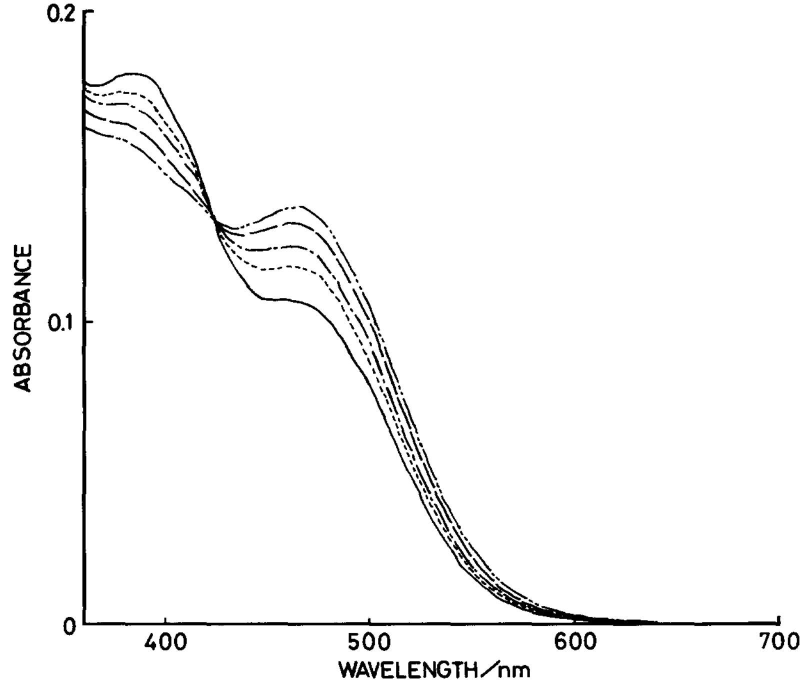


Fig. 1. Spectral change of 5 on silica gel with the rise in temperature. ——, 21.5°C; - - - -, 30.8°C; — - — -, 41.1°C; — —, 61.0°C; — - - —, 80.5°C.

reversible spectral change with a change in temperature, where the absorption near 390 nm (MR) and 440 nm (NR) increased, and that near 520 nm (MR) and 535 nm (NR) decreased, with rise in temperature (Fig. 2). The spectral change of NR had an isosbestic point at 454 nm, while no isosbestic point existed in the case of MR. The maximum wavelengths of absorption increasing with rise in temperature were estimated from the difference spectra between lower and higher temperature (Table 1); they were about the same as those of the basic form of the dyes in methanol. Therefore, the spectral changes of the dyes on silica gel are based on the shift of the acid-base equilibrium.

The following indicators (the pKa values of which in water at 25°C [8] are quoted in parentheses) were also examined: Methyl Orange (pKa = 3.40), Bromocresol Green (pKa = 4.68), Bromocresol Purple (pKa = 6.3), Phenol Red (pKa = 7.9), Phenolphthalein (pKa = 9.4), and Thimolphthalein (pKa = 10.0). Methyl Orange and Bromocresol Green did not change in color, and the other indicators showed a slight color change. The reason why Methyl Orange and Bromocresol Green are not thermochromic is considered to be that the acidity of these indicators is strong enough for them to convert

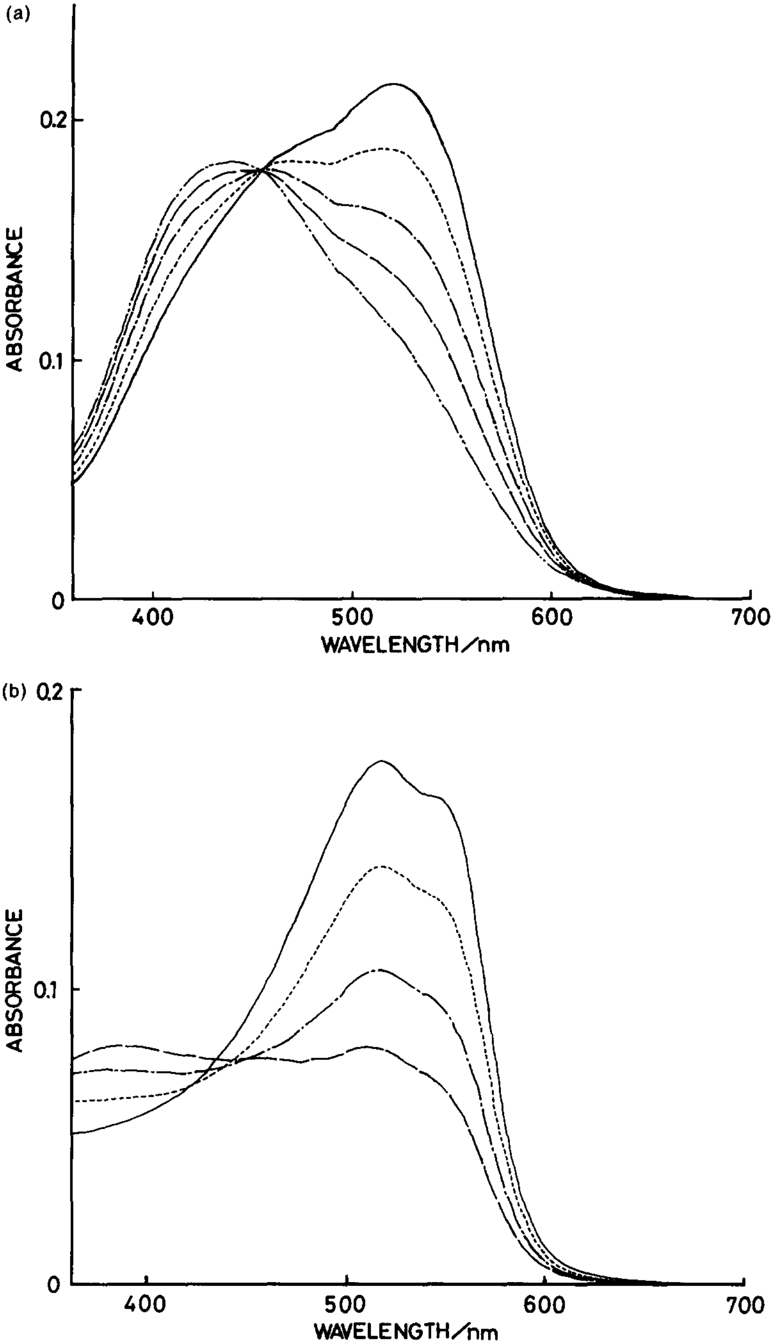
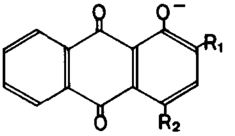


Fig. 2. Spectral change of NR and MR on silica gel with the rise in temperature. (a) NR: ——, 21.0°C; - - - -, 29.9°C; — - —, 40.0°C; — —, 50.8°C; — - - —, 70.6°C. (b) MR: ——, 20.2°C; - - - - - - -, 41.3°C; — - —, 61.0°C; — —, 81.3°C.

TABLE 1
Maximum Absorption Wavelength of Basic Form of the Dyes



Compounds	λ_{max} (nm) Estimated from differential spectra on silica gel	λ_{max} (nm) Basic form in methanol
1 $R_1 = R_2 = H$	475	485
2 $R_1 = CH_3$, $R_2 = H$	490	—[a]
3 $R_1 = Br$, $R_2 = H$	479	487
4 $R_1 = R_2 = Br$	488	493
5 $R_1 = H$, $R_2 = NO_2$	468	482
Neutral Red (NR)	411	447
Methyl Red (MR)	375	398

[a] Because of low acidity, the spectrum of the basic form was difficult to be measured.

completely into their basic forms on silica gel, even at low temperature. The pKa values of MR and NR in water at 25°C are 4.95 [8] and 7.4 [8], respectively.

Assuming that the pKa values on silica gel are parallel to those in water, Bromocresol Purple was expected to reveal a clear color change. However, as noted above, it showed only a slight color change. The results for the phthaleins and sulphonphthaleins reveal that these indicators are insufficiently thermochromic. A structural change after ring opening is necessary for these indicators to be colored in their basic form. This structural change may be considerably restricted in the adsorbed state on silica gel. The insufficient thermochromic character of the phthaleins and sulphonphthaleins may be caused by this structural restriction in the adsorbed state on silica gel. On the other hand, only deprotonation, which easily occurs, is needed for the 1-hydroxyanthraquinones MR and NR, to be colored in their basic form.

Analysis of absorption spectra of the dyes

To estimate the dependency of the acid-base equilibrium of the dyes with change in temperature, the following analytical procedure for the absorption spectra was carried out.

$$AH \rightleftharpoons A^- \quad (1)$$

In the acid-base equilibrium [eqn (1)], when the analytical concentration and degree of dissociation of the dye are C_0 and α, respectively, the absorbances at wavelengths of λ_1 and λ_2 are expressed by eqns (2) and (3).

$$\mathrm{A}_{\lambda 1} = C_0\varepsilon_{\mathrm{AH}}^{\lambda 1}(1-\alpha) + C_0\varepsilon_{\mathrm{A}^-}^{\lambda 1} - \alpha \tag{2}$$

$$\mathrm{A}_{\lambda 2} = C_0\varepsilon_{\mathrm{AH}}^{\lambda 2}(1-\alpha) + C_0\varepsilon_{\mathrm{A}^-}^{\lambda 2} - \alpha \tag{3}$$

where $\varepsilon_{\mathrm{AH}}$ and ε_{A} are the extinction coefficients of AH and A^-.

The relation between the differences in the absorbances at λ_1 and λ_2 ($D_{\lambda 1}$ and $D_{\lambda 2}$) accompanied by a change in the degree of dye dissociation from α_0 to α_1 is derived from eqns (2) and (3) as eqn (4).

$$D_{\lambda 1} = \frac{\left(\varepsilon_{\mathrm{A}-}^{\lambda 1} - \varepsilon_{\mathrm{AH}}^{\lambda 1}\right)}{\left(\varepsilon_{\mathrm{A}-}^{\lambda 2} - \varepsilon_{\mathrm{AH}}^{\lambda 2}\right)} D_{\lambda 2} \tag{4}$$

When $D_{\lambda 2}$ in eqn (4) is substituted by $-\mathrm{A}_{\lambda 2}\left(= -C_0\varepsilon_{\mathrm{AH}}^{\lambda 2} - C_0\alpha_0\left(\varepsilon_{\mathrm{A}-}^{\lambda 2} - \varepsilon_{\mathrm{AH}}^{\lambda 2}\right)\right)$, the negative value of $\mathrm{A}_{\lambda 2}$ at $\alpha = \alpha_0$, then the value of $D_{\lambda 1}$ obtained, $D'_{\lambda 1}$ is expressed as eqn (5):

$$D'_{\lambda 1} = -C_0\left(\varepsilon_{\mathrm{A}-}^{\lambda 1} - \varepsilon_{\mathrm{AH}}^{\lambda 1}\right)\left(\frac{\varepsilon_{\mathrm{AH}}^{\lambda 2}}{\varepsilon_{\mathrm{A}-}^{\lambda 2} - \varepsilon_{\mathrm{AH}}^{\lambda 2}} - \alpha_0\right) \tag{5}$$

From the summation of $\mathrm{A}_{\lambda 1}^0$, the value of $\mathrm{A}_{\lambda 1}$ at $\alpha = \alpha_0$, and $D'_{\lambda 1}$, the following two relations are obtained:

$$C_0\varepsilon_{\mathrm{AH}}^{\lambda 2} = \frac{D'_{\lambda 1} + \mathrm{A}_{\lambda 1}^0}{a - \beta} \tag{6}$$

and

$$C_0\varepsilon_{\mathrm{A}-}^{\lambda 2} = \frac{D'_{\lambda 1} + \mathrm{A}_{\lambda 1}^0}{b - \beta} \tag{7}$$

where $a = \varepsilon_{\mathrm{AH}}^{\lambda 1}/\varepsilon_{\mathrm{AH}}^{\lambda 2}$, $b = \varepsilon_{\mathrm{A}-}^{\lambda 1}/\varepsilon_{\mathrm{A}-}^{\lambda 2}$, and $\beta = \left(\varepsilon_{\mathrm{A}-}^{\lambda 1} - \varepsilon_{\mathrm{AH}}^{\lambda 1}\right)/\varepsilon_{\mathrm{A}-}^{\lambda 2} - \varepsilon_{\mathrm{AH}}^{\lambda 2})$. The degree of dissociation of the dye, α, is derived from eqn (3) as eqn (8):

$$\alpha = \frac{A_{\lambda 2} - \varepsilon^{\lambda 2}_{AH}}{C_0\left(\varepsilon^{\lambda 2}_{A-} - \varepsilon^{\lambda 2}_{AH}\right)} \qquad (8)$$

and then α is estimated from the values of $C_0\varepsilon^{\lambda 2}_{AH}$ and $C_0\varepsilon^{\lambda 2}_{A-}$, which are calculated by eqns (6) and (7), and $A_{\lambda 2}$.

In the case of the 1-hydroxyanthraquinones, because of the existence of the wavelength λ_2 where $\varepsilon^{\lambda 2}_{AH} = 0$ in the measurement range, eqns (7) and (8) are reduced to eqns (9) and (10), respectively.

$$C_0\varepsilon^{\lambda 2}_{A-} = \frac{D'_{\lambda 1} + A^0_{\lambda 1}}{b - \gamma} \qquad (9)$$

where $\gamma = \left(\varepsilon^{\lambda 1}_{A-} - \varepsilon^{\lambda 1}_{AH}\right)/\varepsilon^{\lambda 2}_{A-}$ and

$$\alpha = A_{\lambda 2}/C_0\varepsilon^{\lambda 2}_{A-} \qquad (10)$$

$D_{\lambda 1}$ and $D_{\lambda 2}$ were obtained based on the absorbances at the lowest temperature in the measurement range. Plots of $D_{\lambda 1}$ vs $D_{\lambda 2}$ were found to be linear and passing through the origin except for Methyl Red, in which case the linear plot broke at about 40°C. Because of the absence of an isosbestic point in the spectral change (Fig. 2), the absorption coefficient of Methyl Red seems apparently to change at about this temperature. The temperature dependence of the degree of dissociation of the dyes is shown in Fig. 3.

The pKa values of the 1-hydroxyanthraquinones in methanol at 20°C are 14.3 (**1**)*, 15.3 (**2**, 16°C)*, 12.8 (**3**)*, 12.4 (**4**)*, and 12.2 (**5**)† and those at 63°C are 13.6 (**1**)*, 14.3 (**2**)*, 12.1 (**3**)*, 11.7 (**4**)* and 11.6 (**5**)†. The order of the pKa values between 20 and 63°C is unchanged†**. Therefore, the order of the degrees of dissociation in Fig. 3 is considered to reflect that of acidity in methanol, except **5** for the 1-hydroxyanthraquinones. Although the reason for the disorder of **5** is not clear, the electron-withdrawing property of the nitro group at the **4** position might not sufficiently emerge, or the basic form of **5** on silica gel might not be as stable as that in methanol.

MR is expected to show a higher degree of dissociation than that of NR, if the acidity of the former indicator is considered higher than that of the latter, which is considerably based on the pKa values in water as described above. Dye NR, however, showed a higher degree of dissociation than that of dye MR, contrary to the presumption. Because the acid form of MR has two

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*Tajma, M., unpublished data..

†See footnote to Table 2.

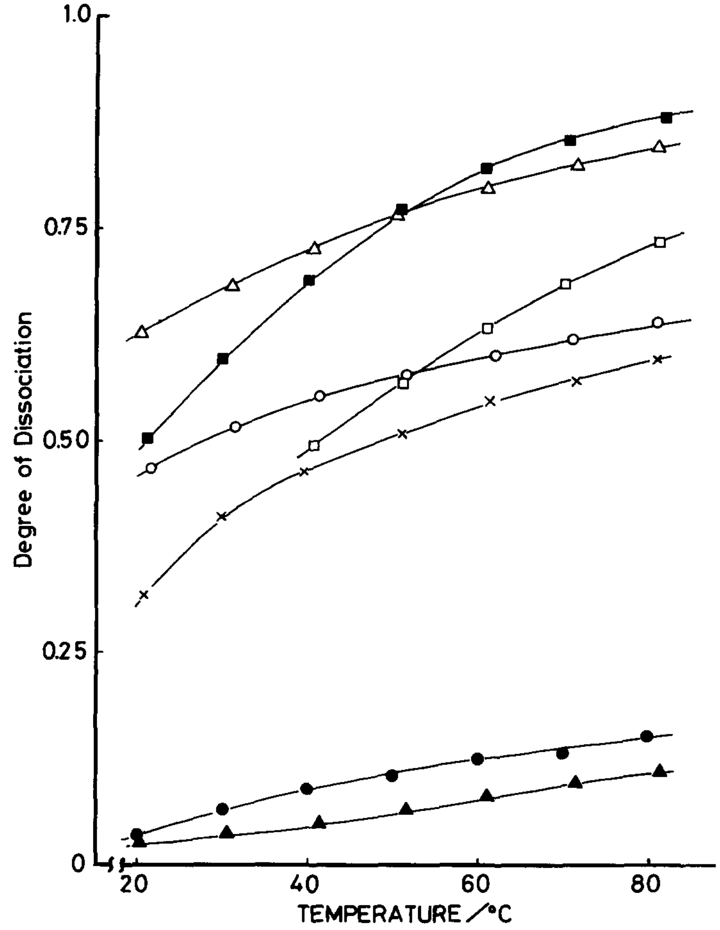

Fig. 3. Temperature dependence of the degree of dissociation of the dyes. ●, 1; ▲, 2; ×, 3; △, 4; ○, 5; ■, NR; □, MR.

parts, a carboxyl group and a protonated diazo group, which strongly adsorb on silica gel, it may be more stable than the acid form of NR.

Driving force for the shift in the acid-base equilibrium

Let the acidic and basic sites on silica gel be expressed as Acid and Base. Because the numbers of Acid and Base sites are considered large enough to be unchanged even after the dye's dissociation, the acid-base equilibrium of the dye on silica gel is expressed as

$$AH + \mathrm{Base} \rightleftharpoons A^- + \mathrm{Acid} \qquad (11)$$

Therefore, the equilibrium constant, K, is

$$K = \frac{[\mathrm{AH}][\mathrm{Base}]}{[\mathrm{A}^-][\mathrm{Acid}]} = \frac{\alpha[\mathrm{Base}]}{1 - \alpha[\mathrm{Acid}]} \tag{12}$$

where α is the degree of dissociation of the dye. From the logarithm of eqn (12), the following equation is derived:

$$\ln\frac{\alpha}{1-\alpha} = \ln K - \ln\frac{[\mathrm{Base}]}{[\mathrm{Acid}]} = -\frac{\Delta\mathrm{H}}{\mathrm{R}T} + \frac{\Delta\mathrm{S}}{\mathrm{R}} - \ln\frac{[\mathrm{Base}]}{[\mathrm{Acid}]} \tag{13}$$

When ΔH, ΔS and the value of [Base]/[Acid] are constant, regardless of temperature, the relation between $\ln\{\alpha/(1-\alpha)\}$ and $1/T$ is expected to be linear.

As shown in Fig. 4, the plots of $\ln(\alpha/(1-\alpha)\}$ vs $1/T$ tend to deviate downward from a linear relation below 30~40°C. In particular, **1**, **5**, and NR show a pronounced deviation. Because it is reasonable to assume that the thermodynamic quantities for the acid-base equilibrium are independent of temperature in a narrow range (which is at least assured in methanol for the anthraquinones [6]*) the deviations are considered to be referred to the change in [Base]/[Acid] with that of temperature. By considering that the value of [Base]/[Acid] increases with the rise in temperature up to 30~40°C and becomes constant above this temperature, the deviations can be explained. That is to say, the increase in the degree of dissociation up to 30~40°C is mainly caused by that of the basic site on silica gel, and the increment above 30~40°C is contributed by that of the dyes' acidity with increase in temperature.

The result of DSC measurement of the silica gel used showed an endothermic process centered at ca 30°C (Fig. 5), and this is considered to indicate that water adhering on the silica gel is released at about this temperature. The increase in basic sites as a result of releasing water below 40°C is a promotive force for large acid dissociation of the dyes. In spite of the temperature, samples situated under nitrogen after evacuation for 30 min at room temperature to release water adhering on silica gel actually showed unchanged absorption spectra, which corresponds to the state at higher temperature in air. The reason why the plot of $D_{\lambda 1}$ vs $D_{\lambda 2}$ for Methyl Red

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*See footnote to Table 2.

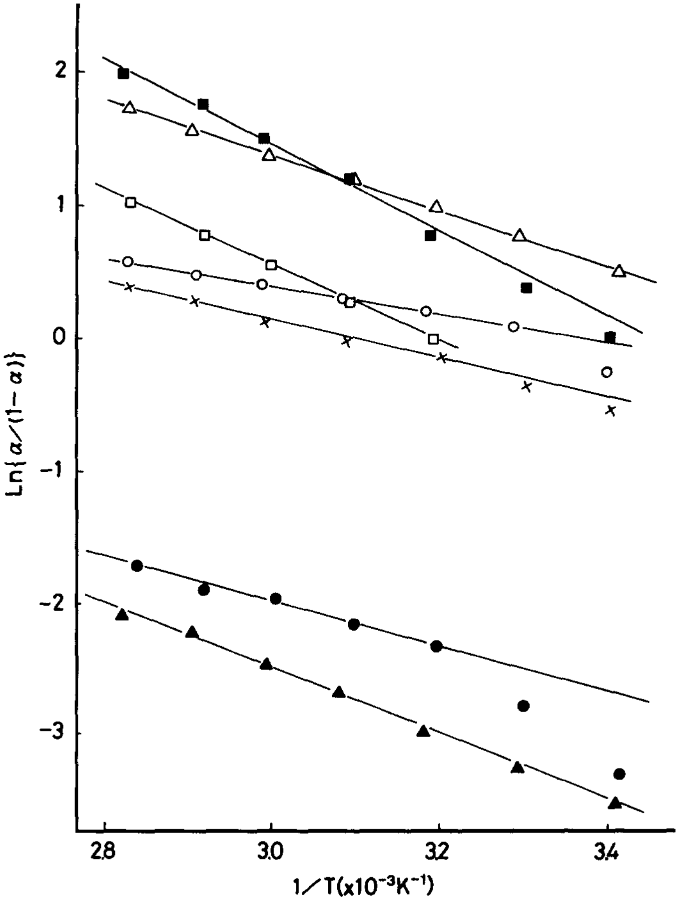

Fig. 4. Plots of $\ln\{\alpha/(1-\alpha)\}$ vs $1/T$. ●, 1; ▲, 2; ×, 3; △, 4; ○, 5; ■, NR; □, MR.

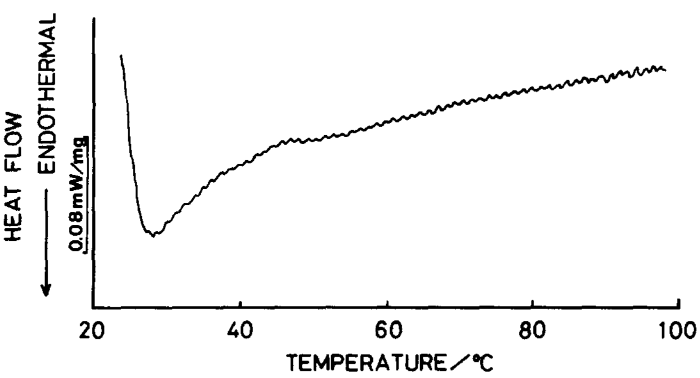

Fig. 5. DSC curve of silica gel.

broke at about 40°C might be the apparent change in the absorption coefficients based on the environmental change as a result of the release of water. The enthaplies of acid ionization of the 1-hydroxyanthraquinones obtained from the linear part of the plots (Fig. 4) are compared with those in methanol in Table 2. The order of magnitude of the enthaplies on silica gel is

$$2 > 4 > 1 \geq 3 > 5$$

which is considered to substantially correspond to the order in methanol

$$2 > 1 \geq 3 \geq 4 > 5$$

This supports the fact that the change of the dissociation of the dyes above 30~40°C is due to that of the acidity of the dyes.

EXPERIMENTAL

Materials

1-Hydroxyanthraquinone (**1**) and its derivatives, 2-methyl (**2**), 2-bromo (**3**), and 2,4-dibromoanthraquinone (**4**), were prepared by methods described elsewhere [6] [9]. 1-Hydroxy-4-nitroanthraquinone (**5**) was synthesized by the nitration of **1** in the presence of boric acid [10]. These compounds were purified by column chromatography and recrystallization. Methyl Red (guaranteed reagent, Junsi Pure Chemicals Co., Ltd.) was used without further purification. The basic form of Neutral Red (3-amino-6-dimethylamino-2-methylphenazine) was obtained as a precipitate by basifying an aqueous solution of Neutral Red (Tokyo Kasei Kogyo Co., Ltd.). The resulting precipitate was washed and dried.

TABLE 2
Enthalpies of the Acid Ionization of 1-Hydroxyanthraquinones

Compounds	ΔH ($kJ mol^{-1}$)	
	On silica gel	*In methanol [6]*
1	13	35
2	21	40
3	12	34
4	17	33
5	8.5	30[a]

[a] Estimated for the temperature range from 10 to 63°C by a conventional indicator method using a spectrometric measurement adopting bromothymol blue the pKa of which had been known [6] as a standard. The resulting pKa values were 12.5 (10°C), 12.3 (20°C), 12.2 (25°C), 12.0 (35°C), 11.9 (45°C), 11.8 (56°C) and 11.6 (63°C). Plot of pKa vs $1/T$ was linear.

Other indicators of guaranteed reagent grade (Kanto Chemicals Co., Inc.) were used without further purification. Silica gel for t.l.c contained no binder (Wakogel B-0, Wako Pure Chemical Industries, Ltd.). Benzene was dried over calcium chloride and distilled using of a Widmer fraction column. Methanol was dried with magnesium and freed from basic impurities by distillation from sulfanilic acid.

Sample preparation

A thin layer of silica gel about 0.3 mm in thickness was made on a glass plate. Adsorption of the dyes was carried out by soaking the plate once in benzene solutions of the dyes, the concentrations of which were 1×10^{-3} mol dm^{-3} for the anthraquinone derivatives and 1×10^{-4} mol dm^{-3} for Methyl Red and the basic form of neutral red. Methanol, or a mixture of methanol and benzene, was used for dyes insoluble in benzene. The silica gel thin-layer plate prepared using 10% aqueous sodium hydroxide was used for adsorption of only the basic form of the dyes. Silica gel thin-layer plates adsorbing the acidic form of Methyl Red and that of Neutral Red, were obtained by soaking the plate treated with a mixture of benzene and acetic acid (9:1) in benzene solutions of the indicators.

Measurement of absorption spectra

Absorption spectra were recorded on a Shimadzu Multipurpose Spectrophotometer MPS-2000, using glass cells maintained at a constant temperature by a water-circulating device. The temperature range of the measurement was from 20 to 80°C.

Measurement of DSC

A DSC measurement of silica gel was carried out in air atmosphere using a Shimadzu Differential Scanning Calorimeter DSC-50 at a heating rate of 1°C min^{-1}.

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