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Evaluation of disperse dye sublimation via gas chromatography

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Abstract

Gas chromatography has been examined as a method for characterising the sublimation property of disperse dyes. In this regard, the vapor pressure of azo and anthraquinone dyes were recorded and the Arrhenius plots utilising the experimental vapor pressures formed straight lines. Heats of sublimation (ΔH_{sub}) and heats of vaporization (ΔH_{vap}) were calculated using experimental data from GC measurements and were compared with ΔH_{sub} and ΔH_{vap} values obtained from previous methods. The results indicate that vapor pressure values arising from the GC method were only slightly different from the values measured by the Knudsen effusion and transpiration methods. It is believed that the observed differences are due to irregularities in the crystalline state of dyes in the methods employed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sublimation; Disperse dye; Gas chromatography; Heat of sublimation; Vapor pressure

1. Introduction

Vapor pressure and heat of sublimation data for disperse dyes provide important information for studies involving thermal transfer printing and supercritical fluid dyeing, both of which continue to attract attention. The vapor pressures of compounds that have low vapor pressures (e.g. disperse dyes) are difficult to determine at high levels of accuracy, unless special techniques such as the Knudsen effusion [1,2], Knudsen torque [3,4], or transpiration method [5,6] are employed.

In previous work from our laboratories, we reported results from dye sublimation into polyester films using microcapsules containing disperse dyes and a ferromagnetic material [7,8]. To further develop this technology, we decided that it would be worthwhile to study the sublimation behavior of disperse dyes inside the microcapsule, with the development of a method for dyeing textiles using these microcapsules in mind.

The temperature dependency of vapor (sublimation) pressure of a given compound is expressed by the Eq. (1) [5,6,9]. Thus, the slope of the Arrhenius plots for the sublimation pressure measured at each temperature gives the heat of sublimation below the melting point and the heat

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of vaporization at temperatures above the melting point.

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1}$$

where P = vapor pressure (Pa) and ΔH = heat of sublimation (J/mol)

Further, Eq. (1) and the entropy change (ΔS) of sublimation may be related to Eq. (2):

$$\Delta S = \frac{\Delta H + \{RT \ln(P/P_0)}{T} \tag{2}$$

In the present study, measurements of sublimation pressure and vaporization pressure for model and commercial disperse dyes have been conducted, using data from gas chromatography [10] and calculated heats of sublimation. We have studied the sublimation behavior of disperse dyes, by comparing the vapor pressure and heats of sublimation values obtained from our GC method with those obtained using conventional methods.

2. Experimental

2.1. General

A gas chromatography G180 (Yanagimoto Co., Ltd.) instrument equipped with a dual pass system was used, and nitrogen or helium was utilized as the carrier gas. The flow rate of carrier gas was measured by using a soap film flowmeter and vapor pressure measurements were conducted using a 15–40 ml/min flow rate. A gas chromatopack C-R1B data processor (Shimazu Works Co., Ltd.) was used.

For vapor pressure measurements, glass columns of 3 mm diameter and 10, 20, 50 and 75 cm lengths were used on the sample and reference sides. Flusin GH glass beads (60–80 mm mesh, GL Sciences Co., Ltd.) were used as the stationary phase. To enhance peak resolution, we used Chromosorb W AW-DMCS (60–80 mesh), from Yanagimoto Co., Ltd.) coated with polystyrene (3% w/w).

4-*N*,*N*-Dimethylaminoazobenzene (*p*-DMAAB) was employed as a model compound using the following experimental conditions: sample solution = 0.033 mol/l(EtOH), injected amount = 0.6–8.0×10^{-3} ml, column temperature = 170 °C, column length = 20 cm, and the flow rate of carrier gas (helium) = 40 (ml/min).

The experimental disperse dyes had purities of 95–99%, and the commercial dyes were used after Soxhlet extraction with acetone and recrystalisation from ethanol (azo dyes) or benzene (anthraquinone dyes). Where necessary, the dyes were used after purification by column chromatography. Acetone (Ace), *N*,*N*-dimethylformamide (DMF), and ethyl alcohol (EtOH) were analytical grade.

2.2. DSC measurements

A DSC2O differential scanning calorimeter (Seiko Electronic Industry Co., Ltd.) was used to measure the heats of fusion. Approximately 2 mg of dye were used and the measurements were conducted under a N_2 gas flow, raising the temperature at 10 °C/min. ΔH_{melt} values were calculated from the peak areas using Eq. (3).

$$\Delta H_{\mathrm{melt}} = \frac{S}{m} \times \frac{C}{v} \times \frac{Y}{D} \tag{3}$$

ΔH_{melt} = heat of fusion (mJ/mg), S = peak area (cm^2), m = amount of sample (mg), C = 60 (s/min), v = chart speed (cm/min), Y = range (mJ/s), and D = chart paper width (cm).

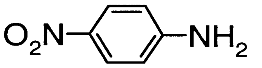
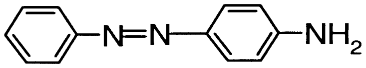
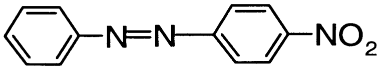
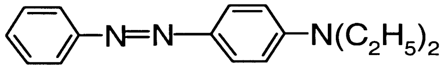
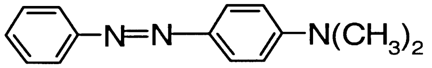
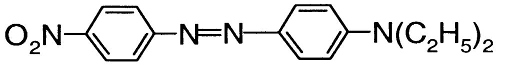
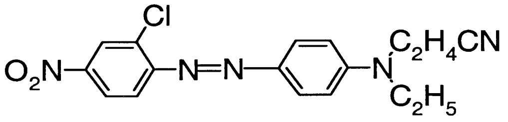
3. Results and discussion

Structures of compounds used in this study are given in Tables 1 and 2, and vapor pressure data are given in Table 3. Arrhenius plots derived from the vapor pressure data gave a linear graph (Figs. 1 and 2). Values for A and B in Eq. (4) were determined using the method of least squares. The resultant data are summarised in Tables 4 and 5 along with ΔH and ΔS values.

$$\ln P = B - \frac{A}{T} \tag{4}$$

P = vapor pressure (Pa),
A and B = constants

Table 1
Characteristics of model disperse dyes (monoazo compounds) and disperse dyes used

Dye No.	Code	Formula	Mol wt.	M.p.[a] (°C)	Solvent
p-Nitroaniline **1**	*p*-NA		138	148 [9]	Ace
p-Aminoazobenzene **2**	*p*-AAB		197	124 [11]	DMF
p-Nitroazobenzene **3**	*p*-NAB		227	132–134 [12]	DMF
4-*N*,*N*-Diethylaminoazobenzene **4**	*p*-DEAAB		253	97–98 [12]	EtOH
4-*N*,*N*-Dimethylaminoazobenzene **5**	*p*-DMAAB		225	117 [9]	EtOH
4′-Nitro-4-*N*,*N*-diethylaminoazobenzene **6**	NDEAAB		298	150–151 [6]	DMF
C.I. Disperse Red 50 **7**	Red 50		358	140[b]	Ace

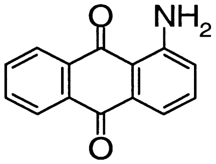
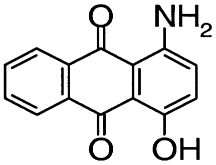
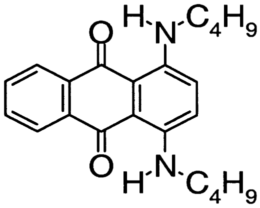
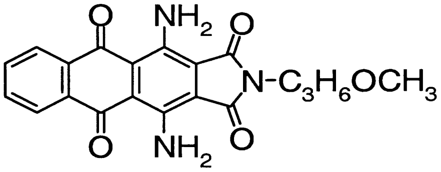
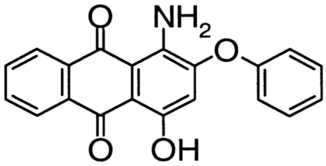
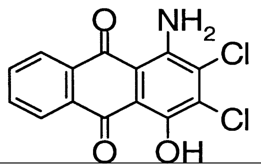
[a] Ref.
[b] Measured data.

3.1. Monoazo dyes

When a comparison of heats of sublimation values for compounds **1**–**13** using the transpiration [6,14], Knudsen effusion [9], and GC methods was made only small differences were apparent. A comparison of our results involving the temperature dependence of disperse dye vapor pressure with data from the literature [6,9,14] was also made. In this regard, we found that the vapor pressure of compound **1** was 19.6 Pa at 125 °C, a value that is significantly smaller than the value obtained using the transpiration method [6], but only slightly smaller than the value reported using the Knudsen effusion method [9] (Table 3). The vapor pressure we obtained for compound **2** was 7.23 Pa at 120 °C, which was larger than the value obtained using the transpiration method [6] and the Knudsen effusion method [9]. Similar comparisons were made for the other compounds employed in this study and the results of those comparisons indicated that there was no significant difference between the values of vapor pressure obtained by the GC method and those by other methods (Table 3), though some dyes give slightly different values from prior literature.

Some comparisons of heats of fusion data obtained via GC analysis and differential scanning calorimetry (DSC) measurements are given in Table 6. It can be seen that the heats of fusion values are quite close in the case of *p*-AAB, but significantly less so in the case of the anthraquinone dye Red 50. The reason for the observed differences may be that the compounds are dissolved in a solvent for GC studies, whereas DSC studies are conducted in the crystalline state. In this regard, the crystalline nature of disperse dyes is known to affect vapor pressure [16]. Like DSC analysis, the Knudsen effusion and transpiration methods

Table 2
Characteristics of model disperse dyes (anthraquinone compounds) and disperse dyes used

Dye No.	Code	Formula	Mol wt.	M.p.[a] (°C)	Solvent
1-Aminoanthraquinone **8**	1-AAQ		223	251–252 [13]	DMF
1-Amino-4-hydroxyanthraquinone **9**	1-A-4-HAQ		239	210–211 [11]	Ace
C.I. Solvent Blue 35 **10**	Blue 35		351	120–122 [12]	DMF
C.I. Disperse Blue 60 **11**	Blue 60		365	183[b]	DMF
C.I. Disperse Red 60 **12**	Red 60		331	183–184 [5]	DMF
C.I. Disperse Violet 28 **13**	Violet 28		307	292[b]	DMF

[a] Ref.

[b] Measured data.

measure the vapor pressure of dyes in their crystallized state.

We also found that the heat of sublimation values obtained via the GC method were comparable to those from other methods (Table 4). It was determined, for example, that compound **7** had a vapor pressure of 0.44 Pa at 200 °C, which is lower (0.58×) than the value (0.76 Pa) using the transpiration method and was lower by a factor of 0.59 than the value obtained at 150 °C using this method [14]. This constant difference in vapor pressure as a function of temperature suggests that

Table 3
Comparison of vapor pressure values (Pa) for compounds used in this study

Compound	Temperature (°C)	Transpiration[a]	Knudsen effusion[b]	GC
1	125	26.9	20.6	19.6
2	120	5.70	5.34	7.23
3	115	4.60	–[c]	6.61
4	95	0.26	–	0.26
5	95	–	0.35	0.34
6	130	0.079	0.086	0.079
7	150	0.032	–	0.019
8	150	1.34	0.98	1.30
9	160	1.85	1.94	1.51
10	200	–	–	3.30
11	200	–	–	0.26
12	200	2.94	–	2.53
13	200	–	–	1.95

[a] Refs. [5–6,14].
[b] Refs. [1,2,9,15].
[c] Blank shows no data in Ref.

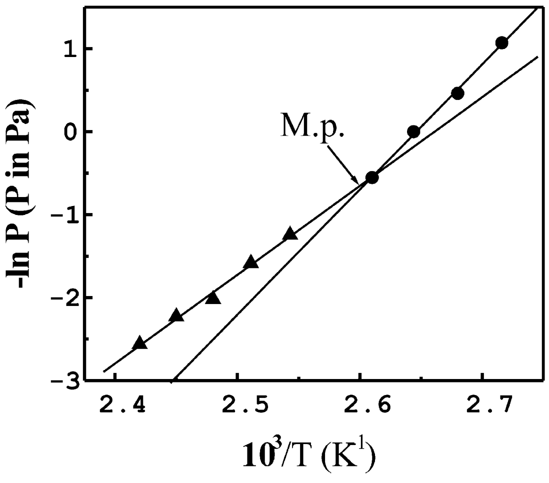


Fig. 1. Plots of −ln P against $10^3/T$ for *p*-DMAAB.

the difference between the heat of sublimation values obtained via GC and transpiration measurements is not significant.

3.2. Anthraquinone dyes

With regard to anthraquinone dyes, the vapor pressure values obtained from GC experiments were compared with data from the transpiration and Knudsen effusion methods [6,15]. Dye **8** had a vapor pressure of 1.30 Pa at 150 °C, which is nearly equal to the value from the transpiration method [6] but larger than the value from the Knudsen effusion method [15] (Table 3). The vapor pressure we obtained for dye **9** at 160 °C was smaller than the values from either the transpiration method [6] or Knudsen effusion method [15]. However, dyes **8** and **9** gave heats of sublimation values from GC experiments that were quite similar to those obtained from the transpiration and Knudsen effusion methods [6,15]. These results suggest that the present vapor pressure changes are influenced by temperature, as observed for the azo dyes employed in this study.

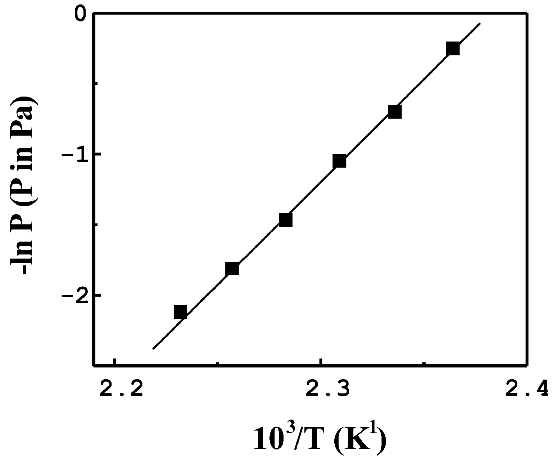


Fig. 2. Plots of −ln P against $10^3/T$ for 1-AAQ.

In heat transfer printing and dyeing processes utilizing microcapsules, the sublimation behavior of dyes at 200 °C is commercially important. In the present study, the vapor pressures of azo dye **7** and anthraquinone dyes **10**–**13** were found to be 0.26–3.30 Pa. These values are nearly equal to those calculated from the vapor pressure temperature dependency equation for azo [14] and anthraquinone [5] commercial disperse dyes. It was also found that disperse dyes **12** and **13** gave smaller heats of sublimation than anthraquinone dyes **8** and **9**, despite the larger molecular weight of the former dyes. This indicates that intermolecular forces are stronger between molecules

Table 4
Thermodynamic properties of monoazo disperse dyes

No.	Code	Range of temperature (°C)	A[a]	B[a]	r[b]	Method[c]	Ref.	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/mol K)
1	*p*-NA	125–145	11,823	32.68	0.9982	G		98.3	175.9
						T	6	94.6	168.6
		73–93				E	9	97.5	
2	*p*-AAB	100–120	11,280	30.68	0.9993	G		93.8	159.2
						T	6	106.3	188.7
		83–100				E	9	110.9	
		130–170	9084	25.26	0.999	G		75.5[e]	114.2[e]
3	*p*-NAB	100–115	12,653	34.50	0.995	G		105.2	191.0
		90—120[d]				T	6	110.0	200.4
4	*p*-DEAAB	80–95	15,790	41.55	0.9999	G		131.3	249.6
						T	6	132.2	249.4
		100–120	12,159	31.63	0.9999	G		101.1[e]	167.1[e]
5	*p*-DMAAB	95–110	15,070	39.88	0.9987	G		125.3	235.7
		86–108				E	9	120.9	
		120–140	10,696	28.46	0.9961	G		88.9[e]	140.8[e]
6	NDEAAB	130–145	18,842	44.21	0.9982	G		156.6	271.7
						T	6	146.0	245.2
		155–175	11,404	25.07	0.9884	G		94.8[e]	112.6[e]
7	Red 50	125–135	15,289	32.33	0.9999	G		127.1	173.0
		150–230	12,617	25.85	0.9995	G		104.9[e]	119.1[e]
						T	14	105.0[e]	121.0[e]

[a] See Eq. (4).
[b] Correlation coefficient given by linear regression.
[c] Measurement method: G = gas chromatography, T = transpiration, E = Knudsen effusion.
[d] Values obtained by the reverse calculation from Ref. 6.
[e] Values from vaporization of liquid.

Table 5
Thermodynamic properties of anthraquinone disperse dyes

No.	Code	Range of temperature (°C)	A[a]	B[a]	r[b]	Method[c]	Ref.	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/mol K)
8	1-AAQ	150–170	14,571	34.71	0.9994	G		121.1	192.7
						T	6	121.8	194.6
		140–156				E	15	125.6	
		255–275	12,130	28.47	0.9985	G		100.8[d]	140.9[d]
9	1-A-4-HAQ	160–180	15,548	36.32	0.9955	G		129.3	206.1
						T	6	127.2	203.3
		146–165				E	15	135.6	
10	Blue 35	125–190	13,147	28.99	0.997	G		109.3[d]	145.2[d]
11	Blue 60	190–240	12,763	25.62	0.999	G		106.1[d]	117.2
12	Red 60	150–175	12,622	27.49	0.9997	G		104.9	132.7
						T	5	103.8	132.2
		195–230	11,642	25.54	0.9992	G		96.8[d]	116.5[d]
13	Violet 28	100–220	7806	17.17	0.9949	G		64.9	46.9

[a] See Eq. (4).
[b] Correlation coefficient given by linear regression.
[c] Measurement method: G = gas chromatography, T = transpiration, E = Knudsen effusion.
[d] Values from vaporization of liquid.

Table 6
The comparison of heats of fusion from (GC) and DSC methods

	ΔH_{melt} (kJ/mol)	
Code	GC method	DSC method
p-AAB	18.5	18.1
p-DEAAB	29.8	25.7
Red 50	22.1	31.2
1-AAQ	20.1	26.3

of dyes **8** and **9** than dyes **12** and **13**. In this regard, it has been suggested that dispersion forces are predominant in anthraquinone dyes and that the presence of hydrogen bonds can play a vital role in dye properties [6].

4. Conclusions

It has been shown that gas chromatography is an effective method for assessing the sublimation properties of disperse dyes. Further, it has been shown that heats of sublimation can be determined from the temperature dependency of the sublimation pressure data generated by this method.

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