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Color Photographic Development Accelerators. Part IV: Adsorption of Hydrazines Containing the 1,3,4-Thiadiazole Heterocyclic System on Silver Halides

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ABSTRACT

In order to clarify the nature of the interaction with silver halides of the selective-development accelerators based on hydrazines containing a 1,3,4-thiadiazole system, the adsorption of these compounds on silver chloride and bromide was studied. The results of the measurement of adsorption isotherms, values of heat of adsorption, and the saturation maximum of adsorbate indicated that the compounds chemically interact with the surface of silver halides.

1 INTRODUCTION

Hydrazine compounds are known to act as development accelerators and behave as selective-development accelerators to increase the photographic speed if a 1,3,4-thiadiazole moiety is introduced into the molecule.[1] Information about the adsorption of the functionalized hydrazine compound on silver halide would therefore be helpful in understanding the mechanism of the development acceleration.

In this work, the adsorption behaviour on silver halides of selective-development accelerators of the above type was studied by examining

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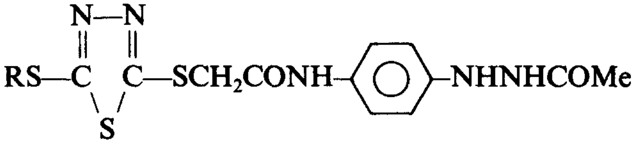
their adsorption isotherms and heats of adsorption. The results obtained are helpful in the understanding of the nature of the interaction between the compounds and the surface of silver halide grains.

2 EXPERIMENTAL

The functionalized hydrazine compounds used in the study are as follows:



Compound	R
1	Me
2	Et
3	n-Bu
4	n-hexyl

For comparison, the adsorption behaviour of *N*'-formyl-*N*-phenylhydrazine (Compound 5) was also studied under the same experimental conditions.

Compounds 1–4 and the reference compound 5 were prepared according to the reported procedures.[1,2] Silver halide grains used were prepared as follows: 1 liter of 1N aqueous silver nitrate was added dropwise into 1·2 liter of 1N aqueous potassium halide at 25°C. After washing to remove small particles, the precipitate that deposited at the bottom of the vessel was collected, dried, and used for the experiments. IR data confirmed the absence of water and nitrate ion in the samples.

The surface area of grains can be measured by various methods.[3] In this present study, the surface area of the silver halide powder was measured by using the BET method, on a Micromeritics ASAP 2400 instrument, and assessing the adsorption of nitrogen gas onto it at liquid-nitrogen temperature.

Compounds 1–5 were absorbed onto the silver halide powder in the following way: 1 g of the silver halide powder and 5 ml of the compound in ethanol (of known concentration) were placed in an airtight vessel; the solution was agitated for more than 6 h at 25°C and the solution was then separated from the solid by centrifuging. The decrease in the concentration of the solution of the test compound gave the amount of the compound adsorbed on the powder. Ultra-violet spectral measurements of the solutions were made by using a Hewlett Packard U-8451A Spectrophotometer, and quantitative measurements of the concentration of solutions of the compounds were made with a Shimadzu UV-120-02 Spectrophotometer.

TABLE 1
Ultra-violet Spectral Data of Compounds 1–5 in Ethanol

Compound	λ_{max} (nm)	ε_{max} (at 25°C) $\times 10^{-4}(M^{-1}\ cm^{-1})$
1	282	1·90
2	276	2·03
3	280	2·03
4	271	2·01
5	232	0·65

3 RESULTS AND DISCUSSION

3.1 General data

The measured surface areas of the silver halide grains were as follows: silver chloride: 0·87 m^2/g; silver bromide: 0·97 m^2/g. The ultra-violet spectral data of Compounds 1–5 are shown in Table 1.

3.2 Adsorption isotherms

Adsorption isotherms of Compounds 1–5 on silver halides from their ethanolic solutions were plotted as the amount of the compounds adsorbed per gram of silver halide against the equilibrium concentration of the compounds (Figs 1 and 2).

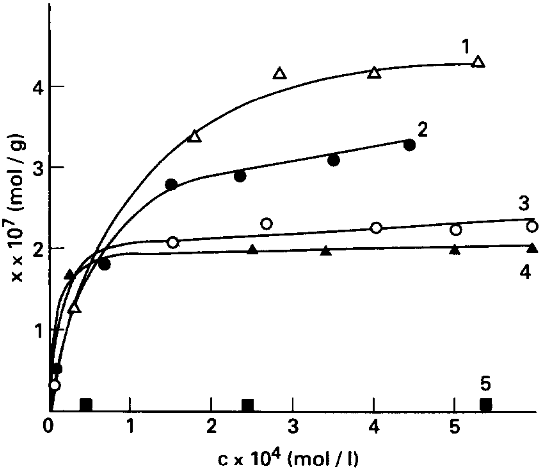


Fig. 1. Isotherm of the adsorption of compounds 1–5 on AgCl powder from ethanolic solution.

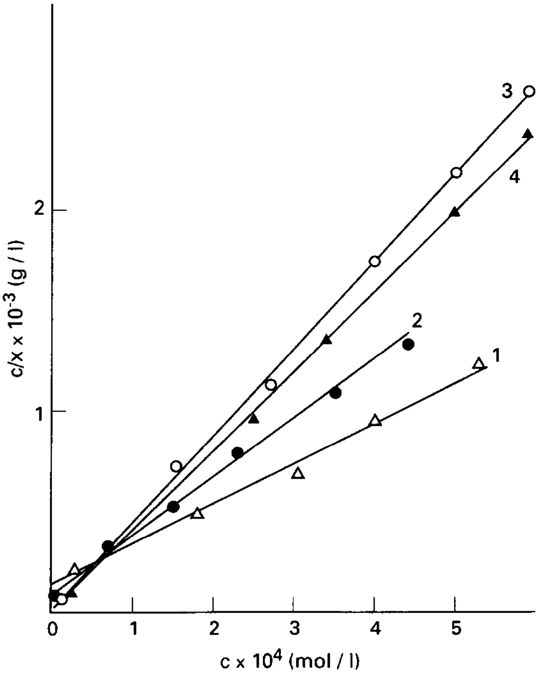


Fig. 2. Langmuir plots for the adsorption of compounds 1–4 on AgCl powder from ethanolic solution.

Figures 1 and 2 show that the adsorption isotherms of compounds 1–4 on silver chloride and silver bromide grains fit the Langmuir isotherm. The relationship between the concentration of free compound in equilibrium and the amount of adsorbed compound is thus expected to be given by eqn (1).

$$\frac{c}{x} = \frac{c}{M} + \frac{b}{M} \tag{1}$$

where c is the concentration of free compound in equilibrium;
x is the amount of the compound adsorbed on silver halide grains;
M is the value of the saturation maximum of the adsorbed compound; and
b is a constant.

In the case of the reference compound 5, no adsorption phenomena was observed, as is shown in Figs 1 and 2.

The results in Figs 3 and 4 indicate a linear relationship between c/x and c, which supports the applicability of eqn. (1) to the adsorption of

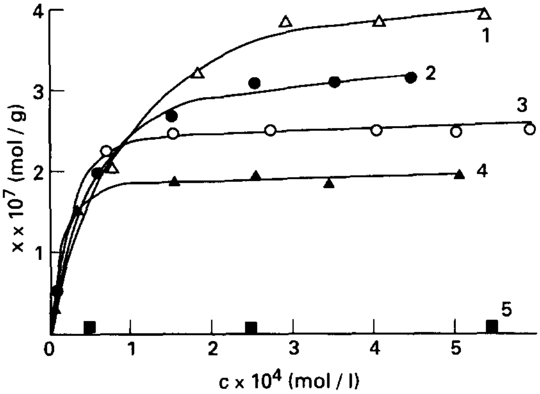


Fig. 3. Isotherms of the adsorption of compounds 1–5 on AgBr powder from ethanolic solution.

compounds 1–4 on silver chloride and silver bromide grains. The slopes of the straight lines in Figs 3 and 4 give the values for the saturation maximum of the adsorbed compounds and the areas occupied by each compound on silver chloride and silver bromide grains, respectively. The relevant results are given in Table 2.

The results in Table 2 indicate that the value of the saturation maximum of adsorption depends on the length of the alkyl chain in the compound. The longer the alkyl chain, the smaller is the value of the saturation maximum. These results may explain why the development acceleration

TABLE 2
Saturation Maximum and Area Occupied by Compounds 1–4 Adsorbed on Silver Chloride and Silver Bromide

Compound	Saturation maximum of adsorbate $\times 10^7$ (mol/g)	$\times 10^7$ (mol/m^2)	Area occupied by one molecule (Å^2)
Adsorbent: AgCl			
1	5·00	6·17	269
2	3·45	4·26	390
3	2·38	2·94	565
4	2·00	2·47	672
Adsorbent: AgBr			
1	4·54	4·68	355
2	3·38	3·48	477
3	2·63	2·71	613
4	1·96	2·02	822

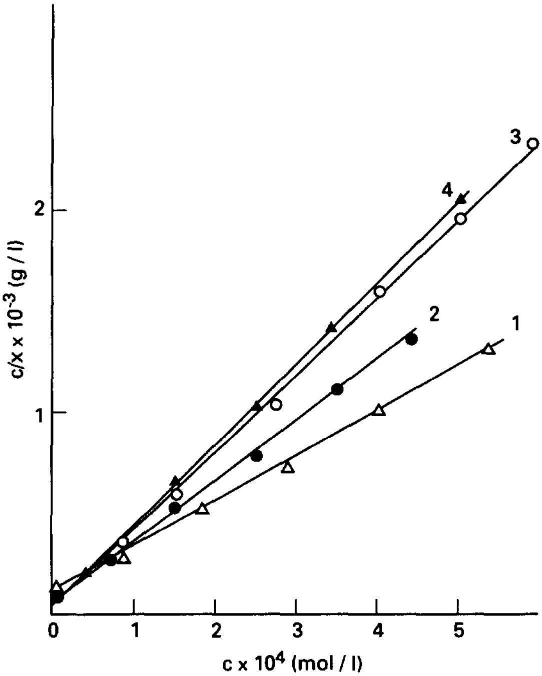


Fig. 4. Langmuir plots for the adsorption of compounds 1–4 on AgBr powder from ethanolic solution.

of the compound becomes weaker with an increase in the length of the alkyl chain when the compound is incorporated into a colour-negative photographic material.[1]

Usually, the adsorption of organic-compound molecules on silver halide is classified into three types: flat-on, edge-on, and end-on.[4] By assuming that the compound molecules are adsorbed on the surface of the adsorbent forming a monomolecular layer, the area occupied by one compound molecule should be as shown in Table 3.

On the basis of the data in Tables 2 and 3, the adsorption of compounds 1–4 on silver chloride and silver bromide are thought to be ascribed to the flat-on type of adsorption.

3.3 Heat of adsorption

As mentioned in Section 3.2, the adsorption isotherms of compounds 1–4 on silver halides fit the Langmuir isotherm. The plot of c/x against c therefore gives a straight line that intersects with the ordinate at a point at which the value for c/x is positive, as can be seen in Figs 3 and 4.

TABLE 3
Area Occupied by One Molecule for Compounds 1—4

Compound	Area occupied by one molecule (Å^2)[a]		
	Flat-on	Edge-on	End-on
1	97	32	9
2	101	33	9
3	114	37	9
4	125	41	9

[a] Calculated according to the average values of bond lengths and bond angles of each compound.[5]

According to eqn (2), proposed by Eucken,[6] the heat of adsorption of the compounds on silver halides can be calculated:

$$Q = -2{\cdot}3RT \log\left(\frac{b}{M}2ra\right) \tag{2}$$

In eqn (2), b/M has the same value as that of c/x at the intersecting point, and $2ra$ is the width of the adsorption layer of the molecule of the compound on the surface of the silver halide, as given in Table 4. On the assumption that compounds 1–4 are adsorbed on silver halide according to the Langmuir isotherm, the heats of adsorption of the compounds were calculated by using eqn (2) and are listed in Table 5.

According to previous investigations,[7] by the nature of the interaction between an organic compound and silver halide can be reflected by the heat of adsorption. If the compound is absorbed on silver halide by physical forces, the heat of absorption of the compound will depend on the polarizability of the compound and adsorbent. Thus the larger the polarizability of the compound and absorbent, the greater is the heat of adsorption of the compound. The results shown in Table 5 are not in accord with this and imply that compounds 1–4 are adsorbed on silver halide by some chemical interaction. Investigation of the chemical

TABLE 4
Width of the Adsorption Layer for Flat-on Type of Adsorption of Compounds 1—4 on the Surface of Silver Halide

Compound	1	2	3	4
Width of adsorption layer (Å)[a]	18·6	19·3	21·9	24·0

[a] Calculated according to the average values of bond lengths and angles of each compound.[5]

TABLE 5
Heat of Adsorption of Compounds 1—4 Adsorbed on Silver Halide

Compound	Heat of adsorption (kcal/mol)	
	AgCl	AgBr
1	14·2	14·1
2	14·4	14·4
3	14·9	14·6
4	15·2	14·7

properties of 1,3,4-thiadiazole derivatives has shown that the heterocyclic system may be co-ordinated to the silver ion by both the N and S atoms in the heterocyclic ring.[8] It is therefore concluded that the interaction between the compounds 1–4 and silver halides may be ascribed to complexation of the 1,3,4-thiadiazole heterocyclic system in the compounds examined with the silver ion on the surface of the silver halide grains.

4 CONCLUSIONS

Hydrazine compounds containing the 1,3,4-thiadiazole heterocyclic system are adsorbed from their ethanolic solutions onto the surface of silver halide grains according to the Langmuir isotherm and form a monomolecular adsorbed layer on the surface of the grains. Determination of heats of adsorption indicated that the compounds examined in this work are adsorbed on the surface of silver halides by chemical interactions.

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