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Influence of non-stoichiometry of sulphides on adsorption isotherms of dyes

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Abstract. Depending on their non-stoichiometry, sulphides are classified as n-type or p-type semiconductors. Adsorption of dyes from aqueous and non-aqueous solutions has been made use of to study the surface characteristics of solid adsorbents. Their use in flotation as collectors or depressants is also reported. Adsorption of anionic tartrazine on CdS-doped Ag_2S shows a lower value compared to undoped Ag_2S. The dye adsorption characteristics on these sulphides has been explained on the basis of their defect-structures.

Keywords. Non-stoichiometry; dye adsorption; isotherms.

1. Introduction

Minerals can be separated by flotation if the surface of the particles can be made selectively hydrophobic by use of surfactants (e.g. collectors) which are selectively adsorbed. Any organic acid, base or salts may be suitable as collectors, if it has specific reactivity, dispersibility and availability (Gaudin 1957). Non-ionic agents are also used as collectors. A number of dyes have been used as flotation collectors (Spedden 1951) and depressants (Taggart 1954; Schubert 1981). Adsorption of dyes from aqueous and non-aqueous solutions is also used to study the surface characteristics of solid adsorbents.

The present study reports the adsorption behaviour of tartrazine (an anionic dye) and safranine-T (a cationic dye) on n-type sulphides such as Ag_2S, Ag_2S doped with CdS and ZnS and a p-type sulphide such as PbS. Safranine-T has been found to float sulphide minerals effectively (Sengupta *et al* 1988).

2. Experimental

2.1 *Materials*

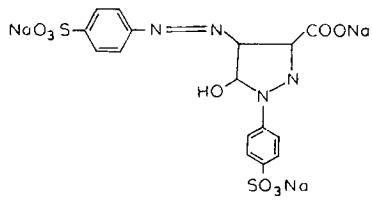
Ag_2S (Mellor 1961) was prepared by passing H_2S gas into a solution of $AgNO_3$. In order to dope Ag_2S with CdS, a specific quantity of $AgNO_3$ solution was added to get a product containing 0·1 wt.% CdS. ZnS was prepared (Mellor 1963) from an ammoniacal solution of $ZnCl_2$ which was precipitated as ZnS by adding a solution of Na_2S held in an ice bath. PbS was prepared (Rao *et al* 1976) from a solution of lead acetate. Lead was precipitated as PbS in the ice bath by adding Na_2S solution.

All the sulphides were thoroughly washed, dried at 343 K, stored in well-stoppered bottles and kept in a dessicator.

Semiconductor types were determined for ZnS and PbS using a hot probe method (Balachandran *et al* 1987). The circuit consisted of a galvanometer connected in series with a copper plate which carried the sulphide specimen in the form of a pellet

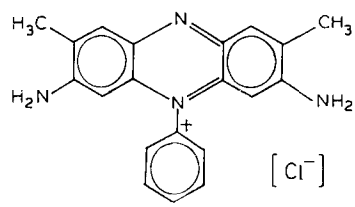
and electrically heated probe. The difference in temperature across the specimen generated a thermoelectric-emf which caused the current to flow. The direction of the current flow indicated the semiconductor type. The above measurement indicated that ZnS was an n-type semiconductor and PbS used for the study was p-type semiconductor.

The anionic dye used in the study was tartrazine (GR). Its structure is shown below:



$C_{16}H_9N_4Na_3O_9S_2$ (mol. wt 534·37).

This dye has a molecular area of 471 Å^2 (Orr 1950). The cationic dye used is safranine-T with the following structure



$C_{20}H_{19}N_4Cl$ (mol. wt 350).

The molecular area of safranine-T was reported to be 148 Å^2 (Mishra *et al* 1984).

Since the molecular areas of these dyes are larger than that of nitrogen, the BET method for the measurement of surface area was not used. The surface area was calculated from the size distribution data obtained on a sedigraph (Micromeritics Corporation, USA, model 5000D) using the method suggested by Allen (1963). However, measurements with a high speed surface area analyser (Micromeritics, USA, model 2200) based on BET principle showed zero area for Ag_2S as well as CdS-doped Ag_2S. Therefore, the surface areas for all the sulphides were calculated from the size distribution data and they were as follows: 1402, 1586, 4182 and 776 cm^2 g^{-1} for Ag_2S, Ag_2S doped with CdS, ZnS and PbS respectively.

2.2 *Adsorption measurement*

Adsorption of dyes from aqueous solutions has been determined by the difference between their concentrations before and after adsorption using a photoelectric colorimeter (Klett Summerson, USA). The time required for attaining equilibrium adsorption of the dyes and the time provided in the experiments are presented in table 1.

The amount of dye chemisorbed on Ag_2S, CdS-doped Ag_2S and PbS has been estimated by a difference method. After equilibrium adsorption of the dyes, the

Table 1. Time required for equilibrium adsorption of dyes.

Sample	Tartrazine adsorption: Minimum time requirement (h)	Tartrazine adsorption: Time provided (h)	Safranine-T adsorption: Minimum time requirement (h)	Safranine-T adsorption: Time provided (h)
Silver sulphide system	40	72	6	16
Zinc sulphide	48	96	24	48
Lead sulphide	60	120	40	72

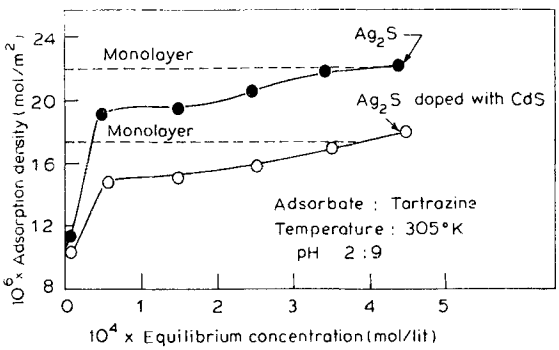


Figure 1. Adsorption isotherms of tartrazine on Ag_2S and its doped variety.

adsorbents were washed with distilled water till the washed water showed no coloration. The total dye content in the washed water was deducted from the initial amount to determine the amount of dye chemisorbed on the surfaces or not desorbed from the surface. In the case of ZnS, it was dissolved in 1:1 HCl after thorough washing. Chemisorption was estimated according to the method of Norman (1970).

3. Results

Adsorption isotherms of tartrazine on Ag_2S and CdS-doped Ag_2S are shown in figure 1. The pH of tartrazine in contact with the powder samples of Ag_2S and Ag_2S doped with CdS did not show any significant change within the range of dye concentration studied. The pH was around 2·9 for tartrazine and varied between 2·8 and 3·0 for safranine-T. The adsorption isotherms of safranine-T on Ag_2S and CdS-doped Ag_2S are shown in figure 2. In the case of tartrazine adsorption, isotherms for both the samples were of H-type according to the classification given by Giles *et al* (1960). The Langmuir plots (figure 3) were based on the equation

$$C/M = (C/M') + (b/a)(1/M'), \tag{1}$$

where C is the equilibrium concentration in mol/l, M the amount adsorbed in mol/g of the sample, M' the amount adsorbed to form a monolayer in mole/g of the sample and a, b the constants referring to monolayer adsorption. Figure 3 shows the plots between C/M in g/l vs C in mol/l. The monolayer capacities obtained from the

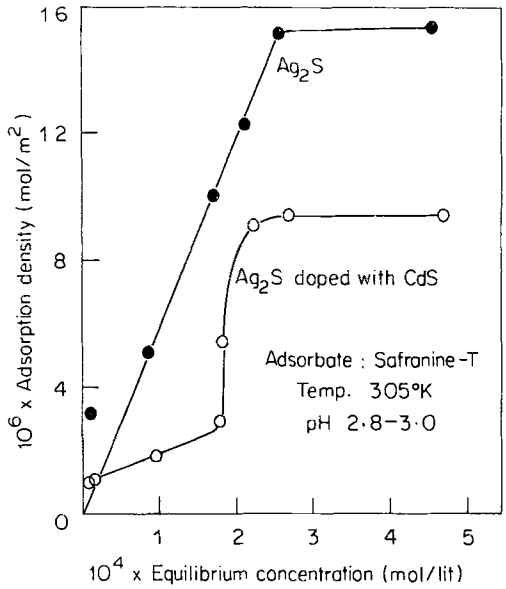


Figure 2. Adsorption isotherms of safranine-T on Ag_2S and its doped variety.

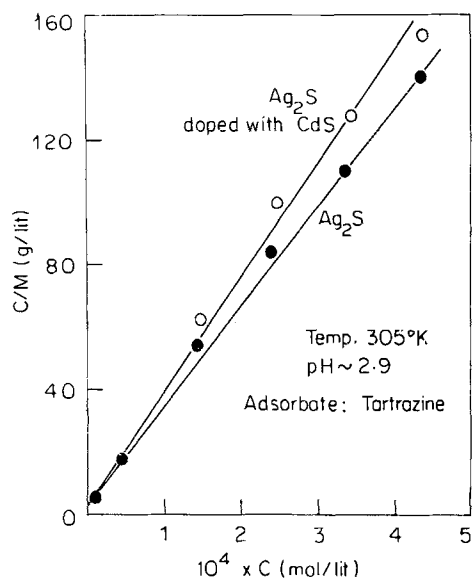


Figure 3. Langmuir plots for adsorption of tartrazine on Ag_2S and its doped variety.

(slope)$^{-1}$ of the straight lines in figure 3 were found to be $3{\cdot}0941 \times 10^{-6}$ and $2{\cdot}7503 \times 10^{-6}$ mol/g respectively or $22{\cdot}069 \times 10^{-6}$ and $17{\cdot}344 \times 10^{-6}$ mol m^{-2} respectively.

The adsorption isotherms of safranine-T on undoped Ag_2S (figure 2) closely resemble with C-type adsorption curve (Giles *et al* 1960). Beyond the equilibrium concentration of $2{\cdot}75 \times 10^{-4}$ mol/l, the adsorption reached a saturation and the

quantity adsorbed was $2{\cdot}13 \times 10^{-6}$ mol g^{-1} or $15{\cdot}27 \times 10^{-6}$ mol m^{-2}. The CdS-doped Ag_2S showed a two-stage adsorption of safranine-T. The first stage may be compared to C-type curve and around $1{\cdot}9 \times 10^{-4}$ mol/l of equilibrium concentration, it suddenly rises and shows a plateau region beyond $2{\cdot}2 \times 10^{-4}$ mol/l of equilibrium concentration. The amount of safranine-T adsorbed at this stage was $1{\cdot}48 \times 10^{-6}$ mol/g or $9{\cdot}31 \times 10^{-6}$ mol m^{-2}. It is seen that the isotherm of safranine-T does not follow (Sengupta 1985) any of the relations like Freundlich, Langmuir or BET.

The adsorption isotherms of tartrazine and safranine-T on ZnS depicted in figure 4 resemble with S-type curve (Giles *et al* 1960) and both of them follow a more or less Freundlich relation according to the following relation

$$\log(x/m) = \frac{1}{n}\log C + \log k, \tag{2}$$

where x is the amount adsorbed in g by 'm'g of adsorbent, C the equilibrium concentration in g/l and n, k the constants. Figure 5 shows plots between log C vs $\log(x/m)$ which gives slopes of about 1·43 and 1·36 respectively.

The adsorption isotherms of tartrazine and safranine-T on PbS are shown in figure 6. The tartrazine adsorption on PbS shows resemblance to L-type curve (Giles *et al* 1960) and follows a Langmuir relation (figure 5). The monolayer capacity as calculated from $(\text{slope})^{-1}$ is $3{\cdot}0 \times 10^{-5}$ mol/g or $38{\cdot}7 \times 10^{-5}$ mol m^{-2}. The adsorption isotherm of safranine-T on PbS resembles an S-type curve and follows more or less the Freundlich equation with a high slope value of 2·85 (figure 5). For Ag_2S system the pH was around 2·9. In the ZnS/tartrazine system, the pH was within 7·6 to 8·2 in which range the adsorption showed a constant value (Sengupta 1985) starting from 7·2. In the case of ZnS/safranine-T system, the pH was within 7·3 to 7·5 and the variation seen in adsorbed dye was insignificant. In the case of PbS, the pH was within 5·7 to 6·0. A summary of the results is given in table 3.

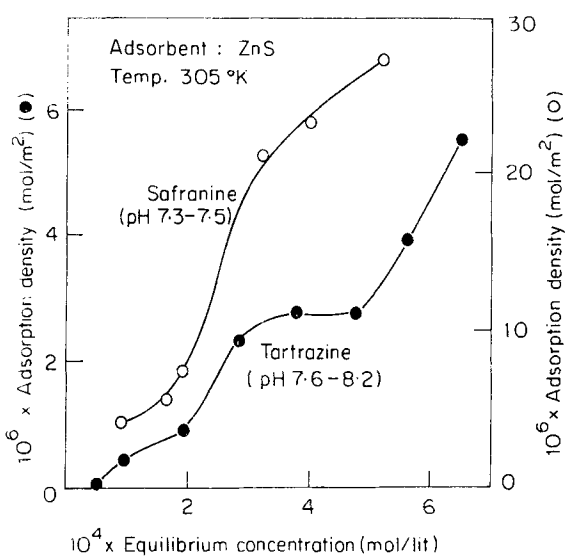


Figure 4. Adsorption isotherms of tartrazine and safranine-T on ZnS.

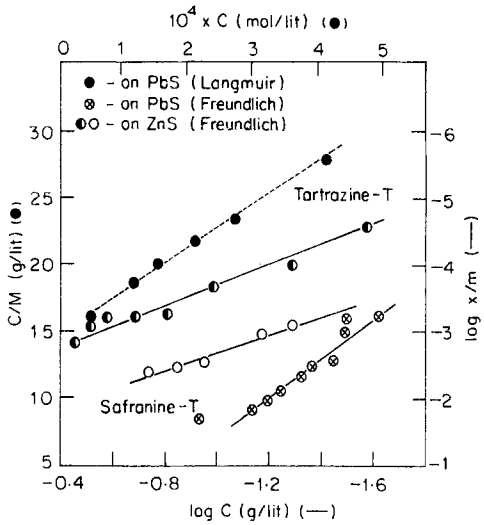


Figure 5. Freundlich and Langmuir plots for adsorption of dyes on ZnS and PbS.

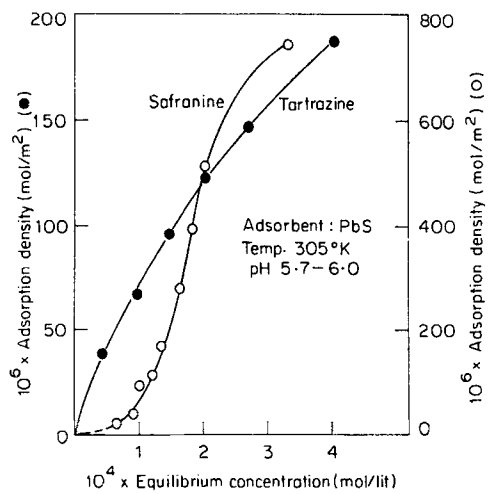


Figure 6. Adsorption isotherms of tartrazine and safranine-T on PbS.

4. Discussion

Adsorption isotherms of tartrazine on Ag_2S and Ag_2S doped with CdS appear to resemble with H-type curve (Giles *et al* 1960) characterizing a high affinity of tartrazine towards both Ag_2S and its doped variety. The chemisorption data (table 2) show that around 60% of the total adsorption is perhaps contributed by the chemisorption process. This implies that there may be some chemical binding force between Ag_2S and the anionic tartrazine. Ag_2S is an n-type semiconductor (Wagner 1953) with slight excess of silver ions and free electron. However, the excess silver ion is expected to occupy interstitial positions as suggested by Hauffe (1965). When Ag_2S

Table 2. Results on chemisorption of dyes on different sulphides.

Adsorbent	Adsorbate	Initial concentration (mol/l)	Total adsorption $\times 10^{-6}$ (mol/m^2)	Amount not desorbed by washing (mol/m^2)
Pure Ag_2S	T	3×10^{-4}	20·6	$12{\cdot}41 \times 10^{-6}$ (60·2%)
CdS-doped Ag_2S	T	3×10^{-4}	15·72	$8{\cdot}93 \times 10^{-6}$ (56·8%)
Pure Ag_2S	S	$2{\cdot}9934 \times 10^{-4}$	15·27	Negligible
CdS-doped Ag_2S	S	$2{\cdot}9934 \times 10^{-4}$	9·31	–do–
PbS	T	$1{\cdot}0769 \times 10^{-6}$	38·46	$15{\cdot}68 \times 10^{-6}$ (40·8%)
PbS	S	1×10^{-4}	20·67	$8{\cdot}28 \times 10^{-7}$ (4·0%)
ZnS	T	6×10^{-4}	3·91	Negligible
ZnS	S	$2{\cdot}1184 \times 10^{-4}$	5·67	$1{\cdot}43 \times 10^{-6}$ (25·3%)

T, tartrazine; S, safranine-T.

is doped with CdS, the defect equilibria may be written as

$$CdS = Cd^{\circ}_{Ag} + e' + S_S$$

or

$$CdS = Cd^{\circ}_{Ag} + V'_{Ag} + S_S,$$

where Cd°_{Ag}, e' and V'_{Ag} represent Cd^{2+} ion occupying Ag^+ ion position with a positive charge, a negatively charged electron and a negatively charged silver vacancy respectively. Excess electron and negatively charged cation vacancy created by doping is expected to decrease the adsorption of anionic tartrazine. The monolayer capacity as calculated from the Langmuir plots is, therefore, smaller for CdS-doped Ag_2S compared to undoped Ag_2S. Therefore the experimental results agree with the surface condition predicted due to the effects brought about by doping with higher valent metal ion.

The C-type curve obtained for the adsorption of safranine-T on Ag_2S is characterized by the constant partition of safranine-T between Ag_2S and dye solution up to the maximum possible adsorption. Such a curve indicates that as more safranine-T is adsorbed, more sites for adsorption are created. The process suddenly stops when highly crystalline regions of the substrate are reached and the isotherm shows a plateau region. This is attributed to the varying degree of crystallinity in Ag_2S system. However, such a curve appears mainly with textile fibres (Kipling 1965).

If the adsorption isotherms of tartrazine and safranine-T on Ag_2S and CdS-doped Ag_2S are compared, it is seen that both tartrazine (anionic) and safranine-T (cationic) are adsorbed less on CdS-doped Ag_2S than on undoped Ag_2S. The basic difference regarding adsorption of dyes as found from the experimental results is that the adsorption of tartrazine on Ag_2S system is perhaps governed mostly by chemisorption whereas the adsorption of safranine-T is purely a physisorption process. When the n-type Ag_2S is increased by Cd^{2+} doping, the surface prefers to adsorb more H^+ ions compared to the cationic dye leading to a decrease in the adsorption of cationic dye, whereas the negatively charged cation vacancies or excess

Table 3. Summary of the results on adsorption of anionic and cationic dyes on sulphides.

		Tartrazine adsorption				Safranine-T adsorption			
Sulphides (semi-conductor type)	Defect	Type of curve	Fits with	Monolayer or slope from Freundlich equation	Washability of the dye from the surface	Type of curve	Fits with	Slope from Freundlich equation	Washability of the dye from the surface
Ag_2S (n-type)	Excess Ag^+ in interstitial position	H	L	$22{\cdot}06 \times 10^{-6}$ mol/m^2	Part	C	—	—	Total
Ag_2S-doped with CdS (n-type)	More negatively charged cation vacancy	H	L	$17{\cdot}34 \times 10^{-6}$ mol/m^2	Part	C partly	—	—	Total
ZnS (n-type)	Sulphur vacancies	S	F	1·43 (slope)	Total	S	F	1·36 (slope)	Considerable
PbS (p-type)	Schottky defect more cation vacancies	L	L	$38{\cdot}698 \times 10^{-5}$ mol/m^2	Considerable	S	F	2·85 (slope)	Almost total

L, Langmuir; F, Freundlich.

electrons arising out of CdS doping decrease the adsorption of anionic tartrazine.

In the case of ZnS which is an n-type semiconductor (Kröger 1974) with sulphur vacancy, the adsorption isotherms of tartrazine and safranine-T resemble the S-type curve. For anionic tartrazine adsorption, the initial part of the S-curve perhaps indicates a strong competition between the dye molecule and water molecule for surface sites on ZnS. Since ZnS is an n-type semiconductor with excess electron, the anionic dye adsorption becomes difficult. With increase in concentration of the dye, the adsorption curve goes up which indicates that one molecule helps the other to get adsorbed on the surface. A further rise beyond the plateau region may be due to adsorption through micelles and therefore, the slope value of the Freundlich plot is quite high.

Adsorption of safranine-T also resembles the S-type curve and the slope value from Freundlich plot is quite high i.e. about 1·36. The contribution due to chemisorption was estimated to be around 25% of the total adsorption and the rest is by physisorption. It has been reported by Fuerstenau (1957) that when Freundlich plots yield slope values more than 0·5, the adsorption process is either through chemical interaction with the surface metal ion or through micelle formation. Safranine-T perhaps first interacts chemically with the surface metal ions and as the concentration of the dye is increased, the adsorption process continues with the micelle formation.

Bloem (1963) reported that PbS exhibits a predominantly Schottky defect. In the present case, cation vacancies are greater compared to anion vacancies imparting a p-type behaviour, viz

$$\frac{1}{2}S_2 = \mathrm{PbS} + V''_{\mathrm{Pb}} + 2\dot{h}.$$

Hence, the doubly-charged negative lead vacancy (V''_{Pb}) and positive hole ($\dot{h}$) are present.

The adsorption isotherm of anionic tartrazine on PbS resembles an L-type curve (Giles *et al* 1960) and this isotherm fits well with the Langmuir relation. Experiments for estimation of chemisorption indicate that a considerable part of the total adsorption, i.e. around 40% is contributed by chemisorption which may be due to the positive holes.

Adsorption isotherm of safranine-T on PbS shows a very good resemblance to S-type curve (Giles *et al* 1960) and it follows more or less a Freundlich relation as shown in figure 5 with a high slope value. Estimation of chemisorption shows that the adsorption is mostly governed by the physical process. The high slope value in the Freundlich plot, therefore, indicates that the greater adsorption of safranine-T is probably due to the adsorption of micelles.

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