Adsorption 6, 349–357, 2000

Static and Kinetic Studies on the Adsorption Behavior of Sulfadiazene

A.K. BAJPAI* AND M. RAJPOOT
Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur 482 001, MP, India

D.D. MISHRA
Department of Chemistry, Rani Durgavati University, Jabalpur 482 001, MP, India

Abstract. To investigate the nature of interactive forces between sulfadiazene molecules and alumina surface the experiments were performed for the adsorption of sulfadiazene (SD) from its aqueous sulution onto the alumina surfaces at $25 \pm 0.2^\circ$C and the influence of factors such as increasing concentration of SD (4.0–20.0×10^{-3} mol cm^{-3}), the time required for adsorption equilibrium, pH (2.0–12.0) and temperature (5–45°C) of the adsorption medium, the presence of ions like Cl^-, SO_4^{2-} and PO_4^{3-} (0.01–0.30 M) and organic solvents (5% v/v) were observed on the course of adsorption of SD. Various adsorption and kinetic parameters such as adsorption coefficient, the rate constants for adsorption and desorption were also evaluated. The results of the above cited studies facilitated to formulate the mechanisms of interaction between SD and alumina surfaces. From application view point the present work may be a potential tool for an effective chromatographic separation of sulfa drugs from industrial effluents.

Keywords: sulfadiazene, adsorption, kinetics

Introduction

Adsorption plays an important role in various biological, industrial and technological processes (Burkhat and Martinez, 1992; Kudelski and Bukowska, 1992; Kapoor et al., 1984). In spite of a great deal of work done in the field of adsorption of low molecular weight compounds, the investigations on the adsorption behaviours of biologically active compounds, such as drugs, are rather few in number. The adsorption studies of drugs onto various surfaces are significant not only in formulating the optimum experimental conditions for their chromatographic separation but also from pharmaceutical view point.

The life saving action of sulfa drugs in fighting against several diseases (Loubatiers, 1957; Franke and Funchs, 1955; Plummer and Smillie, 1944) is well known. It has been found that a large number of infants of those areas which are near the industrial sites commonly suffer from methemoglobenemia (Di Palma, 1971) and hemolytic anemia (Marks and Banks, 1965) due to toxic nature of sulfa drugs. Bearing in mind the water contaminating role of sulfa drugs and extending our previous work on adsorption of sulfonamides (Bajpai and Rajpoot, 1996; Bajpai et al., 1996, 1997) we in the present paper are reporting the results of adsorption of sulfadiazene (SD) onto the alumina.

Experimental

Materials

Adsorbate. Sulfadiazene (abbreviated by SD) used as the adsorbate, was isolated from sulfadiazene tablets, containing 500 mg of SD and less than 20 mg of binding materials.

Preparation of SD Solution. A known number of SD tablets were weighed and ground to fine powder.

---

*To whom correspondence should be addressed.

To a weighed amount of this fine powder was added 0.5 ml of 10% sodium hydroxide to give a paste of SD which was further diluted to 50 ml with doubly distilled water. Insoluble materials were separated out by filteration (Whatman No. 41 filter paper) and than the filterate was diluted to 100 ml in a volumetric flask. The pH of the SD solution so prepared was found to be 7.7.

Adsorbent. The adsorbent alumina was of chromatographic grade and obtained from BDH (Poole England). It had a specific surface area 18.0 $m^2 \, g^{-1}$ as determined by BET method.

Determination of the point of zero charge (PZC) of alumina was carried out by potentiometric titration of 2.0 g of oxide suspended in 50 ml of solution containing 1.0×10^{-3} $mol \, cm^{-3}$ KNO_3 as the supporting electrolyte. The PZC was found to be at pH 9.0. Moreover, independence of the PZC of alumina on the added anions Cl^-, SO_4^{2-} and PO_4^{3-} was also observed as reported by Chibowski (1990) and Lyklema (1961).

All other chemicals and reagents used were of A. R. grade. Doubly distilled water was used throughout the studies.

Methods

Method of Adsorption of Sulfadiazene. Into a glass stoppered flat bottom flask an accurately weighed amount of alumina (0.2 g) and known volume of aqueous solution of SD were placed and the flask kept for shaking untill equilibrium was reached (in the present investigation the required time for adsorption equilibrium was two hours). The adsorbed SD was estimated colorimetrically (Krishna and Shastry, 1979).

Kinetics of Adsorption. Kinetic studies of the adsorption process were carried out by shaking a series of glass stoppered flat-bottom flasks containing identical (in concentrations and volumes) aqueous solutions of SD and equal weights of alumina at the same pH i.e. 7.7. At different time intervals the flasks were taken out and each flask was examined for the remaining SD colorimetrically (Krishna and Shastry, 1979). The amount of adsorbed SD calculated by mass balance equation.

pH Measurement. Every attempt was made to maintain pH of the suspension constant at pH 7.7 before and after the adsorption experiments. In the study of the effect of pH on the adsorption process, the pH was varied by addition of hydrochloric acid and sodium hydroxide.

Results and Discussion

Concentration Effect

Adsorption Isotherm. The adsorption isotherm is the very first and significant parameter of adsorption studies because the shape of the adsorption isotherm not only provides a quantitative relationship between the adsorbed amount and equilibrium concentration of adsorbate, but also reflects the manner in which the adsorbate molecules are adsorbed on the surface of the adsorbent. The adsorption isotherm obtained is shown in Fig. 1, where the amount of SD adsorbed (in $mg \, g^{-1}$) has been plotted against the equilibrium concentration of the SD solution (in mol cm^{-3}). The shape of the adsorption isotherm reveals that it is of the L2 type, i.e. Langmuir type of isotherm. In most of the previous adsorption studies similar type of isotherms have been reported (Viladkar et al., 1996).

Mode of Adsorption. Before explaining the possible mode of adsorption of SD onto the alumina it becomes of important to discuss the characteristics of both the adsorbent and adsorbate.

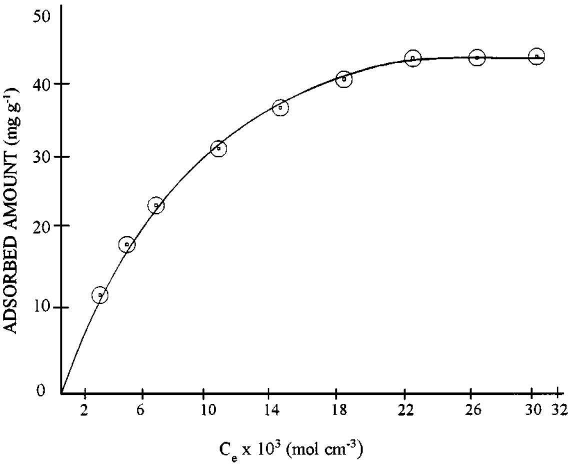


Figure 1. Amount of SD adsorbed (in $mg \, g^{-1}$) versus the equilibrium concentrations of SD solution ($mol \, cm^{-3}$) at fixed pH = 7.7, $Al_2O_3 = 0.2$ g, $[KNO_3] = 1.0 \times 10^{-3}$ $mol \, cm^{-3}$ and temp. = 25 ± 0.2°C.

Characteristics of Alumina and SD Regarding the Present Work

(i) It is generally known (Rudzinski and Charmas, 1996) that metal oxide surface is covered with hydroxyl groups when oxide is placed in water. The presence of the two free electron pairs of oxygen atom and possibility of hydrogen ion dissociation is the evidence of amphoteric character of these groups. On account of this, the most useful parameter in description of the water/metal oxide interface is pH of the solution being in contact with the surface. Adsorption of H^+ or OH^- ions causes protonization or deprotonization of the surface according to the Eqs. (1) and (2).

$$>AlOH + H^+ \rightarrow >AlOH_2^+ \tag{1}$$

$$>AlOH + (OH^-) \rightarrow >AlO^- + H^+(+H_2O - H^+) \tag{2}$$

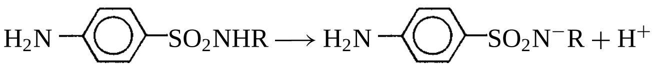
(ii) The point of zero charge (PZC) of alumina is 9.0 i.e. at pH 9.0 on the surfaces of alumina are present only $>AlOH$ groups and, therefore, the surface becomes neutral.

The above discussion reveals that on changing the pH of the aqueous suspension of alumina, from acidic to alkaline pH range following equilibria exist:

$$\begin{array}{ccccc} >AlOH_2^+ & \overset{-H^+}{\rightleftharpoons} & >AlOH & \overset{-H^+}{\rightleftharpoons} & >AlO^- \\ \text{pH} = 9.0 > \text{pH} & & \text{pH}_{\text{PZC}} = 90 & & \text{pH} = 9.0 < \text{pH} \\ \text{positively charged} & & \text{neutral} & & \text{negatively charged} \\ \text{surface complex or} & & \text{surface complex or} & & \text{surface complex or} \\ \text{protonated aluminol group} & & \text{unprotonated aluminol group} & & \text{deprotonated group} \end{array} \tag{3}$$

(iii) In the acidic pH range sulfonamides commonly undergo protonation (via $-NH_2$ group) because of basic nature of the amino group and ionize in the alkaline pH range (via $-SO_2$ NHR group) by relasing hydrogen atom grom sulfonamide group).

Since the adsorption was carried out at pH 7.7, both $>AlOH$ and $>AlOH_2^+$ groups are present on the surface of the alumina giving it a net positive charge. At the same time the SD molecules will be almost completely ionized (25% at pH 6.0, 75% at pH 7.0 and 95% at pH 8.0, Paul and Richard, 1942) because its pK_a value is 6.48. Thus the two species (alumina and SD) will be present in the following forms contacting with each other at pH 7.7:



(4)

SD molecule — SD ion

$>AlOH$ and $>AlOH_2^+$

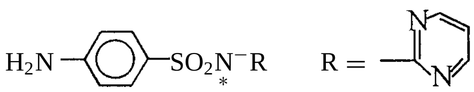
Alumina surface hydroxyl group — Alumina surface protonated hydroxyl group

Now, to discuss the mode of adsorption the following points deserve attention:

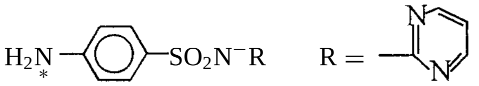
(i) $>AlOH_2^+$ groups may form an electrostatic type of bond with SD whereas the $>AlOH$ group can take part only in H-bond formation.

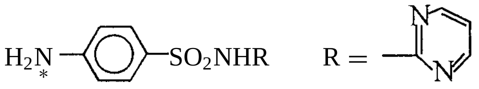
(ii) There are three active centres in the SD molecule which can participate in either type of bond formation i.e., electrostatic or H-bond. These centres are:

  (a) Negatively charged nitrogen atom of SD ion,



(b) Nitrogen atom of $-NH_2$ group of either SD molecule or its ion,



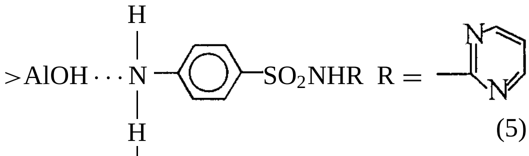


(c) Either of the two oxygen atoms of the $-SO_2$ NHR group of SD molecule due to their partial negative charge (Pouling, 1940),

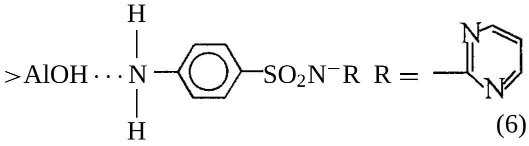
However, in the case of SD ion these centres can't take part in interaction with alumina surface because the negatively charged nitrogen atom ($-SO_2N^-R$) has a greater affinity for bond formation with the surface than the partially negative charged oxygen atom.

The following type of interactions between SD and alumina surfaces are possible:

(i) H-bonding between $>$AlOH group and the $-NH_2$ group of either SD molecule or SD ion,

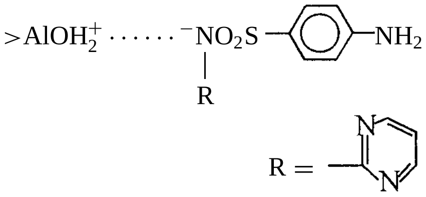


(5)



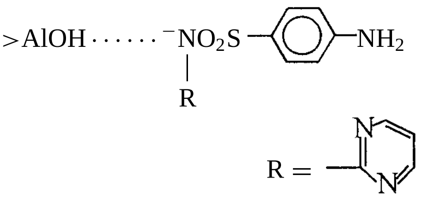
(6)

(ii) Electrostatic bonding between the negatively charged nitrogen atom of the SD ion and the $>AlOH_2^+$ group,



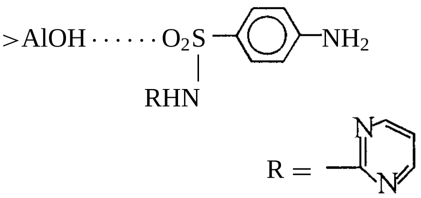
(7)

(iii) H-bonding between the negatively charged nitrogen atom and the $>$AlOH group,



(8)

(iv) H-bonding between the SD molecule, and the $>$AlOH group, via the oxygen atom,



(9)

Evaluation of Adsorption Coefficient. The linearized Langmuir adsorption equation, i.e. Eq. (10), is

$$\frac{C_e}{a} = \frac{1}{a_s K} + \frac{C_e}{a_s} \tag{10}$$

where, C_e = equilibrium concentration of the adsorbate solution; K = adsorption coefficient; $K = k_1/k_2$; k_1 = rate constant for adsorption; k_2 = rate constant for desorption; a and a_s represent the amount adsorbed (in mg g^{-1}) at equilibrium concentration and at saturation (monolayer capacity) respectively. The theoritical value of a_s has been calculated from Fig. 2 and found to be 47.0 mg g^{-1} which is quite near to the experimental value of 44.0 mg g^{-1}.

A plot between C_e and C_e/a (Fig. 2) yields a straight line and the adsorption coefficient evaluated from its slope and intercept is found to be 5.45×10^2 cm^3 mol^{-1}.

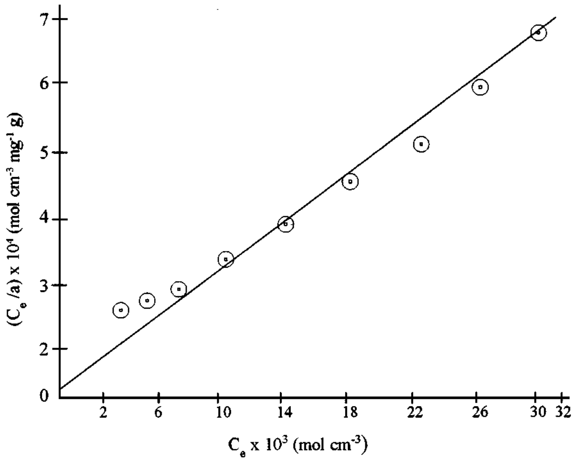


Figure 2. Equilibrium concentration of the SD solution (mol cm^{-3}) versus (C_e/a) for calculating the adsorption coefficient at fixed pH = 7.7, Al_2O_3 = 0.2 g, [KNO_3] = 1.0×10^{-3} mol cm^{-3} and temp. = 25 ± 0.2°C.

Kinetics of Adsorption

A common practice for studying the kinetics of the adsorption process is to monitor the change in concentration of the adsorbate solution with the time period of adsorption. The adsorbed amount of SD at different time intervals was determined colorimetrically (Krishna and Shastry, 1979) and plotted against time as shown in Fig. 3. The shape of the plot suggests that the adsorption is almost constant up to 120 minutes and after that it levels off. During the period of constant adsorption rate the kinetic scheme described elswhere in detailed (Bajpai and Bajpai, 1993) may be applied. Thus by employing the kinetic scheme various kinetic parameters such as the rate constants for adsorption and desorption can be evaluated.

Evaluation of k_1 and k_2. The rate constant for adsorption was calculated from the Eq. (11).

$$\frac{1}{C} = \frac{k_1}{C_0} \cdot t + \frac{1}{C_0} \qquad (11)$$

where, C = concentration of adsorbate solution at any time t; C_0 = initial concentration of adsorbate solution.

The slope of the linear plot ($1/C$ vs. time), provided evaluation of k_1 and was found to be $2.0 \times 10^{-6}\ s^{-1}$. Since $K = k_1/k_2$ it becomes easy to compute the value of k_2, as found to be 0.36×10^{-8} mol $cm^{-3}\ s^{-1}$.

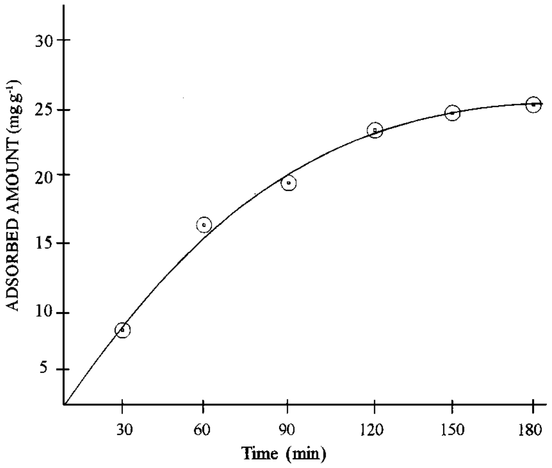


Figure 3. Variation in amount of SD adsorbed (mg g^{-1}) with time (min.) at fixed [SD] = 8.0×10^{-3} mol cm^{-3}, pH = 7.7, Al_2O_3 = 0.2 g [KNO_3] = 1.0×10^{-3} mol cm^{-3} and temp. = 25 ± 0.2°C.

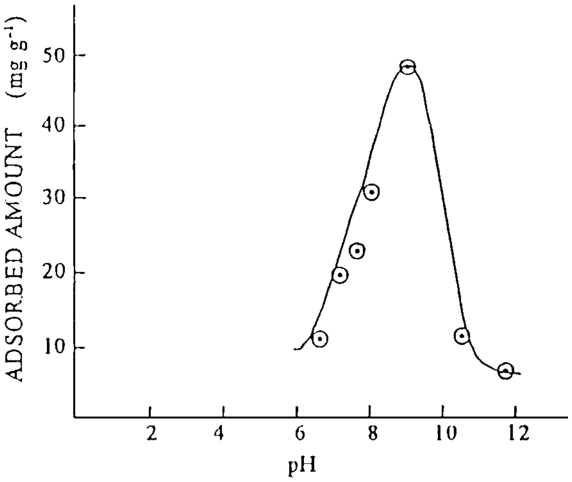


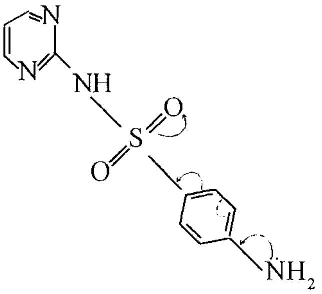
Figure 4. Effect of varying pH of the SD solution on its plateau adsorption (mg g^{-1}) at fixed [SD] = 8.0×10^{-3} mol cm^{-3}, Al_2O_3 = 0.2 g, [KNO_3] = 1.0×10^{-3} mol cm^{-3} and temp. = 25 ± 0.2°C.

pH Effect

The pH of a suspension is one of the most important parameter in those adsorption investigations where oxides are involved as adsorbent. Moreover, a change in pH also results in change in charge profile of the adsorbate molecule which consequently influences the interactions between the adsorbate and adsorbent molecules.

To investigate the effect of pH on adsorption behaviour experiments were carried out over the pH range 2.0–12.0, by additing appropriate volume of hydrochloric acid or sodium hydroxide. The results are depicted in Fig. 4 which indicate that maximum adsoption is obtained at pH 9.0 while it decreases on both sides. In addition to the results one remarkable point is that in the acidic pH range the SD precipitated out. The results obtained may be explained as below:

In acidic pH range SD is feebly soluble, and, therefore gets precipitated out from solution in this range. It is due to the fact that in sulfadiazene molecule the amino group (—NH_2) is only weakly basic apparently due to the combined electron withdrawing nature of the diazene group and sulfonamide group present in para position with respect to the —NH_2 group (as shown in the following scheme). This makes sulfadiazene feebly soluble in acidic pH range. In the lower acidic pH range ionization of SD beings and increases with increase in pH (as given in characteristics of SD) so that SD again comes into solution. During the adsroption experiment interaction takes place as shown in Eqs. (5–9). In this manner interactions between SD and alumina surface increase up to pH 9.0.



At pH 9.0 alumina surface becomes uncharged i.e. only >AlOH groups are present and SD is present in its almost completely ionized form. This consequently results in a maximum adsorption at this pH.

According to Eq. (3) beyond pH 9.0 the alumina surface hydroxyl groups convert into deprotonated form and the formation of $>AlO^-$ groups on the surface of alumina creats electrostatic repulsion between the surface and the negatively charged SD ion so that adsorption decreases.

Salt Effect

The addition of inorganic salts to the system causes a noteworthy change in adsorption behavior. If the size of added ions is smaller than adsorbate molecules, added ions may be preferentially adsorbed on the surfaces. The adsorbate molecules although not directly linked with surface can interact with ions on the surface to make a double layer in the following manner,

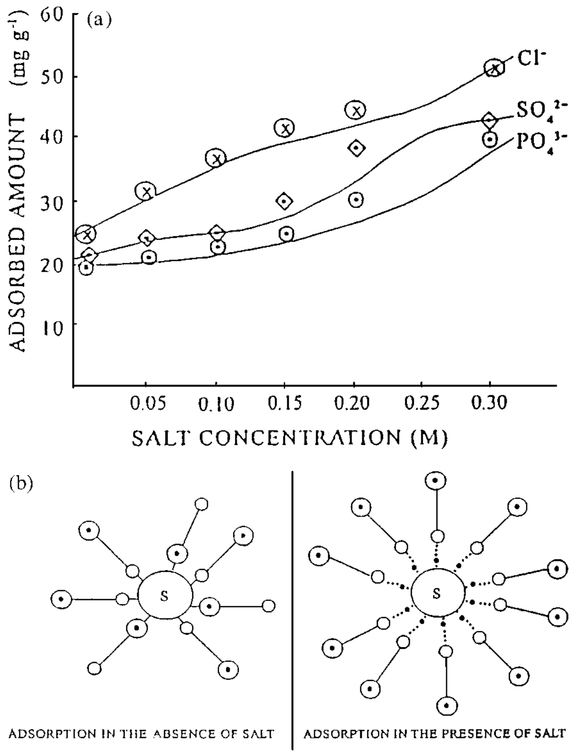


Figure 5. (a) Effect of addition of salts on the plateau adsorption ($mg\,g^{-1}$) of SD at fixed $[SD] = 8.0 \times 10^{-3}$ $mol\,cm^{-3}$, $pH = 7.7$, $Al_2O_3 = 0.2$ g and temp. $= 25 \pm 0.2$°C. (b) Schematic representation of the adsorption of sulfadiazene onto the alumina surface in the presence and absence of salt at fixed $[SD] = 8.0 \times 10^{-3}$ $mol\,cm^{-3}$, pH = 7.7, $Al_2O_3 = 0.2$ g and temp. $= 25 \pm 0.2$°C.
● = Anions, ○ = $^-NH_2$, ⊙ = $^-SO_2NHR$, Ⓢ = Surface,
··· = Interactions either electrostatic or H-bond type.
—— = -⌬-

$$\boxed{S}\cdots\cdots\boxed{I}\cdots\cdots\boxed{AM}$$

where, S = surface, I = ions and AM = adsorbate molecule.

In the present investigation experiments were carried out in the concentration of range 0.01 M to 0.3 M of different salts such as NaCl, Na_2SO_4 and Na_3PO_4. Results are shown in Fig. 5(a), which reveals the following points:

1. The adsorption of SD increases with rise in concentration of the added inorganic salts.

2. In the presence of NaCl, Na_2SO_4 and Na_3PO_4 increased adsorption of SD obeys the following order:

$$\mathrm{Cl^-} > \mathrm{SO_4^{2-}} > \mathrm{PO_4^{3-}}$$

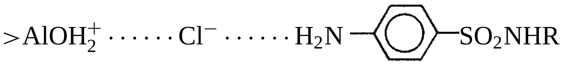
The results may be explained as below:

As the experiments were carried out at pH 7.7 both $>\mathrm{AlOH}$ and $>\mathrm{AlOH_2^+}$ groups are present on the surface of alumina. Anions like $\mathrm{Cl^-}$ are preferentially adsorbed on the surface of the alumina either by electrostatic attraction or by H-bonding:

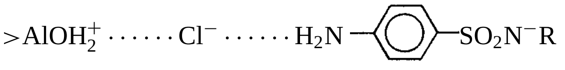
$$>\mathrm{AlOH_2^+}\cdots\cdots\mathrm{Cl^-} \qquad >\mathrm{AlOH}\cdots\cdots\mathrm{Cl^-}$$

A similar type of preferential adsorption of $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$ and $\mathrm{PO_4^{3-}}$ ions onto iron oxide has been shown by Lee et al. (1991).

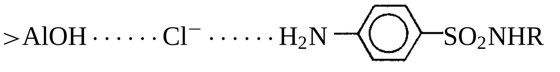
As the experimental pH was 7.7, Eqs. (5–9) reveal that groups $-\mathrm{NH_2}$, $-\mathrm{SO_2N^-R}$ and $-\mathrm{SO_2NHR}$ can participate in bond formation with the alumina surface, but here because of the presence of anions only the smaller groups i.e. $-\mathrm{NH_2}$ can interact with the surface via the H-bonds, as shown below:



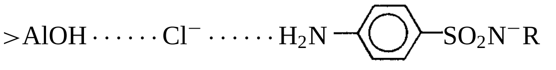
$$>\mathrm{AlOH_2^+}\cdots\cdots\mathrm{Cl^-}\cdots\cdots\mathrm{H_2N{-}C_6H_4{-}SO_2NHR} \tag{12}$$



$$>\mathrm{AlOH_2^+}\cdots\cdots\mathrm{Cl^-}\cdots\cdots\mathrm{H_2N{-}C_6H_4{-}SO_2N^-R} \tag{13}$$



$$>\mathrm{AlOH}\cdots\cdots\mathrm{Cl^-}\cdots\cdots\mathrm{H_2N{-}C_6H_4{-}SO_2NHR} \tag{14}$$



$$>\mathrm{AlOH}\cdots\cdots\mathrm{Cl^-}\cdots\cdots\mathrm{H_2N{-}C_6H_4{-}SO_2N^-R} \tag{15}$$

From the above equations it is clear that with rise in the concentration of added salts the extent of interaction increases, which results in a gradual increase in the adsorption of SD. The reason for the greater adsorption observed in the presence of salts may be depicted as shown in Fig. 5(b).

It is worthwhile mentioning that the depression in the adsorption curve for $\mathrm{PO_4^{3-}}$ ions (in Fig. 5(a)) may be due to their trivalency as compared to the monovalent $\mathrm{Cl^-}$ ions and bivalent $\mathrm{SO_4^{2-}}$ ions. The size of the anions may also be another factor for this depression. Due to their larger size $\mathrm{PO_4^{3-}}$ ions sterically hindered the approach of SD molecules, which consequently lowers the increase in the adsroption of SD.

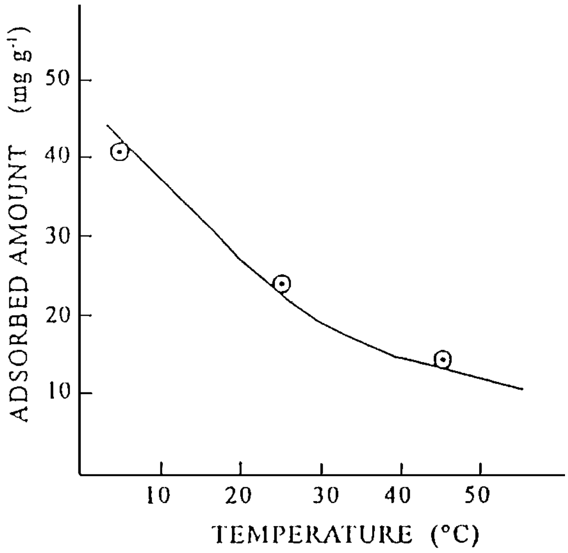


Figure 6. Effect of temperature (°C) on the plateau adsorption ($\mathrm{mg\,g^{-1}}$) of SD at fixed $[\mathrm{SD}] = 8.0 \times 10^{-3}\ \mathrm{mol\,cm^{-3}}$, pH = 7.7, $\mathrm{Al_2O_3} = 0.2$ g and $[\mathrm{KNO_3}] = 1.0 \times 10^{-3}\ \mathrm{mol\,cm^{-3}}$.

Temperature Effect

The range of temperature studied was 5–45°C. From Fig. 6, it is easy to see the decrease in the adsorbed amount of SD with increasing temperature. The results can be interpreted as below:

1. As the adsorption isotherm is of Langmuir type it is clear that the intermolecular forces responsible for adsorption are purely physical and, therefore, at lower temperature these forces become prominant and result in a greater adsorption (Singh and Rawat, 1994).
2. In earlier reports (Giles et al., 1964) it was mentioned that lowering the temperature increases the agglomeration of dye molecules. This may also cause an increase in the extent of adsorption.
3. The solubility of the adsorbate increases with increase in temperature so that adsorbate molecules go into the bulk phase and move away from the solid surface (Gupta et al., 1992).
4. Singh and Rawat (1994) have reported that at lower temperature there is an increase in the number of active sites on the solid surface, which will cause an increase in the amount adsorbed.

Table 1. Adsorbed amount of sulfadiazene (in mg g^{-1}) at various media.

S. no.	Solvent	Adsorbed amount of SD (mg g^{-1})
1.	Methyl alcohol	16.8
2.	Ethyl alcohol	13.9
3.	iso-Propyl alcohol	12.7
4.	Butyl alcohol	10.2
5.	iso-Butyl alcohol	8.4

5. We have also calculated the energy of activation by Arrhenius equation and it has been found to be 14.8 KJ mol^{-1}.

Solvent Effect

In order to study the influence of solvent on the adsorption behaviour, adsorption experiments have been carried out in the presence of water miscible aliphatic alcohols (5% v/v, C_1 to C_4). The results are summarized in Table 1, from which it is clear that the adsorption of SD decreases with increasing number of carbon atoms in the alkyl group. In the case of *n*-butyl and iso-butyl alcohols, adsorption is greater in the presence of *n*-butyl alcohol. The results so obtained may be explained in the following manner:

Syrkin and Poliokow (1931) in their studies of the adsorption of tetraethylammonium iodide (TEAT) on a purified wood charcol found that the adsorption was higher in the presence of solvent having the higher surface tension. In the present study the surface tension of the solvents was:

$$\text{MeOH} > \text{EtOH} > \text{iso-PrOH} > n\text{-BuOH} > \text{iso-BuOH}.$$

The amount of SD adsorbed is greater in the presence of MeOH and lowest in the presence of iso-BuOH. The results adequately resemble with those reported by Syrkin and Poliokow (1931).

From the work on the adsorption of benzophenone and other substances onto alumina in the presence of different solvents, Jacques and Mathieu (1945) postulated that in a binary mixture, as the difference in dielectric constant of the two solvents increases, the adsorption also decraeses. In the present investigation the dielectric constant of water and different alcohols obey the following order:

$$\text{water} > \text{MeOH} > \text{EtOH} > \text{iso-PrOH} > n\text{-BuOH} > \text{iso-BuOH}$$

It is clear that difference between dielectric constant of water and MeOH is the smallest and is the highest in case of iso-BuOH. Table 1 clearly implies that the adsorption of SD obey a similar sequence of effectiveness of alcohols as reported elsewhere (Jacques and Mathieu, 1945).

Conclusion

Sulfadiazene adsorbs onto the alumina surfaces via H-bonding and electrostatics forces following a Langmuir type of adsorption model and belonging to the L2 category of adsorption isotherms. This clearly indicates about the physical nature of the adsorption process and is further supported by the value of the energy of activation (14.8 KJ mol^{-1}) which falls in to the range of physical adsorption. The adsorption exhibits a strong dependence on pH thus showing a maximum adsorption at the point of zero charge of the alumina (9.0) and a decreasing adsorption on both the sides. With addition of anions the adsorption is enhanced, obeying the following sequence, of effectiveness.

$$\text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$$

The adsorption decreases with increasing temperature of the adsorption mediam. It is found that adsorption decreases with added alcohols and the effectiveness of the added solvent increases with increasing number of carbon atoms in the added alcohoals.

Acknowledgment

The authers are greatful to Dr. K.K. Verma, Professor, Department of Post-Graduate Studies and Research in Chemistry, Rani Durgavati University, Jabalpur, for discussions and suggestions regarding this work. One of the authors, M. Rajpoot, gratefully acknowledges the financial support by the Council of Scientific and Industrial Research (CSIR), New Delhi, India.

References

Bajpai, A.K. and M. Rajpoot, *Bull. Chem. Soc. Jpn.*, **69**(3), 521 (1996).

Bajpai, A.K., M. Rajpoot, and D.D. Mishra, *Indian J. Chem.*, **35**(A), 560 (1996).

Bajpai, A.K., M. Rajpoot, and D.D. Mishra, *J. Colloid Interf. Sci.*, **187**, 96 (1997).

Bajpai, U.D.N. and A.K. Bajpai, *Polym. Int.*, **32**, 43 (1993).

Burkhat, K.K. and A.M. Martinez, *J. Toxicol. Clin. Toxicol*., **30**, 371 (1992).

Chibowski, S., *J. Colloid Interface Sci*., **140**, 444 (1990).

DiPalma, J.R. (ed.), *Drill's Pharmacology in Medicine*, 4th edn., ch. 58, McGraw-Hill, New York, 1971.

Franke, H. and J. Fuchs, *Deut. Med. Wochensch*, **80**, 1449 (1955).

Giles, C.H., I.A. Easton, and R.B. McKay, *J. Chem. Soc*., **4**, 4495 (1964).

Gupta, G.S., S.P. Shukla, and V.N. Singh, *Environ. Technol*., **13**, 925 (1992).

Jacques and Mathieu, *Compt. Rend*., **221**, 293 (1945).

Kapoor, R.C., A. Prakash, and S.L. Kalani, *J. Indian Chem. Soc*., **LXI**, 600 (1984).

Krishna, R.R. and C.S.P. Shastry, *Talenta*, **26**, 861 (1979).

Kudelski, A. and J. Bukowska, *J. Molec. Struct*., **275**, 145 (1992).

Lee, L.T. and P. Somasundaran, *J. Colloid Interface Sci*., **142**, 470 (1991).

Loubatienes, A., *Ann. N.Y. Acad. Sci*., **71**, 4 (1957).

Lyklema, J., *Kolloid-Z*, **175**, 129 (1961).

Marks, P.A. and J. Banks, *Ann. N.Y. Acad. Sci*., **123**, 198 (1965).

Paul, H.B. and O.R. Richard Jr., *J. Am. Chem. Soc*., **64**, 2905 (1942).

Plummer, C.H. and W.G. Smillie, *J. Am. Med. Assoc*., **124**, 8 (1944).

Pouling, L.C., *The Nature of Chemical Bond*, 2nd edn., Cornell University Press, Ithaca, NY, 1940.

Rudzinski, R. and R. Charmas, *Adsorption*, **2**, 248 (1996).

Singh, B.K. and N.S. Rawat, *J. Chem. Tech. Biotech*., **61**, 57 (1994).

Syrkin and Poliokow, *Kolloid-Z*, **55**, 33 (1931).

Viladkar, S., R. Agarwal, and Kamaluddin, *Bull. Chem. Soc. Jpn*., **69**, 95 (1996).