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TITROMETRIC STUDIES OF THE ADSORPTION OF SOME ALIPHATIC ORGANIC ACIDS FROM AQUEOUS SOLUTIONS ON THE SURFACE OF ACTIVATED CHARCOAL

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Adsorption of acrylic acid and crotonic acid from aqueous solutions on the surface of activated charcoal by titrometric method has been undertaken. The rate of adsorption of acrylic acid on activated charcoal is higher than crotonic acid. The Langmuir and Freundlich plots have been drawn and the constants involved in Langmuir and Freundlich isotherms are calculated. A possible explaination of the adsorption of aliphatic organic acids from aqueous solutions on the surface of activated charcoal has been given.

Key words: Adsorption, Uncovered surface, Partial balance force

Introduction

Some organic compounds like charcoal, starch and sucrose are useful adsorbents. Charcoal is one of the good adsorbent but it has a dis-advantage of being coloured. On the other hand starch and sucrose are rather weak adsorbents useful for separating high molecular weight compounds like chlorophyll and xanthophylls. Adsorption of various organic acids (monobasic and dibasic) from aqueous solutions on the charcoal has been studied by so many researchers [1-7]. It has been found that polarizability of the compounds plays a significant role in the adsorption process and the adsorption of organic substances from aqueous solutions increases strongly and regularly as the homologous series is ascended [8]. Further the adsorption process may be reversed if polar adsorbents and non polar solvents are used [9].

Adsorption by solids from aqueous or non aqueous solutions always accurs when solutions and adsorbents are brought into contact. The adsorption process is used in estimating the surface area of adsorbents and finding the changes in this area. Further, the extent of adsorption may provide valuable informations about the adsorbents and adsorbate.

This paper describes the adsorption of unsaturated aliphatic organic acids (vinyl monomers) like acryllic acid and crotonic acid at the surface of the activated charcoal.

Experimental

Materials. Activated charcoal (animal), acrylic acid, crotonic acid, sodium hydroxide, phenolphthalene and ethyl alcohol of E. Merck were used without further purification.

Procedure. All experiments were made in stoppered reagent bottles. Nine reagents bottles were taken and numbered as 1,2,3,4,5,6,7,8,9. Solutions of acids were prepared in distilled water. Required volume of acid (0.1 mol dm^{-3}) according to Tables 1 and 2 was added to each bottle already containing 1 mg activated charcoal. The volume of each bottles was than made 100 ml by adding distilled water. These bottles were kept in a thermostatically controlled bath at 30°. The reagent bottles were continously shaken for an hour and then filtered. Filtrate from each reagent bottle was titrated against standard sodium hydroxide solution using phenophthalene as indicator. The amount of acid which could not be adsorbed on the surface of activated charcoal was determined from these titrations by taking the mean of the values obtained.

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Results and Discussions

The results of the adsorption of acrylic acid and crotonic acid from aqueous solutions on activated charcoal are summarized in Table 1 and 2 respectively. The results shown in these tables and Fig. 1 indicate that the adsorption of monobasic unsaturated organic acid from aqueous solutions on the surface of activated charcoal increases with increase in concentration of acids. The rate of adsorption of acrylic acid from aqueous solution on the surface of charcoal is higher

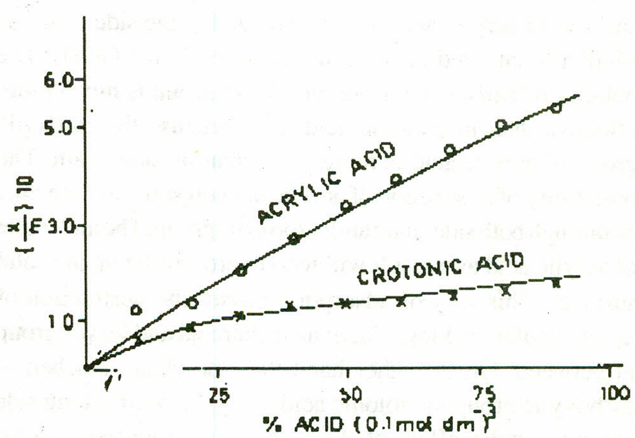


Fig 1. A plot of (x/m) x 10 against % acid mol.dm^{-3}) for the titrometric studies of the adsorption of some aliphatic acids from aqueous solutions on the surface of activated charcoal.

TABLE 1. ADSORPTION OF ACRYLIC ACID (0.1 MOL.DM^{-3}) ON THE SURFACE OF 1 GM. ACTIVATED CHARCOAL A+30°C

Expt No.	Acrylic acid %	Amount of acid adsorbed xg	Equilibrium concentration of acid cx10^3 mol. dm^{-3}	C/x/m x 10^2
1.	90	0.5346	15.808	2.957
2.	80	0.4973	10.032	2.017
3.	70	0.4491	7.600	1.692
4.	60	0.3888	6.080	1.563
5.	50	0.3319	3.952	1.191
6.	40	0.2673	22.888	1.080
7.	30	0.2004	2.128	1.060
8.	20	0.1325	1.672	1.261
9.	10	0.1194	1.216	1.018

TABLE 2. ADSORPTION OF CROTONIC ACID (0.1 MOLE DM^{-3}) ON THE SURFACE OF 1 GM ACTIVATED CHARCOAL A+30°

Expt No.	Acrylic acid %	Amount of acid adsorbed xgm	Equilibrium concentration of acid cx10^3 mol. dm^{-3}	C/x/m x 10^2
1.	90	0.1784	6.922	3.879
2.	80	0.1589	6.156	3.872
3.	70	0.1514	5.238	3.460
4.	60	0.1459	4.309	2.952
5.	50	0.1352	3.429	2.537
6.	40	0.1297	2.487	1.917
7.	30	0.1124	1.696	1.508
8.	20	0.951	0.892	0.937
9.	10	0.649	0.251	0.387

than crotonic acid. The degree of adsorption of the acrylic acid and crotonic acid on the solid surface may be controlled by the carboxylic group and the side chain to which it is attached. Furthermore, the nature of bonding (π or α) also affects the trend of adsorption or absorption on the solid surface. In acrylic acid (CH_2=CHCOOH), the side chain is small as compared to crotonic acid (CH_3 CH=COOH). The polarity of carboxylic group in acrylic group is much more effective than in crotonic acid. It is because the caroxylic group of acrylic acid is more polar than its side chain. The possibility of adsorption of acrylic acid on solid surface may be through both side chain and carboxylic group. The molecules of acrylic acid as a result will tend to erect or lie on the solid surface. This way of adsorption causes the destruction of unimolecular packing of activated charcoal and leaves group in between. On the other hand the side chain attached to carboxylic group in crotonic acid is bigger. With a long side chain the polar effect of the carboxylic group will not be transmitted through the side chain. The molecules of crotonic acid will be adsorbed on the surface of the activated charcoal through carboxylic group. In the adsorption of formic, acetic, propionic and butyric acids from aqueous solution on activated charcoal, similar results were obtained. The order of adsorption depends upon the length of the side chain (formic > acetic propionic > butyric). The partially polar end of the molecules have a tendency to attach themselves to the active sites of the solid surface [6]. The effect of unsaturation (bonding) of these acids on adsorption cannot be reglected. The double bond of these acids strikes the uncovered surface of activated charcoal and produce radicals resulting the formation of dimers, trimers etc. of these acids. The prominent site of the adsorption on solid surface is carbon which is in the vicinity of carboxylic group. Similarly styrene (CH_2=CHC_6H_5) adsorbs on the surface of charcoal from methylethyl ketone through carbon attached to the phenyl group in the form of polystyrene as a dimer or trimer [10].

Freundlich and Langmuir adsorption isotherms have been drawn for unsaturated organic acids like crotonic acid and acrylic acid. In terms of concentrations langmuir equation [11] can be written as

$$C/(\frac{x}{m}) = \frac{1}{ab} + \frac{1}{a} C \text{ ....(1)}$$

where c is the equilibium concentration of the solution, x is the amount of molecule adsorbed on m gm of solid 1/a and 1/ab are the langmuir constants, where 'a' is the measure of the surface area of the solid and 'b' is intensity or the strength of the adsorption. Thus the slope of the plot c/x/m versus c in Figures 2 and 3 respectively for the adsorption of acrylic acid

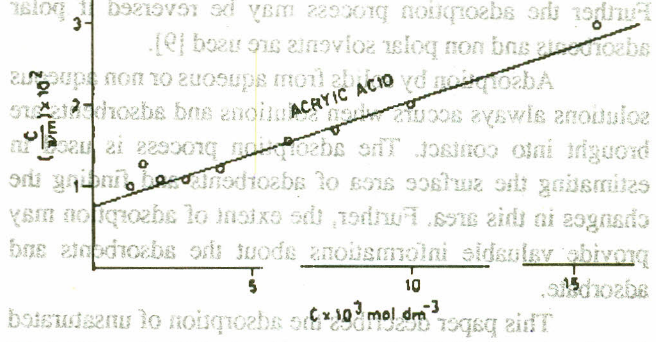


Fig 2. Langmuir plot for the sitrometric studies of the adsorption of acrylic acid from aqueous solutions on the surface of activated charcoal.

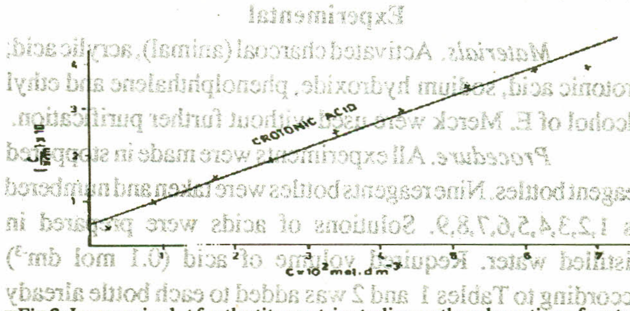


Fig 3. Langmuir plot for the titrometric studies on the adsorption of crotonic acid from aqueous solutions on the surface of activated charcoal.

and crotonic acid determines the value of 1/a and intercept of this plot measures the value of 1/ab. These values for crotonic acid and acrylic acid are summarized in table 3. The value of 1/a for acrylic acid is 1.3 whereas for crotonic acid it is 5.7.

TABLE 3. FREUNDLICH AND LANGMUIRPARAMETERSINTHEADSORPTION OF ACRYLIC ACID AND CROTONIC ACID FROM AQUEOUS SOLUTION ON THE SURFACE OF ACTIVATED CHARCOAL.

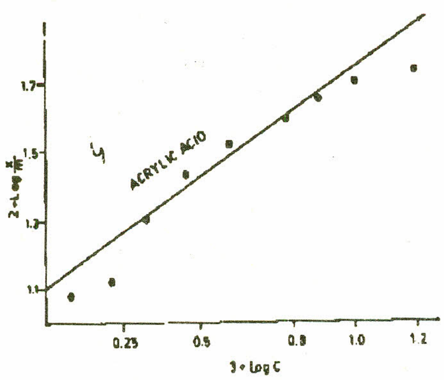
Name of acid	Freundlich constants		Langmuir constants	
	1/n	Log a	1/a	1/ab
Acrylic acid	0.640	1.100	1.30	0.0075
Crotonic acid	0.2830	0.700	5.70	0.050

Similarly the values of 1/ab for acrylic acid and crotonic acid are obtained respectively as 0.0075 and 0.05. The difference in the value of 1/a and 1/ab for these acids may be due to the length of the side chain attached to the carboxylic group of the acids which makes the acid more or less polar. It indicates that polarity of the adsorbing compounds play an important role in the process of adsorption on the solid surface. The more polar compound will be adsorbed more on the solid surface of the activated charcoal.

The linear form of Freundlich isotherm [12] may be written as

Log (x/m) = 1/n log c + log a ....(2)

Where 'a and 'n' are constants. As a first approximation 'a' is a measure of the intensity of adsorption. since adsorption isotherms are generally convex to the C-axis, the value of n is correspondingly greater then unity. A plot of log (x/m) versus log c gives a straight line of intercept a and slope 1/n. In Figs. 4 and 5 [2+log (x/m)] is plotted against)3+log C) respectively for acrylic acid and crotonic acid. The slope of the plot determing the value of 1/n whereas intercept measures the value of log a. The values obtained from these plots are shown in Table 3. It is obvious from the values of 1/n and log a that as the side chain increases, the values of 1/n decreases from



Fog 4. Freundlich plot for the titrometric studies of the adsorption of acrylic acid on the surface of activated charcoal.

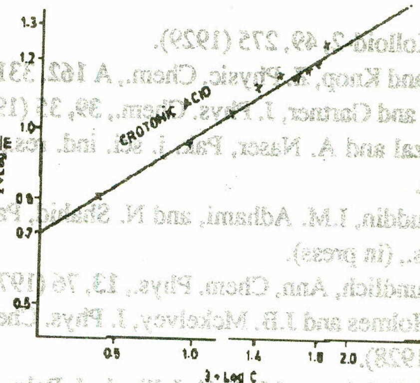


Fig 5. Freundlich plot for the titrometric studies of the adsorption of crotonic acid on the surface of activated charcoal.

0.64 for acrylic acid to 0.283 for crotonic acid. Similarly the values of log a for acrylic acid (1.10) is greater than for crotonic acid (0.7).

Conclusion

In summery when activated charcoal is added to an aqueous solution of crotonic acid or acrylic acid of the solute adsorbs on the solid surface preferentially as compared with solvent (water). The adsorption may be due to the action of partial valence forces at the boundary or surface of the adsorbent. The adsorption of these acids from aqueous solution on the surface of the activated charcoal mostly depends upon solubility of acids in water, the polarity of solvent (water), surface area of the activated charcoal and nature of organic acid. Charcoal is particularly effective in adsorbing compounds having aromatic rings whereas aliphatic compounds like acrylic or crotonic acid are usually less adsorbed on the surface of charcoal. This is because charcoal has no polar group which participates in hydrogen bonding. Only the polarity of the compound to be adsorbed is important. Acrylic acid and crotonic acid as compared with aromatic acids are less polarizable. The surfac area of the adsorbent is another factor which facilitates in adsorption. The surface area of activated charcoal has been reported in literature [14] being as 3600 sq. ft per gm. though not in every case. This in parts explains why if is possible to adsorb measureable quantities of these acids. However rate of adsorption of acrylic acid is higher than crotonic acid since the side chain of acrylic acid is small. Lengthening of side chain changes the polarity of functional group (carboxylic group). The carboxylic group in acrylic acid is more polar than the carboxylic group of crotonic acid. Hence charcoal is a suitable adsorbent for the adsorption of acrylic and crotonic acids from aqueous solution.

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