ADSORPTION STUDIES OF SOME SURFACE ACTIVE AGENTS ON LIGNIN

A THESIS

submitted in fulfilment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY

By

ANUJA GUPTA

INSTITUTE OF PAPER TECHNOLOGY
(UNIVERSITY OF ROORKEE)
SAHARANPUR-247 001 (INDIA)

AUGUST, 1992

DEDICATED

TO

THE MEMORY OF

MY RESPECTED MOTHER

LATE SMT. DAYA WATI AGARWAL

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**ADSORPTION STUDIES OF SOME SURFACE ACTIVE AGENTS ON LIGNIN**" in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy and submitted in the Department of Institute of Paper Technology, Saharanpur of the University is an authentic record of my own work carried out during a period from March, 1988 to August, 1992 under the supervision of Dr. A.K. Jindal and Dr. Satish Kumar.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other University.

Anuja Gupta
(ANUJA GUPTA)
Signature of the Candidate

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

AJindal	Satish Kumar
(Dr. A.K. Jindal)	(Dr. Satish Kumar)
Lecturer	Lecturer
Institute of Paper	Institute of Paper
Technology, Saharanpur	Technology, Saharanpur
(India)	(India)

Date : 29th Aug., 1992

The Ph.D. Viva-Voce examination of ANUJA GUPTA, Research Scholar, has been held on..................

Signature of Supervisors   Signature of External Examiner

Signature of H.O.D.

Head of Department
Institute of Paper Technology (U.O.R.)
SAHARANPUR-247001

ABSTRACT

INTRODUCTION

Biochemically resistant detergents present some of the most wide spread and severe problems in wastes and receiving waters. A regular discharge of synthetic surfactants into municipal sewage causes frothing troubles in operation tanks. The toxicity of the synthetic surfactants to fish and aquatic flora as well as human beings is well known.

Of the various treatment methods adsorption method appears to offer the best overall treatment especially for those which can not be removed by other methods. Activated carbon, the most effective adsorbent has not found favour in view of regeneration difficulties and economic considerations. A number of other adsorbents like fly ash, alumina, lime stone, solids, sludge, ash etc. have also been tried but the results are not encouraging.

Lignin is a waste material present in the black liquor of pulp and paper industry which possess problems for its disposal. Studies have shown that it can adsorb a number of dyes and other compounds from their aqueous solutions. Hence lignin has been chosen for the study of adsorption of synthetic surfactants, to explore its utility for the removal of surfactants from waste water.

EXPERIMENTAL

Kraft lignin has been isolated from spent liquor obtained by pulping of Eucalyptus chips in the laboratory. The pulp was filtered and the filterate was acidified with dilute hydrochloric

acid to precipitate crude lignin. It was purified by Ahlm's method.

Two cationic surfactants namely Cetyl pyridinium chloride (CPC) and Cetyl trimethyl ammonium bromide (CTAB) and two nonionic surfactants namely Tween20 (T20) and Tween40 (T40) have been chosen for adsorption studies. The estimation of cationic surfactants have been performed by the method of Few and Ottewill. The method involves the extraction of cationic surfactant OrangeII dye complex into chloroform and measuring spectrophotometrically the colour intensity of chloroform phase at 485 nm. The estimation of nonionic surfactants have been performed by standard method. The method essentially involve the extraction of nonionic surfactant cobaltothiocyanate complex into dichloro methane and measuring spectrophotometrically the colour intensity of dichloromethane phase at 620 nm.

The study of sorption characteristics and sorption kinetics provide very useful information for fully exploiting the potential of an adsorbent. Batch method because of simplicity and ease of evaluation of adsorption parameters, has been used for the study of adsorption and adsorption kinetics experiments. Adsorption isotherms are shown by determining the adsorption at different concentration of surfactants (1-14 mg/l and 16-112 mg/l in cases of cationic and nonionic surfactants respectively). The isotherms have been plotted to study the effect of temperature, pH, particle size of lignin and salt solutions on adsorption.

RESULTS

Adsorption studies

The plots of surfactant removal vs time of contact indicate that the removal of surfactant occurs in two phases. In the first phase the uptake of solute is fast while in the second phase rate of removal becomes quite slow and subsiquent removal of solute continues over longer period of time. The uptake seems to be complete in two hours in case of cationic and four and half hours in nonionic surfactants. As such all observations have been made after equilibrating the solution with adsorbent for three and six hours in cases of cationic and nonionic surfactants respectively.

The logarithmic plots between surfactant removal and time of contact are linear and may be represented mathematically as —

$$P_s = K_t . t^m$$

or

$$\log P_s = m \log t + \log K_t$$

where, P_s is the percent solute removal and t is the time of contact. The intercept K_t of linear plot is indicative of rate factor while the slope m reflects the mechanism of adsorption.

The results show a positive adsorption in all adsorption isotherms. These are regular and concave to equilibrium concentration axis. The extent of adsorption increases with increasing concentration of surfactants. A rapid adsorption at low surfactant concentration which markedly decreases at high surfactant concentrations with slow approach towards saturation. At low surfactant concentrations, about 60-90% of the surfactant gets adsorbed showing that lignin is quite suitable for the removal of trace quantities of cationic and nonionic surfactants.

Among the two cationic surfactants CPC and CTAB, the uptake of CPC is much higher than CTAB. Since the carbon hydrogen chain length is same in both the molecules, the hydrophobicity of two compounds would be almost similar. As such the difference in the extent of adsorption of CPC and CTAB is due to spatial geometery of the moleculer structure. CPC is a planner molecule and positive charge at nitrogen is more accessible to adsorbents thereby causing a higher uptake of this compound. Substituents in CTAB are tetrahedrally oriented and the bulky groups sterically hinder the positive sites on the adsorbate molecule to come in effective interaction with the adsorbent resulting in a lesser uptake of CTAB as compared to CPC.

The uptake of Tween20 is higher than Tween40. The longer carbon hydrogen chain length in Tween40 molecule leads to higher hydrophobicity which results in lower uptake of Tween40.

The sorption of cationic surfactants is much higher than nonionic surfactants. The lignin particles are negatively charged which attracts more strongly the positively charged organic surfactants thereby giving a higher uptake of cationic surfactants.

The sorption of both cationic and nonionic surfactants increase marginally with increasing pH, resulting in the increased negative charge on lignin surface. The adsorption is also found to increase with decrease of particle size of lignin. As particle size is reduced, the surface area of lignin particle is increased, which results in increased chance of contact between lignin particle and surfactant molecule.

In the presence of salts, the adsorption of surfactants decrese in the order of $Al^{3+} > Ca^{2+} > Na^{+}$. The adsorption has also been found to increase with increasing temperature of adsorption for both cationic and nonionic surfactants. The heat of adsorption is exothermic and the values increase with extent of adsorption. The values being higher for CTAB than CPC and Tween20 than Tween40.

The adsorption data has been correlated with both Langmuir and BET adsorption models. A good linerization of data is not observed if it is plotted for BET models for the entire concentration range of surfactants studied. As such plots have been limited only to low concentration of surfactants. It has also not been possible to make BET plots of the sorption data of Tween40. The values of Q^{o}, the amount of surfactants adsorbed for forming a complete monolayer on adsorbent surface, for both cationic and nonionic surfactants as calculated from BET plots are lesser than the one oriented from Langmuir plots. The values of Q^{o} are in the same order in which these are adsorbed on lignin. The values of constant "A" which reflect the energy of interaction with the surface are also in the same order in which these surfactants are adsorbed on lignin.

The entire data is much better represented by Langmuir model. The values of "b" are lower than those obtained from BET plots. The values being higher for cationic surfactants than nonionic surfactants. CPC has higher value of "b" than CTAB and Tween20 higher than Tween40. The value of "b" reflects the steepness of approach to saturation, more specifically "b" is the reciprocal of concentration at which half saturation of the adsorbent is obtained. Thus greater values of "b" for cationic surfatants indicate a greater tendency towards adsorption.

Adsorption kinetic studies

The sorption kinetic studies (F vs t plots) indicate that for both the cationic and nonionic surfactants, the sorption process is quite rapid and about 50-80% of the adsorption occurs in the first 20-30 minutes of contact. This initial rapid adsorption subsequently gives a slow approach to equilibrium. These curves also indicate that the amount of solute removed during the first ten minutes of contact increases with increase in concentration of adsorbate. However the time required for 50% adsorption is more or less unaffected by the entire adsorbate concentration. This suggests particle diffusion may be the rate controlling step.

The Bt vs t plots for both cationic and nonionic surfactants are linear and passing through origin. These plots are independent of initial solution concentration at and above 11 and 80 mg/l in case of cationic surfactants and nonionic surfactants respectively. However at lower concentration, the curves deviate from linear behaviour. This shows that the adsorption of cationic and nonionic surfactants is particle diffusion controlled at and above 11 and 80 mg/l respectively while at low solution concentration, the film diffusion also affects the adsorption.

The adsorption rate has been found to increase with increase of temperature for both cationic and nonionic surfactants. Increase in mobility of the sorbing species at higher temperature results in increased sorption rate. The increase in sorption rate with increase in temperature further support particle diffusion as the rate controlling process.

The shapes of McKay plots for both cationic and nonionic surfactants are similar to those obtained for independently decaying radioactivities. The initial portion of these plots are convex to log(1-F) axis while the later portion lies on a straight line. It indicates that in the sorption of both cationic and nonionic surfactants, mainly two interdiffusion processes, contribute to the overall rate of sorption.

(i) a faster process, corresponding to residual curve

(ii) a slower process, corresponding to later straight line portion of the plot.

The nonlinear behaviour of McKay plots is also an evidence in favour of particle diffusion mechanism as the rate controlling step.

The values of D_i, the effective diffusion coefficient are in the same order in which these surfactants are adsorbed on lignin i.e., CPC > CTAB > Tween20 > Tween40. The geometry and bigger size of CTAB as compared to CPC and higher size of Tween40 as compared to Tween20 causes more hinderance with in the pores of the sorbent.

The energy of activation, E_a has been evaluated from the linear behaviour of $\log D_i$ vs $1/T$ plots and D_o values have been used to calculate ΔS^*, entrpy of activation. A higher value of E_a has been observed for cationic surfactants than nonionic surfactants. The value being higher for CTAB than CPC among cationic and Tween20 higher than Tween40 among nonionic surfactants. The entropy of activation values are negative for all the surfactants except for CTAB, where a positive entropy of activation has been observed. The negative value of ΔS^* for CPC, T20 and T40 indicates that these surfactants do not cause any structural changes in the sorbent material. A positive ΔS^* associated with CTAB indicates the disorder produced as a result of the uptake of surfactant cation.

ACKNOWLEDGEMENT

It is a great privilege of mine that I have got an opportunity to express my gratitudes to my guide Dr. A.K. Jindal, Lecturer, I.P.T., Saharanpur for his precious pieces of advise and guidance to me.

I fell indebted to my guide Dr. Satish Kumar, Lecturer, I.P.T., Saharanpur for his sincere help and single hearted devotion in providing me all the facilities and encouragement in the completion of this work.

I owe to Dr. A.K. Singh, Dr. S.P. Singh, Dr. A.K. Ray, Mr. R.S. Malik as well as Mr. S.C. Sharma for their co-operation during my work.

I also feel thankful to my elder brother Mr. R.K. Gupta for his motivation to undertake this work. I express my gratitudes to my teacher Dr. M.K. Maheshwari who inspired me to set out for this task.

Similarly, I am quite unable to express my feelings in words to my life partner, Mr. Rajendra Agarwal, Lecturer, G.I.C., Thatyur who extended all his co-operation and support in the fulfilment of this work.

Lastly, I can't forget the love and blessings of my parents who always wish me sucess in every field of life. I am equally thankful to my family and my accepted brother Mr. Ashok Maheshwari who have helped me a lot by giving invaluable co-operation in obtaining my goal.

In the end, I once again thank all the gentlemen for all that they did for me and I pray to God Almighty to fill in me the ability and persevarence so that in future I may also in return help somebody and be a model in this light.

(ANUJA GUPTA)

CONTENTS

CHAPTER - 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Growing urbanization and industrialization has resulted in increased discharge of polluted water i.e., water contaminated with acids, bases, oils, greasy materials, tarry matters, floated and suspended solids and a whole range of obnoxious solid materials. In contrast with domestic wastes of metabolic origin, these pollutants are resistant to biochemical oxidation or are biochemically degraded very slowly. Thus, these persist in water for longer period and reach obnoxious concentrations with multiple reuse of water.

The presence of such pollutants is objectionable and damaging for many reasons. These cause foaming and impart undesirable taste and odour to water and are source of hazard to public health and safety. Impairment of coagulation, fouling of ion exchange resins and potential toxicity are other factors of concern which are caused by their presence.

Of the known organic substances, biochemically resistant surfactants are the most frequently occurring group of compounds which present some of the most wide spread and severe problems in wastes and receiving waters. A regular discharge of synthetic surfactants into municipal sewage causes frothing troubles in operation tanks. Besides their tendencies to cause persistent foam, the possible toxicity of some of their constituents to fish and other aquatic flora as well as on human beings is quite alarming.

1.1 THE NATURE OF SURFACTANTS

By definition a detergent is anything that cleans. All the detergent formulations as part of their chemical make up include surface active compounds or surfactants. The surfactant tends to lower surface tension, which in turn permits dirt particles to be lifted or floated off the article to be cleaned by the wash water. Surfactants derive their properties from the presence of the same molecule of a strong hydrophilic group and a hydrophobic moiety which causes them to aggregate at the surface of an aqueous solution, thus reducing its surface tension properties. The surfactants can be divided mainly into three groups — cationic, anionic and nonionic surfactants.

Cationic surfactants have a positively charged surfactant ion in solution and are mainly quaternary nitrogen compounds such as $RN^+(CH_3)_3$ (tetra alkyl ammonium ion) or $C_5H_5N^+(CH_2)_nCH_3$ (N-alkyl pyridinium ion). These are being used as sanitizers, disinfectants etc. These are not widely used as household detergents due to their higher costs compared to anionic detergents. They react directly with molecules of odorants and kill the micro organisms that might cause odours.

Anionic surfactants have a negatively charged surfactant ion in aqueous solution, usually derived from a sulphate, carboxylate or sulphonate grouping. The alkyl benzene sulphonates have been the most widely used of the synthetic surfactants, because of their excellent cleaning properties, chemical stability and low cost.

Nonionic surfactants have increased in importance in the last fifteen years, gradually replacing the alkyl benzene sulphonates in detergent formulations. Their removal in waste waters is thus of considerable importance, but apart from the fact that these are known to biodegrade (1,2), many details of the intermediary metabolism of these polymeric glycol like surfactants is unclear. In nonionic surfactants, both the hydrophilic and hydrophobic groups are organic, and do not ionise, so their surface active properties are due to the cumulative effect of the multiple weak organic hydrophils. Their manufacture is achieved by polymerisation of several ethylene oxide molecules on to substrates with a labile H-atom, such as alcohol, to yield alcohol ethoxylates, alkyl phenols to form alkyl phenol ethoxylates or high molecular weight carboxylic acids, usually fatty acids, to produce polyoxyethylene esters.

1.2 WASTE WATER PROBLEM

Surfactants create problems in waste water and sewage treatment plants (3,4). ABS residues (5,6) could foam at very low levels (1 mg/l). In India ABS levels in waste water are in the range of 20-25 mg/l. In the case of cationic surfactants noticeable disturbing effects have been observed at a concentration of 3.0 mg/l.

Adelson et al. (7) and Mackenzie (8) have reported the toxicity of surfactants. They have reported that even a small dose (less than 1 oz) containing ten percent cationic surfactant proved fatal. In some cases sodium alkyl sulphonates have been found to be responsible for gastroduodenal ulceration (9).

The detergents may cause the pollution of ground waters as well. When sewage effluents containing these surfactants are dumped into rivers or streams, pollution of ground water may occur through natural infiltration. Likewise the septic tank effluents may also pollute ground water. Where drinking water is drawn from shallow wells near septic tanks, ABS and other pollutants may appear in water.

1.3 SURFACTANT BIODEGRADATION

Biodegradation is the destruction of a chemical compound by the action of a living organism, usually a microbe, i.e., compound is utilized by the organism to promote its growth. It means either the complete mineralization of compound into carbon dioxide and water or the formation of altered substance, through oxidative microbial action that has lost its characteristic properties.

Quite a significant amount of literature exists on the biodegradation of surfactants. Orsanco (10), Hettche (11), Heinz (12), Cohen (13), Fischer (14) and Keefer (15) have studied the pollution of water vis a vis synthetic surfactants. Garshenin (16) has studied the physical, biochemical and toxicological properties of ABS. The effect of detergents on water supplies and on irrigation waters has been reviewed by Harris et al. (17) and Masche (18). Long term effects of surfactants on fish have been studied by Mann (19) and Cairns (20).

Studies (21-24) on the biodegradation of detergents reveal that their decomposition is slow and these are never completely removed by this process. Since the offending substances are of molecular size and are not amenable to biological degradation some other form of treatment for economic removal of these substances from wastes is necessary. Possible methods include coagulation, sedimentation, filtration, adsorption and ion-exchange.

1.4 TREATMENT METHODS

Impurities in water vary in size and largely removed by sedimentation. Many of the impurities are too small for gravitational settling alone and the agglomeration of these particles into large aggregates which would settle readily is essential for successful separation by sedimentation. The process of aggregation is termed coagulation. Efficacy of some coagulants (25-27) e.g., synthetic organic polymers, activated silica, aluminium and iron salts etc. have been investigated. Gravitational separation by sedimentation is also an effective technique for removal of unstable suspended solids.

Filtration is used for the removal of solids present in surface waters, precipitated hardness from lime softened water and precipitated iron and manganese present in many well water supplies. Granular media which have been used by other workers for filtration is sand, crushed anthracite coal, powdered or granular activated carbon (28,29). A combination of these media are also in use. The most common medium, by far, is a graded bed of silica sand.

1.5 ADSORPTION

Adsorption, first observed by Scheele in 1773 for gases and subsequently by Lowitz in 1785 for solutions, is now a well recognized phenomenon in most biological and chemical processes. Sorption on activated carbon is a well known method for the purification of water.

Clays, some inorganic ion exchangers are used in the removal and recovery of radioactive material, but, at present, synthetic organic resins are used as ion exchangers.

Of all the methods adsorption appears to offer best prospects for overall treatment. Broadly speaking, the term sorption also includes ion exchange adsorption. The process is useful for a broad range of substances and is normally expected to be reversible so that regeneration of the adsorbent with resultant economy of operation may be possible. Middleton has shown it to be one of the most promising techniques for removal of organic refractories (30). Accordingly research was undertaken and in most of the studies activated carbon has been used as adsorbent and the potentialities for using this material for the renovation of water and the final treatment of wastes have been explored. The work has primarily been directed to study the characteristics of adsorption of typical pollutants e.g., rates and capacities for adsorption, adsorptive equilibria as functions of the nature and concentration of adsorbate etc. Temperature and pH effects have also been evaluated. (31-34).

Weber and Morris (35), carberry and Geyer (36), Sundstrom (37), Mohamed et al. (38) and Belfort (39) utilized activated carbon for the removal of organic pollutants. There are two problems associated with the use of carbon for the adsorption of pollutants from water, especially if it is to be used on a regular basis for a large volume of water. One is its relatively high cost, making renovation of water rather expensive if carbon is used once and then discarded. The other is the fragility of activated carbon particles, thus making their regeneration and reuse difficult.

1.6 OTHER ADSORBENTS

In view of the economic drawbacks involved with the use of activated carbon, a search was made for materials which might be more suitable than carbon, either because of lower initial cost or because of potentially greater ease of regeneration.

Renn and Barada (40) have studied a variety of substances e.g., ground lime stone, diatomaceous earth and talc etc., but none were found comparable to carbon as far as the adsorption capacity was concerned.

Pitter (41) studied the adsorption of alkyl sulphate and alkyl aryl sulphonate using the generator ash. Sand has also been used for the removal of non ionic surfactants (42,43) and some heavy metal ions (44). Ferric hydroxide and activated bauxite exhibited good potentialities for the sorption of surfactants (45). Activated and digested sludge has also been tried by Malz (46) as adsorbent. Fly ash which is the waste product of electrical power plants and also obtainable in large quantities during burning of coal at high temperature, has been tried by few investigators (47-50). Soil has also been utilized for the removal of surfactants (51-55), Phenols (56) and fatty acids (57) etc., from aqueous media. Kaolinite (58-60), Calcite (61) have been used to remove surfactants from their aqueous solutions. A study has been made for the sorption of nonionic surfactants on silica gel (61-64). Sorption of anionic surfactants has also been carried out by using silicate (65) as sorbent. Organic matter, humus, has also been used by some workers as adsorbent (66,67). Page and Wayman (68) and Jackson et al. (69) have reported the adsorptive characteristics of humus. Lenhard et al. (70) also used humic acid as an adsorbent for anionic surfactants. Aerosil (71), Zeolites (72-76), alumina (77) have also been utilized as adsorbents by some workers.

The results with sludge and flyash are not very promising. Capacities of adsorption are quite low. In case of fly ash, adsorption increases with time but the capacity even after a long period of contact was very small. Activated bauxite, however, has comparable adsorption properties as that of activated carbon.

Organic ion exchangers have also been used as adsorbents for the removal of phenols (78,79). Attempts have also been made for the removal of anionic surfactants by using a strong base resin in chloride form by Abrams and Lewon (80). The application of synthetic organic resins for the sorption of organic compounds have been reviewed by Kim, Snoeyink and Saunders (81).

Organic resins although possess good sorption properties and selectivity, are mechanically and chemically less stable and undergo degradation as well as loss in exchange capacity especially at elevated temperatures.

Inorganic gels, exhibiting ion exchange properties, are mechanically and chemically more stable, have high exchange capacity and are stable at high temperatures and in presence of highly ionizing radiations. Numerous papers have appeared on the synthesis and properties of a variety of compounds e.g., metal hydrous oxides (82,83), metal ferrocyanogen complexes (84,85) complexes of polyacids (86,87) and heteropoly acid salts (88,89). Removal of surfactants by using adsorption techniques have recently been reviewed by some workers (90-92).

1.7 THE PROBLEM

A survey of existing literature reveals the necessity to explore some suitable adsorbents. It is all the more necessary, in view of the drawbacks involved with adsorbents like activated carbon and fly ash. The initial cost of activated carbon and the difficulty as well as the cost associated with its regeneration makes it economically unsuitable. Although fly ash is a waste product of electrical power industry, its sorption capacity is low and it can not be regenerated. Naturally there would be a problem of disposal of used fly ash.

Lignin is another material which possesses adsorption properties. Kleinert (93) has shown that the uptake of sulphurous acid at room temperature by proto lignin follows the Freundlich equation. Some phenolic compounds are also adsorbed in a similar manner. The uptake of formaldehyde follows Henry's solution equilibria and furfural follows the Frendlich adsorption equation.

Wedekind and Garre (94,95) studied the sorption of some dyes like Water (light) blue, Congo red, Nile blue and Neutral blue and showed that these dyes are completely taken up by lignin and can be completely removed by hot water. Lignin is also shown to sorb water and a number of other organic compounds (96-99).

Lignin is a bye product obtained as black liquor during the manufacture of paper. Small paper industries in India face problems for its disposal. This material has not been tried for the removal of surfactants from waste waters. Keeping this in mind, it was thought worth while to investigate the use of lignin as adsorbent for the removal of surfactants from waste water.

The two cationic adsorbates used are Cetyl pyridinium chloride (CPC) and Cetyl trimethyl ammonium bromide (CTAB) and two nonionic adsorbates are Tween20 (T20) and Tween40 (T40).

In order to make the interpretation of the results less complicated as far as possible, the experiments have been carried out with solutions of pure adsorbates. However some measurements of adsorption in presence of salts etc. have also been made.

The second chapter of this thesis deals with the characterisation of materials including methods used for isolation of lignin, equilibrium sorption as well as kinetic studies.

Equilibria of adsorption, optimum conditions for the removal of surfactants by lignin are described in third chapter. Adsoption studies have been performed by Batch procedure. The amount of uptake of surfactants as a function of adsorbate concentration, pH, temperature have studied and all are included in this chapter.

The kinetics of uptake of surfactants as a function of adsorbate concentration and temperature are given in fourth chapter. The kinetic and thermodynamic parameters of the process have also been evaluated.

REFERENCES

1. C.D. Frazee, Q.W. Osburn, and R.O. Crisler, J. Amer. Oil Chemists Soc., 41, 808 (1964).
2. Q.W. Osburn and J.H. Benedict, J. Amer. Oil Chemists Soc., 43, 141 (1966).
3. Task Group Report, J. Amer. Water Works Assocn., 46, 770 (1954).
4. J.M. Flynn, A. Andreoli, and A.A. Guerrera, J. Amer. Water Works Assocn., 50, 1551 (1958).
5. M. Elton, Journal and Proc. of Institute of Sewage Purification., page 351 (1966).
6. R.D. Swisher, Arch. Environ. Health, 17, 232 (1968).
7. L. Adelson and I. Sunshine, J. Clinical Path., 22, 656 (1952).
8. E.F.W. Mackenzie, J. Brit. Water Works Assocn., 35, 75 (1953).
9. S.J. Fogelson and D.E. Shock, Arch. Int. Med., 73, 212 (1954).
10. Orsanco Comittee Report, J. Amer. Water Works Assocn., 55(3),369 (1963).
11. H.O. Hettche, Water Polln. Abs., 35, 378 (1962).
12. H.J. Heinz and W.K. Fischer, Public Health Engg. Abs., 58, 1531 (1963).
13. M.M. Cohen, J. Amer. Oil Chem. Soc., 40, 645 (1963).
14. W.K. Fischer, Fette, Seifen Anstrichmittel (Germany), 66, 51 (1964).
15. C.E. Keefer, Public Works, 95 (1), 82 (1964).
16. V.F. Garshenin, Maslob. Zhir Prom., 29, 20 (1963).
17. A.J. Harris, J. Amer. Water Works Assocn., 63, 795 (1971).
18. H. Masche, Chemical Abstracts, 74, 140178s (1971).
19. H. Mann and O. J. Schmid, Int. Rev. Ges, Hydrobiol., 46, 419 (1961).
20. J. Cairns, Ind. Water and Wastes, 9, (1), 22 (1964).

21. H. Knopp, Water Polln. Abs., 35, 1019 (1962).

22. P. Pitter, Pub. Health Engg. Abs., 44, 1760 (1964).

23. R.D. Barbaro and J.V. Hunter, Proc. XX Ind. Waste Conf., 118, 189 (1965).

24. P.N. Degens and H. Van Der Zee, J. App. Chem., 5, 517 (1955).

25. W. Stumm, Environ, Sci. and Tech., 1, 221 (1967).

26. H.H. Hahn, J. Colloid and Int. Sci., 28, 134 (1968).

27. C.R. O'Melia, Public Works, 100, 87 (1969).

28. J.L. Cleasby, J. Amer. Water Works Assocn., 61, 181 (1969).

29. D.E. Burns, Engg. Res. Inst. Prep., 382, Iowa State Univ., (1969).

30. F.M. Middleton, Proc. Seminar on Advanced Waste Treatment Research, Cincinnati, Ohio, (May 1962).

31. R.S. Joyce, J.B. Allen, and V.A. Sukenik, J. Water Polln. Control Fedn., 38(5), 813 (1966).

32. J.S. Mattson and H.B. Mark, J. Colloid and Int. Sci., 31, 116 (1969).

33. W.J. Weber, Jr. and J.C. Morris, J. San. Engg. Div., 90 79 (1964).

34. W.J. Weber, Jr. and J.C. Morris, J. Amer. Water Works Assocn., 56(4), 447 (1964).

35. W.J. Weber, Jr. and J.C. Morris, J. Water Polln. Control Fedn., 37, 425 (1965).

36. J.B. Carberry and A. T. Geyer, J. Water Polln. Control Fedn. 49, 452 (1977).

37. D.W. Sundstrom, H.E. Klei, and T. Tsui, Water Research, 13, 1225 (1979).

38. A. Mohamed, EL-Dib, and I.B. Mohamed, Water Research, 13, 225 (1979).

39. G. Belfort, Environ. Sci. and Tech. 13, 1939 (1979).

40. C.E. Renn and M.F. Barada, J. Amer. Water Works Assocn., 53, 129 (1964).

41. P. Pitter, Pub. Health Engg. Abs. 44, 1758 (1964).

42. R.A. Musaev and G.A. Babalyan, Pub. Health. Engg. Abs., 61, 9666 (1964).

43. Rouquerol et al., J. Chem. Technol. Biotechnol, 31(10), 584 (1981).

44. A. Netzer and P. Wilkinson, Proc. 29th Ind. Waste Conf. Purdue, 841 (1974).

45. C.H. Wayman and J.B. Robertson, Amer. Chem. Soc., Div. of Water and Wastes Chem., 4, 190 (1966).

46. F. Malz, Water Polln. Abs., 37, 27 (1964).

47. P.K. Deb, Proc. 21st Ind. Waste Conf. Purdue, 848 (1966).

48. W.J. Weber, J. Water Polln. Control Fedn., 1905 (1969).

49. J.N. Williamson, A.H. Heit, and C. Calmon, Final Tech. Report, Ionac Chemical Co., (1962).

50. Mancy et al., Proc. 19th Ind. Waste Conf. Purdue, 46 (1964).

51. M.J. Suess, J. Water Polln. Control Fedn., 36, 1393 (1964).

52. D.H. Fink, G.W. Thomas, and W.J. Meyer, J. Water Polln. Control Fedn., 42, 265 (1970).

53. B.F. Hajek, J. Water Polln. Control Fedn., 41, 1775 (1969).

54. Abe et al., Nippon Kagaku Kaishi, (5), 814 (1985).

55. Abe et al., Nippon Kagaku Kaishi, (5), 820 (1985).

56. M.D. Luh and R.A. Baker, Proc. 25th Ind. Waste Conf. Purdue, 534 (1970).

57. L. Hemphill and W.S. SwanSon, Proc. 18th Ind. Waste Conf. Purdue, 204 (1963).

58. F.D. Ovcharenko, Ukr. Khim. Zh., 51(10), 1018 (1985).

59. Kronberg et al., Colloids Surf., 18(2-4), 411 (1986).

60. Siracusa et al., Colloids Surf., 26, 55 (1987).

61. N.I. Ivanova et al., Kolloidn. Zh., 49(1), 148 (1987).

62. S. Partyka et al., Colloids Surf., 12(3-4), 255 (1984).

63. Gu, Tiren, J. Colloid Interface Sci., 85(2), 601 (1982).

64. B. Brun et al., J. Chim. Phys. Phys.-Chim. Biol, 85(7-8), 821 (1988).

65. N.A. Klimenko, A.E. Bortnitskii, Kolloidn. Zh., 47(3), 487 (1985).

66. C.H. Wayman and J.B. Robertson, Proc. 18th Ind. Waste Conference, 115, 523 (1964).

67. R.D. Barbaro and J.V. Hunter, Water Research, 1, 157 (1967).

68. H.G. Page and C.H. Wayman, Ground Water, 3, 10 (1966).

69. M.L. Jackson, V.V. Volk, and Krishna Murti, Soil Sci. Soc. Amer. Proc. 30, 685 (1966).

70. G. Lenhard and A. Du Plooy, Hydrobiologia, 22, 317 (1963).

71. S.A. Savintseva et al., Kolloidn. Zh., 44(1), 158 (1982).

72. M.J. Schwuger, W. Von Rybinski, P. Krings, Adsorpt. Solution, Symp., 185 (1983).

73. H.D. Doerfler et al., Tenside Deterg., 21(3), 117 (1984).

74. K.H. Bergk et al., Tenside Deterg., 21(3), 123 (1984).

75. W. Schirmer, Khim. Fiz., (9), 1256 (1982).

76. M.J. Schwuger et al., Prog. Colloid Polym. Sci., 69, 167 (1984).

77. S. Partyka et al., Calorim. Anal. Therm., 16, 76 (1985).

78. F.X. Pollio and R. Kunin, Environ. Sci and Tech., 1, 160 (1967).

79. J.S. Kumagai and W.J. Kaufman, SERL Rap. No. 68-8, San. Engg. Res. Lab., California, (1968).

80. I.M. Abrams and S.M. Lewon, J. Amer. Water Works Assocn., 54, 537 (1962).

81. B.R. Kim, V.L. Snoeyink, and F.M. Saunders, J. Water Polln. Control Fedn., 48, 121 (1976).

82. C.B. Amphlett, L.A. McDonald, and M.J. Redman, Chem. and Ind., 1314 (1956), J. Inorg. Nucl. Chem., 6, 220, 236 (1958)

83. K.A. Kraus, H.O. Phillips, T.A. Carlson, and J.S. Jonnson, Proc. II Intern. Nat. Conf. on 'Peaceful uses of Atomic Energy', Geneva, 28, 3 (1958).

84. W.E. Prout, E.R. Russell, and H.J. Groh, J. Inorg. Nucl. Chem., 27, 473 (1965).

85. J. Scheidhaur, G. Vergnaud, and A. Flamant, Commis. Energy At. France, Rap., No. CEA-R-3585 (1968).

86. C.B. Amphlett, 'Inorganic Ion Exchangers', Elsevier, Amsterdam, (1964).

87. I.S.C. Churms, S. African Ind. Chemists, 19, 26, 48, 68, 87, 148 (1965).

88. J.F. Keggin, Proc. Roy. Soc., (London), A144, 75 (1934).

89. J.W. Illingworth and J.F. Keggin, J. Chem. Soc., 575 (1935).

90. J.S. Clunie, B.T. Ingram, Adsorpt. Solution Solid/Liq. Interface, 105 (1983).

91. D.B. Hough, H.M. Rendall, Adsorpt. Solution Solid/Liq. Interface, 247 (1983).

92. Koopal et al., Colloids Surf., 17(4), 371 (1986).

93. Th. Kleinert, Monatsh, 80, 135 (1949).

94. E. Wedekind, G. Garre, Kolloid-Z., 44, 202 (1928).

95. E. Wedekind, G. Garre, Z. angew chem., 41, 107 (1928).

96. N. A. Ponkina, K.A. Ioileva, E.Yu. Gardin, I.L. Lapides, and N.F. Komshilov, Tr. Karel'sk Filiala Akad, Nauk SSR, 38, 26 (1963).

97. R. Jodl, Brennstoff-Chem, 23, 163 (1942).

98. Hj. Saechtling and H. Zocher, Kolloid-Beiheft, 40, 413 (1934).

99. Hj. Saechtling and H. Zocher, Kolloid-Z, 72, 336 (1935).

CHAPTER -2

MATERIALS AND METHODS

MATERIALS AND METHODS

2.1 ISOLATION OF LIGNIN

As early as in 1939, Hess and coworkers (1) attempted to isolate lignin from plant material finely ground in a vibrational mill to a particle size 1-2 µ. Bjorkman (2) also used wood, ground in an oscillating mill for the isolation of lignin. Schobinger isolated soluble native lignin from wheat straw according to Bjorkman's method. Nord and coworkers (3) isolated lignin from various coniferous and deciduous woods and from bagasse. Pew (4) treated spruce wood with brown rot fungi, using the soil block method and obtained lignin residues in yields.

Willstatter's method for the isolation of lignin with HCl was modified by Hachihama and Jyodai (5). Reviews on the isolation of lignin preparations from the pulp industries have been presented by Aries and Pollak (6). All these methods have also been discussed in two recent reviews (7,8).

The sulphate or kraft cooking process is the most important of those used in the paper industry for the delignification of wood. It obtained its name from the discovery by Dhal that the addition of sodium sulphide to the soda cooking liquor increased not only the yield but also the quality of the pulp. Investigation of what is now called "Thio lignin" was originally carried out by Ahlm (9).

Lignin isolated from spent black liquor by sulphate process is called as thio lignin was prepared as follows — .

Eucalyptus teriticornis was obtained from Shahdol (M.P.). It was debarked, chipped and screened on the pilot plant equipment. The screened chips were then digested in the laboratory auto clave of 25 litres capacity under the following conditions —

Amount of chemicals (NaOH and Na_2S) – 20% (percent based on oven dried chips)
Sulphidity – 25 Percent
Cooking temperature – 160°C
Bath ratio – 1 : 4
Cooking period – 4 hours (including one and half hour to raise the temperature to the maximum.)

After digestion, the cooked material was filtered through a muslin cloth to remove uncooked pulp. The filtrate was acidified with dilute HCl till the precipitation was complete. The precipitate was then allowed to settle and the supernatent liquid was decanted off. The precipitate was washed repeatedly with distilled water till free from chloride ions and dried at room temperature. The product thus obtained is crude thio lignin.

2.11 Purification

Purification of crude thio lignin was carried out according to Ahlm's method (9).

10% solution of the crude thio lignin in dioxane was prepared, filtered and added drop wise from a burrette into vigorously stirred anhydrous ether to precipitate lignin. The precipitate was washed with ether and then benzene. Finally the precipitate was washed with low boiling petroleum ether and dried over anhydrous $CaCl_2$ under vacuum at room temperature.

2.12 Particle size

The sample of pure lignin was ground and passed through different sieves and the fraction (100 to 200) B.S.S. mesh sizes were collected. It was then suspended in water to remove the adhering fine particles of lignin. It was finally dried by placing it in an oven at 90°C for about 12 hours. The average value of sieve openings was taken as the particle radius.

2.2 ESTIMATION OF SURFACTANTS

2.21 Cationic surfactants

The method of Few and Ottewill (10) was used for the estimation of cationic surfactants. An anionic dye (orangeII) having absorption maxima at 485 nm was used for the determination of small concentrations (1 to 14 mg/l) of cationic surfactants in aqueous solutions. This colorimetric method of analysis depends upon the formation of complex between surfactant and the anionic dye and quantitative extractibility of the complex in organic phase (chloroform) in which the dye itself is insoluble. Estimations of the colour intensity of the organic phase were made at 485 nm.

2.22 Nonionic surfactants

A Standard method (11) was used for the estimation of nonionic surfactants. These surfactants react with aqueous cobaltothiocyanate solution to give a cobalt containing product which is extracted quantitatively into organic liquid dichloromethane. Estimations of colour intensity of the organic phase were made at 620 nm for determining the concentrations (16 to 112 mg/l).

2.23 Reagents

Cationic surfactants Cetyl trimethyl ammonium bromide (CTAB),Cetyl pyridinium chloride (CPC) and nonionic surfactants Tween20 (T20) and Tween40 (T40) were supplied by Sisco Research Laboratory, Bombay and Koch Light Laboratory, England respectively. All other reagents were of analytical grade.

2.24 Preparation of solutions

2.241 Surfactants solution :

The solutions of surfactants were prepared in distilled water.

2.242 OrangeII solution :

0.1% solution of orangeII in distilled water was prepared.

2.243 Cobaltothiocyanate reagent :

30 g of $Co(NO_3)_2.6H_2O$ and 200 g NH_4SCN were dissolved in distilled water and the solution was diluted to 1 litre.

2.25 Instrumentation

pH measurements were made with an Elico Digital pH meter model and Shimadzu spectrophotometer UV-2100S was used for spectrophotometric work.

2.26 Calibration curves

2.261 Cationic surfactants :

Aqueous solutions of different concentrations of cationic surfactants were prepared. Aliquots (23 ml) of the surfactant solutions were pipetted into clean dry conical flasks and to each was added orangeII (2ml) and chloroform (5 ml). The contents were shaken vigorously for one minute and the two layers were allowed to separate. The chloroform layer was separated and the absorbance was measured at 485 nm against reagent blank of orangeII.

2.262 Nonionic surfactants :

Aqueous solutions of different concentrations of nonionic surfactants Tween20 and Tween40 were pipetted into clean dry conical flasks and to each was added aqueous cobaltothiocyanate reagent (10 ml) and dichloromethane (5 ml). The contents were shaken for one minute and the two layers were allowed to separate. The dichloromethane layer was separated and the absorbance was measured at 620 nm against reagent blank of cobaltothiocyanate.

In cases, where the optical density exceeded 0.8, the solutions were diluted. The optical density vs concentration plots were then used for determining the concentration of surfactant solutions obtained during adsorption measurements.

Equilibration time, amount of adsorbent as well as the concentration range of adsorbates used in static as well as in kinetic measurements were decided after a good deal of preliminary investigations.

2.3 SORPTION STUDIES

Batch method was used for adsorption studies. A series of Erlenmeyer flasks were used for adsorption studies. 50 ml of aqueous solution of varying concentrations of surfactants was added to each flask, maintained at the desired temperature. Equal amount of lignin (0.1 g in the case of cationic and 0.05 g in the case of nonionic surfactants) was added into each flask. The flasks were shaken for five minutes and equilibrated for three hours (in the case of cationic surfactants) and six hours (in the case of nonionic surfactants) with intermittent shaking. The supernatant liquid was centrifuged and analyzed for surfactant.

The concentration of unadsorbed surfactant was calculated from the calibration curves drawn for this purpose.

2.31 Effect of pH

To study the effect of pH on adsorption, varying amounts of either HCl, NaOH were added to surfactant solutions and the adsorption studies were made as mentioned above.

2.32 Effect of temperature

To investigate the thermodynamics of sorption process, experiments were performed at different temperatures (20,25,30 and 35 $\pm$ 0.1^{o}C).

2.33 Effect of particle size of lignin

To study the effect of particle size of lignin on the adsorption of surfactants, lignin samples of different particle size viz [<52,(52-100),(100-200) mesh] were taken. Each sample was suspended in water to remove the adhering fine particle and finally dried in an oven at 90^{o}C for about 12 hours.

2.34 Effect of salt solutions on the adsorption

The effect of NaCl, $CaCl_2$, $AlCl_3$ (varying concentrations) on the uptake of cationic and nonionic surfactants were also studied.

2.4 DESORPTION EXPERIMENTS

Lignin was equilibrated with 15 mg/l and 120 mg/l of cationic and nonionic surfactants. The quantity of surfactant adsorbed was estimated. The lignin sample was washed with distilled water and 0.1 g of lignin was equilibrated with 20 ml of various desorbing solutions. Aqueous solution of HCl, NaCl, $CaCl_2$ (concentration from 0.1 M to 1.0 M), hot water and methyl alcohol were used as desorbing solutions. After equilibrium the quantity of the various surfactants in the desorbing solution was estimated.

2.5 KINETIC MEASUREMENTS

Two types of experimental procedures have generally been used in studying the kinetics of adsorption (12-14). A column or a shallow bed arrangement in which the adsorbate solution is percolated through the bed of adsorbent with samples being taken periodically from the effluent is known as infinite bath system. A batch operation is one in which the known amounts of the adsorbent and the adsorbate solution are continuously shaken together and the aliquots are withdrawn periodically from the reaction vessel. This is also known as finite bath method.

In the investigations mentioned here, the batch technique (finite bath systems) was selected because of its relative simplicity. Advantages of this technique are its freedom from complex hydraulic parameters indigenous to flow-through systems, its adaptability to small volume work, ease of investigation in various conditions and general facility of operation. A brief description of the batch technique, in general, is given below —

A weighed amount of adsorbent is placed in contact with a standard solution. The solutions are then agitated by shaking or stirring. Sorption rate is determined by measuring the uptake of adsorbate in solution or by an equivalent release of counter ions from the exchanging material. Thus, a number of experiments were carried out and the uptake as a function of time is determined. The concentration change in solution is estimated by analysis of aliquots withdrawn at various intervals of time.

Boyd and Soldano (15) have applied this technique for labelled solutions. The agitation was provided by stirring the solutions. Kressman and Kitchener (16), however, have developed a slightly different technique. They have used centrifugal stirrer in place of ordinary ones used by Boyd et al. (15). Dichel (17) carried out the experiments in a conductivity cell and determined the extent of uptake by recording the change in conductivity of the solution. In this method, the aliquots need not be withdrawn from the solution for analysis.

2.51 Kinetic studies with cationic surfactants

In these investigations the modified technique (18-22) of Kressman and Kitchener (16) was followed. The details of the experimental set up were as follows —

A number of stoppered corning glass conical flasks (100 ml capacity) containing ~~the~~ known volume (50 ml in each case) and concentration of solutions of the cationic surfactants were placed in a thermostat-cum-shaking assembly, when the desired temperature was reached, a known amount of the sorbent was introduced into each flask and the solutions were agitated by mechanical shaking. At pre decided intervals of time, the solution of the specified conical flasks were separated from the sorbent material and analysed to determine the uptake of the surfactant under study. Equilibrium was attained in about 12 hours.

Above experiments were carried out with lignin as adsorbent, and the cationic surfactants cetyl pyridinium chloride (CPC) and cetyl trimethyl ammonium bromide (CTAB) as adsorbates. The amount of the lignin used in these investigations was 0.1 g in each case and particle size was 100 to 200 mesh in each case.

2.511 Effect of concentration :

To observe the influence of concentration on the rate of sorption, experiments were performed for different concentrations of CPC and CTAB. The concentration range studied was 1-20 mg/l.

2.512 Effect of temperature :

To investigate the thermodynamics of the sorption process, experiments were performed at different temperatures (20,25,30 and 35±0.1°C). Other experimental conditions like particle size and concentration etc. were kept identical for each temperature.

2.52 Kinetic measurements with nonionic surfactants

A similar method as given above for cationic surfactants was followed in the case of nonionic surfactants also. In these cases (Tween20 and Tween40), the uptake was smaller as compared to those of cationic surfactants and the equilibration time was quite high. Effect of the concentration of adsorbate and temperature was also observed.

REFERENCES

1. K. Hess, K.P.Jung, and K.E. Heumann, Naturwissenchaften, 27, 770 (1939).

2. A. Bjorkman, Nature, 174, 1057 (1954).

3. S.F.Kudzin, And F.F. Nord, J. Am. Chem. Soc., 73, 690 (1951).

4. J.C. Pew, Tappi, 40, 553 (1957).

5. Y. Hachihama, and S. Jyodai, "Chemistry of Lignin" Nippon Hyoronsha, Tokyo, P 117 (1946).

6. R.S. Aries, and A. Pollak, Chim. and Ind. (Paris), 63, 494 (1950).

7. B.L. Browning, "Methods of Wood Chemistry." Vol-11, Interscience." New York, P802-812, (1967).

8. I.A. Pearl, "The Chemistry of Lignin" Marcel Dekker, Inc. New York, P47-52, (1967).

9. C.E. Ahlm, Paper Trade J., 113, (13), 115 (1941).

10. A.V. Few and R. H. Ottewill, J. Colloid Sci., 11, 34 (195

11. "Standard Method For the Examination of Water and Waste water", Sixteenth Edition, P585-588.

12. W.J. Weber, Jr. and J. Carrell Morris, J. Sanitary Engg. Division, 89,31 (1963).

13. F.A. DiGiano and W. J. Weber Jr., J. Water Polln. Control Federation, 45, 713 (1973).

14. V.L. Snoeyink and W.J. Weber Jr., J.Sanitary Engg. Divisi 98, 1021 (1972).

15. G. E. Boyd and B. A. Soldano, J. Am. Chem. Soc., 75, 6091 (1953).

16. T.R.E. Kressman and J. A. Kitchener, Discussion Faraday Soc., 7, 90 (1949).

17. G. Dickel and A. Meyer, Z. Elektrochem., 57, 901 (1953).

18. D.E. Conway, J.H.S. Green and D. Reichenberg, Trans. Faraday Soc., 50, 511 (1954).

19. G.H. Nancollas and R. Paterson, J. Inorg. Nucl. Chem.,

22, 259 (1961).

20. C. Heitner-Wirguin and G. Markovits, J. Phys. Chem., 67, 2263 (1963).

21. J.P. Rawat and P.S. Thind, J. Phys. Chem., 80, 1384 (1976).

22. I.P. Saraswat, S.K. Srivastava and A.K. Sharma, Can. J. Chem., 57, 1214 (1979).

CHAPTER -3

ADSORPTION OF SURFACTANTS ON LIGNIN

3.1 Introduction

3.2 Results and Disscussion

— Sorption equilibria, isotherms, models and factors affecting sorption

— Evaluation of parameters, necessary for investigating the sorption equilibria by batch process

— Adsorption of cationic surfactants

— Adsorption of nonionic surfactants

ADSORPTION OF SURFACTANTS ON LIGNIN

3.1 INTRODUCTION

Synthetic surface active agents are being increasingly used for cleaning and laundry formulations. The large scale production of these synthetic surfactants became possible in early fifties with the appearance of tetrapropylene alkyl benzenes derived from oil industry. These surfactants after domestic use or industrial use invariably find their way, along with other domestic wastes, either into ground waters or rivers or in sewage treatment plants. These surfactants cause operational problem in the sewage treatment plants as these are not effectively removed in the existing sewage treatment plants.

Various workers have studied the effect of synthetic detergents (1-4) on plants, animals and humans. Subjects included are toxic limits for men and animals, disturbances produced in water treatment plant and pollution of ground water.

Since the offending substances are not amenable to biological degradation the methods of treatment investigated by various workers include coagulation, froth flo~~a~~tation and adsorption.

Of these methods, adsorption appears to offer the best prospects for overall treatment. It is useful for a broad range of substances more so than any of the other listed processes. More over adsorption is generally reversible, so that regeneration of the adsorbent with the resultant economy of operation may be possible.

Middleton (5,6) has shown that activated carbon can be effectively used for the removal of many objectionable materials from laundry wastes. Accordingly further research was undertaken to explore the potentialities of activated carbon for waste water treatment. Joyce (7), Mattson (8), Weber and Morris (9,10), Sundstrom (11) and Belfort (12) have made significant contributions to the use of activated carbon for waste water treatment. A number of successful systems based on adsorption on activated carbon have been developed. The existing commercial systems use activated carbon exclusively. The relatively high cost, regeneration difficulties and reuse are some of the major problems (13) which are yet to be solved.

With a view to find some other suitable adsorbents, a number of adsorbents have been tried. Notable~~s~~ among these are bauxite, fly ash, soils, clays, ion exchangers etc. Bauxite (14) has not find favour as adsorbent. Fly ash (15) like activated carbon also shows regeneration difficulties. A number of workers have studied the adsorption of both cationic and anionic surfactants on soils (16-18) and have tried to correlate the adsorption capacity of surfactants with aluminium or iron content of the soil. Adsorption of some cationic and anionic surfactants have also been studied on montmorillonite and kaolinite clays (19). Some references are also available where ion exchange resins (20,21) have also been tried for the removal of surfactants. The use of inorganic ion exchangers (22-24) e.g., zinc and copper ferrocyanides as adsorbents have also been explored.

Lignin has been shown to adsorb a number of acid-base dyes (25-27) and many other organic compounds viz. amines (28), phenols (29), alcohols (30), acids (31) etc. The use of lignin as adsorbent for the removal of cationic and nonionic surfactants from their aqueous solution have been explored.

This chapter describes investigations on the sorption of two cationic surfactants CPC and CTAB and two nonionic surfactants T20 and T40 on lignin. The chapter has been divided into four parts. The First part describes sorption equilibria, various adsorption models and the factors affecting adsorption. The Second part deals with the description on some preliminary investigations undertaken to fix up necessary parameters for studying the sorption equilibrium by batch process. Results on the sorption of cationic surfactants are given in part three while ~~the~~ part four describes the uptake of nonionic surfactants on lignin.

3.2 RESULTS AND DISCUSSION

3.21 Sorption equilibria and isotherms

The term "adsorption" appears to have been introduced by Kayser in 1881 to connote the condensation of gases on free surfaces, in contradiction to gaseous adsorption where the molecules of gas penetrate into the mass of the adsorbing solid. The wider term "sorption" proposed by McBain in 1909 embraces both types of phenomena.

The suitability of process of adsorption, as a unit operation, for the treatment of wastes can be determined in terms of two aspects viz., the equilibria and the kinetics of adsorption. The rate of adsorption mostly depends on the method in which the adsorbate comes in contact with adsorbent material. The essential requirements for the unit process are rapid separation of pollutants and a longer life of adsorbing material.

Adsorption from solution on to a solid occurs as a result of driving forces of lyophobic character of the solute, relative to the particular solvent, or of a high affinity of the solute for the solid. The mechanism of adsorption process involves three steps. The first is the transport of the adsorbate through a surface film to the exterior of the adsorbent (Film diffusion). In the second step the diffusion of adsorbate takes place with in the pores of adsorbent (Pore diffusion). The third and final step is adsorption of solute at the interior surfaces bounding the pore and capillary spaces of the adsorbent (Intraparticle transport). The overall rate of the process of adsorption depends on the slowest step. For a batch process "pore diffusion" and for continuous flow system "film diffusion" are the most likely rate controlling factors.

The phenomenon of adsorption in general includes, ion exchange, physical adsorption and chemical adsorption. Ion exchange or exchange adsorption is a process in which ions of one substance concentrate at the surface as a result of electrostatic attraction to charged sites at the surface of adsorbent. Exchange adsorption depends on the charge and hydrated size of ions involved. Adsorption occurring as a result of van der Waals' forces (dispersion forces) is generally termed as physical adsorption. Mostly it is reversible and non specific in nature. Chemical adsorption is a result of specific interactions between the sorbing species and sorbent material. In most cases it is irreversible in nature and is effective at high temperature e.g., sorption of phenols on silica or activated carbon involves hydrogen bond formation.

When adsorption is irreversible, solute molecules can not be eluted from the sorbent material. In reversible adsorption the solute is adsorbed at the surface and then moves towards the interior of the adsorbent. This process continues till the equilibrium distribution of the solute between solid and solution phase occurs. In this type of adsorption recovery of solute is possible.

3.22 The factors affecting sorption

3.221 Nature of adsorbate :

Adsorption increases with decrease in solubility of solute in solvent. The solute-solvent bond is to be broken up before adsorption takes place. Normally, solubility of organic compounds decreases with increasing length of carbon chain and consequently adsorption increases with ascending homologous series. Other factors of importance are molecular size, structure and polarity of adsorbate molecules.

3.222 Nature of adsorbent :

As adsorption is a surface phenomenon, portion of the total surface available for adsorption depends on the particle size and shape of the adsorbent material. The adsorption capacity for a nonporous or porous adsorbent varies as the inverse of the particle diameter but for highly porous adsorbents the adsorption rate is independent of particle diameter. Besides this, the chemical nature of the adsorbent material is also a task of interest which determines the rate of adsorption.

3.223 Method of contact :

The uptake of adsorbate material also depends on the type and rate of contact i.e., the rate of adsorption may be different in "Batch mixing" or "Continuous flow system".

3.224 Besides these, the amount of adsorbent, concentration of sorbate in solution, pH, temperature etc. also affect adsorption.

3.3 ADSORPTION MODELS

During adsorption, solute goes to interface till equilibrium is attained between that in bulk and at the surface at a constant temperature. At the position of equilibrium, there is a defined distribution of solute between the two phases. It is conventional to depict the distribution by plotting the amount of solute adsorbed per unit weight of adsorbent vs the concentration of solute remaining in the solution at equilibrium i.e., equilibrium concentration, at constant temperature. An expression of this type is termed as adsorption isotherm. The type of isotherms followed by a system can be any (or a combination) of the following —

3.31 Langmuir adsorption model is valid for monolayer adsorption. This is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant and distributed uniformly at the surface and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented as —

$$q_e = \frac{Q^o\ b\ C}{(1 + b\ C)} \qquad (1)$$

C = remaining concentration of solute in solution at equilibrium.

q_e = amount of solute adsorbed per unit weight of adsorbent.

Q^o = number of moles of solute adsorbed per unit weight of adsorbent, for forming a monolayer on the surface.

b = constant related to energy or enthalpy of adsorption.

It can also be written as —

$$\frac{C}{q_e} = \frac{1}{Q^o\ b} + \frac{C}{Q^o} \qquad (2)$$

and thus a plot of C/q_e vs C gives a straight line of slope $1/Q^o$

and intercept $1/b\ Q^o$.

The assumptions of Langmuir model are not true for most systems of waste water treatment, yet this equation is very useful for the treatment of adsorption data. For example, the value of Q^o for organic wastes on activated carbon does not represent monolayer formation but a fractional limiting capacity for adsorption, which is also a factor of practical utility.

3.32 The Freundlich isotherm is a special case for heterogeneous surface energies in which the energy term, varies as a function of surface coverage due to variations in heat of adsorption. The Freundlich equation can be represented as —

$$q_e = K_f\ C^{1/n} \qquad (3)$$

Data are usually fitted to the logarithmic form of the equation —

$$\log q_e = \log K_f + \frac{1}{n} \log C \qquad (4)$$

$\log q_e$ vs $\log C$ gives a linear plot with a slope of $1/n$ and an intercept equal to $\log K_f$. The intercept is an indicative of sorption capacity and the slope, of adsorption intensity.

3.33 BET isotherm is indicative of sequential multilayer adsorption and is described by the following equation —

$$q_e = \frac{A\ C\ Q^o}{(C_s - C)\ [1 + (A - 1)\ C/C_s]} \qquad (5)$$

where, q_e and C are the same as given above.

C_s = saturation concentration of solute.

Q^o = number of moles of solute adsorbed in forming a complete monolayer on adsorbent surface.

A = constant, expressive of the energy of interaction with the surface.

The BET model can be linearized to yield the following equation —

$$\frac{C}{(C_s - C)\, q_e} = \frac{1}{A\, Q^o} + \frac{A - 1}{A\, Q^o} \; \frac{C}{C_s} \qquad (6)$$

The constants A and Q^o can be evaluated by plotting $C/(C_s - C)\, q_e$ vs C/C_s.

3.4 HEAT OF ADSORPTION

The process may be exothermic or endothermic. If the adsorption increases with temperature, the process is exothermic and if the adsorption decreases with increase of temperature, the process is endothermic. The heat of adsorption is calculated by the equation —

$$Q = R \frac{T_1\, T_2}{T_1 - T_2} \log \frac{C_1}{C_2} \qquad (7)$$

Where C_1 and C_2 are the concentrations of the solute at temperature T_1 and T_2 for the same amount of adsorption.

3.5 EVALUATION OF PARAMETERS, NECESSARY FOR INVESTIGATING THE SORPTION EQUILIBRIA BY BATCH PROCESS

The parameters to be fixed up for investigating the equilibrium by batch process are —

(a) concentration of adsorbate in solution

(b) particle size of adsorbent material

(c) equilibrium time of adsorbate and adsorbent

(d) quantity of adsorbent

(e) pH and temperature.

A moderate concentration of adsorbate 1-14 mg/l in case of cationic surfactants and 16-112 mg/l in case of nonionic surfactants has been chosen for running of adsorption isotherms. This has been decided, keeping in view, the surfactants levels likely to be present in waste water and the concentration ranges at which noticeable change in concentration of surfactants have been observed.

After trying a variety of fractions of particle sizes, it was found that the removal of surfactants is most convenient and maximum when 100 to 200 mesh size of particles is taken. Thus 100 to 200 mesh size of particles has been used throughout these investigations.

The equilibration time and quantity of adsorbent for optimum adsorption have been determined experimentally by observing the effect of the time of contact at a fixed adsorbate concentrations (10 mg/l for CPC and CTAB, 100 mg/l and 80 mg/l for Tween20 and Tween40 respectively). The quantity of adsorbent has been decided after making a few trial runs. 100 mg of adsorbent in case of cationic surfactants and 50 mg in case of nonionic surfactants per 50 ml of solution has been maintained for all the adsorption experiments.

The results of these experiments depicted in Figs. 1 and 2 are the plots of percent surfactant removal vs time of contact. The nature of plot indicate that the removal of surfactants occur in two phases. In first phase the uptake of solute is fast while in second phase rate of removal becomes quite slow and subsequent removal of solute continues over longer period of time.

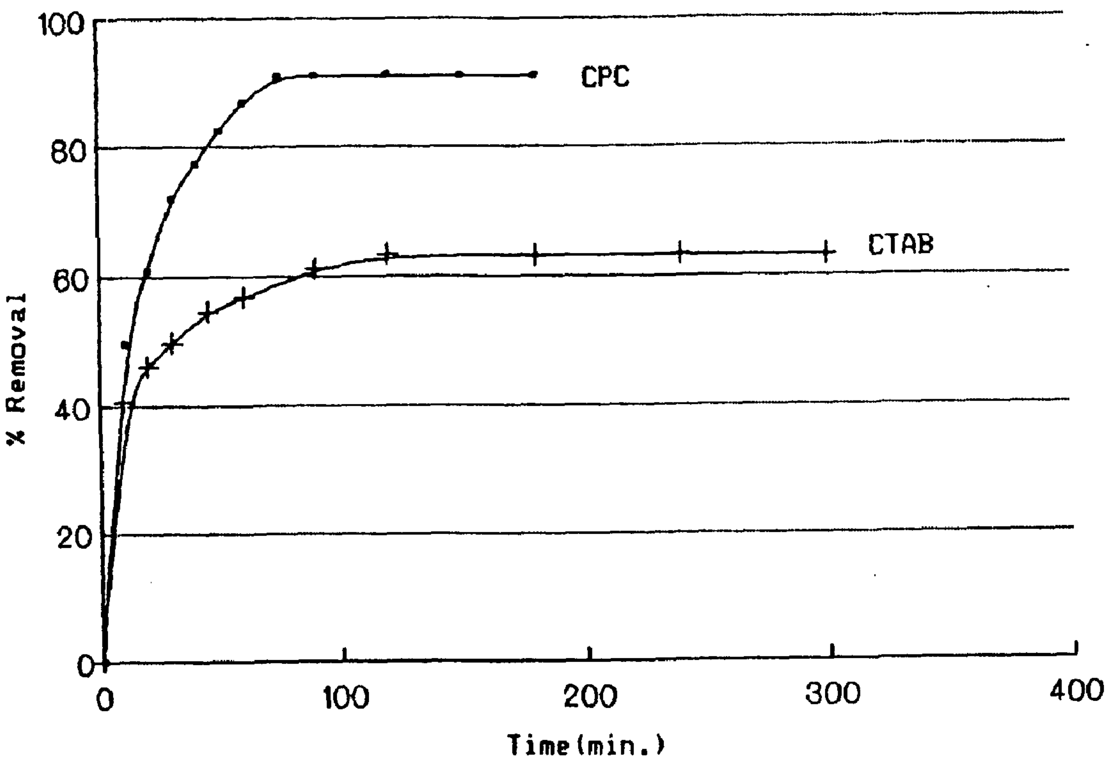


Fig. 1- Plots showing the percentage removal of cationic surfactants vs time.

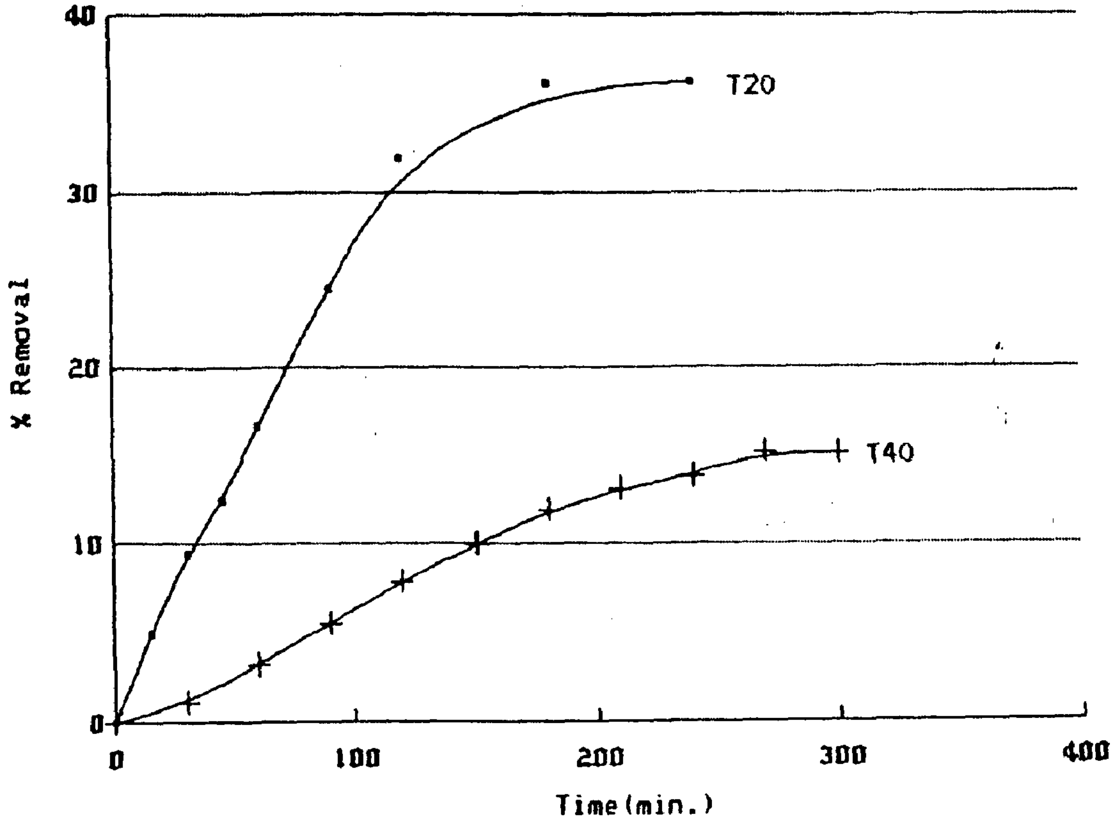


Fig. 2- Plots showing the percentage removal of nonionic surfactants vs time.

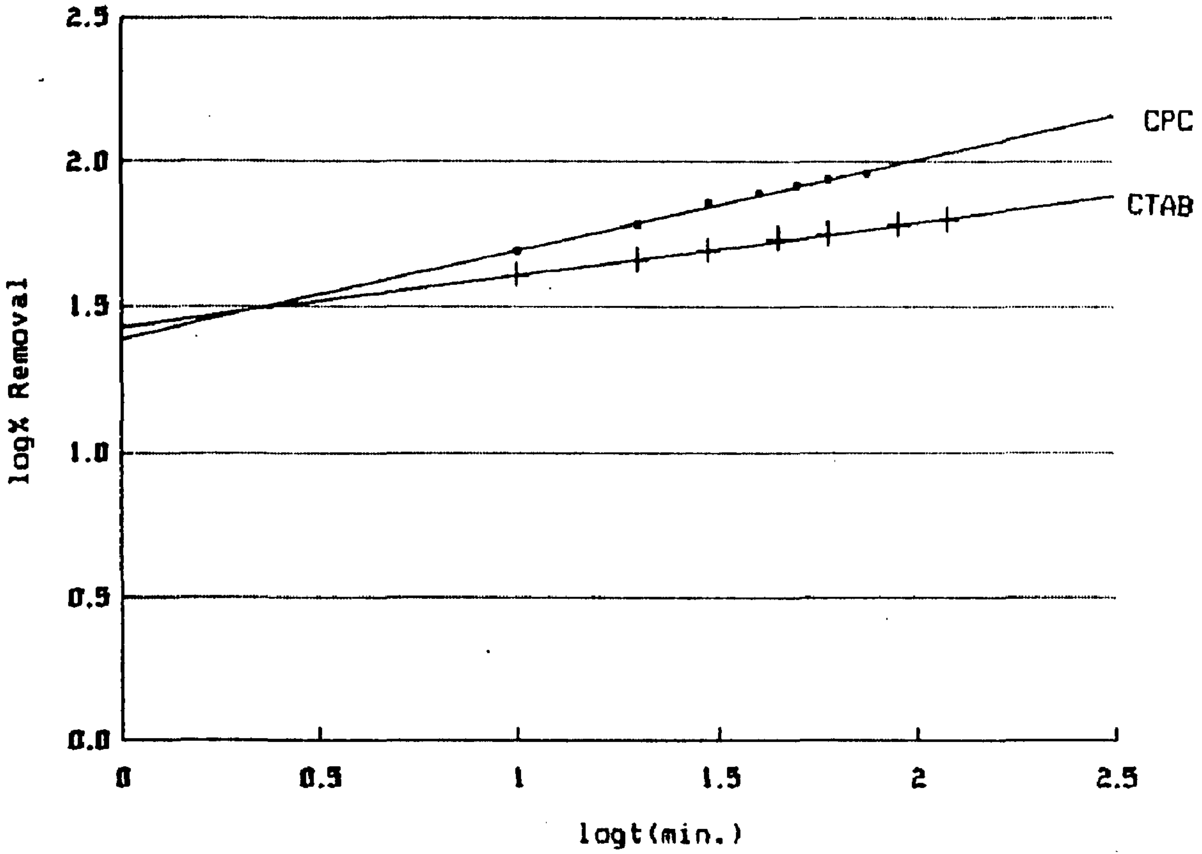


Fig. 3- Plots showing the log percentage removal of cationic surfactants vs log time.

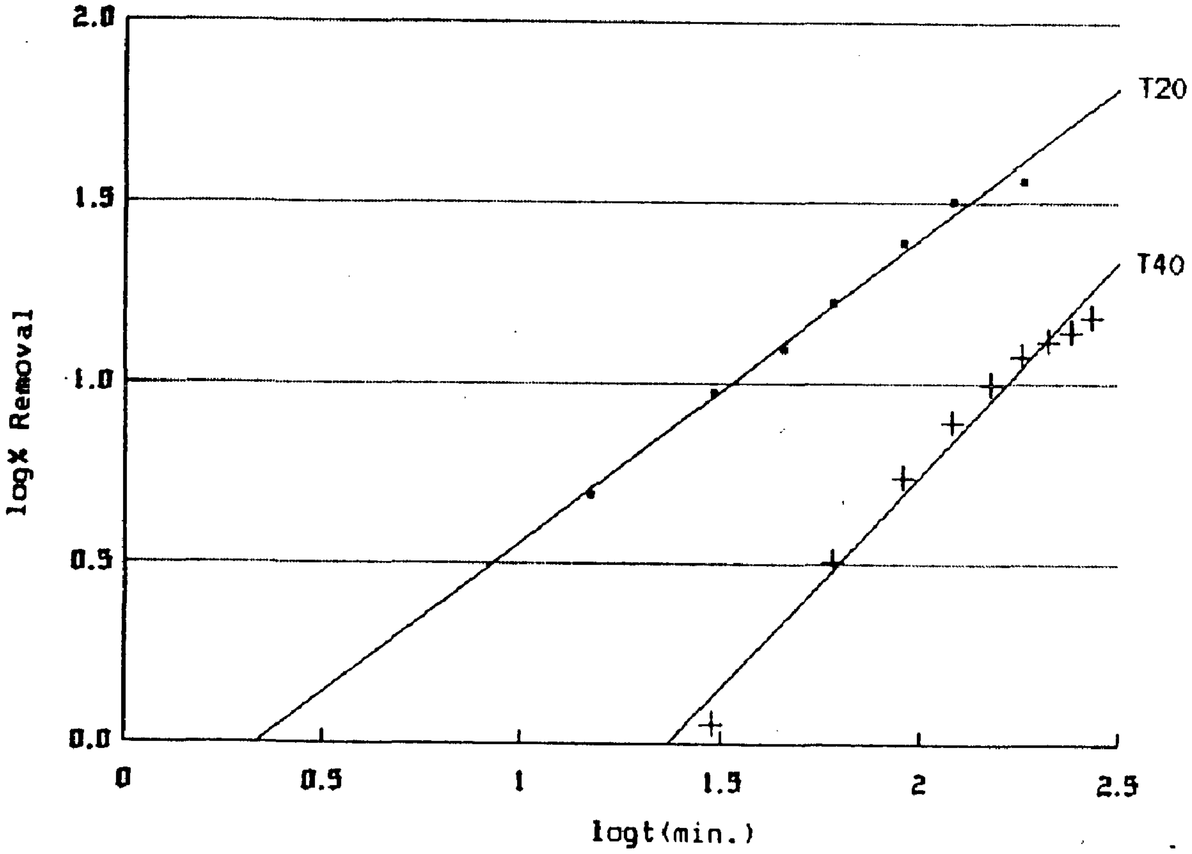


Fig. 4- Plots showing the log percentage removal of nonionic surfactants vs log time.

The uptake of cationic surfactants seems to be complete in one and half hour in case of CPC and two hours in case of CTAB (Fig. 1). As such in case of cationic surfactants all sorption determinations have been made after equilibrating the solution with adsorbent for three hours.

The plots obtained for nonionic surfactants T20 and T40 are shown in Fig. 2. A similar behaviour as observed with cationic surfactants has been noticed with nonionic surfactants but the sorption rate is comparatively slow. The uptake of T20 gets completed in three hours and with T40, in four and half hours. As such, in case of nonionic surfactants, all observations have been made after equilibrating the solution with adsorbent for six hours.

The logarithmic plots between percent surfactant removal and time of contact are shown in Figs. 3 and 4. The plots are linear. Mathematically it may be represented as —

$$P_s = K_t . t^m$$

$$\text{or} \quad \log P_s = m \log t + \log K_t \qquad (8)$$

where, P_s is the percent solute removal and t is the time of contact. The intercept K_t of the linear plot is the indicative of rate factor while the slope m reflects the mechanism of adsorption.

3.6 ADSORPTION OF CATIONIC SURFACTANTS

The adsorption data of cationic surfactants Cetyl pyridinium chloride (CPC) and that of Cetyl trimethyl ammonium bromide (CTAB) are given in Tables 1-4 and Tables 5-8 and isotherms are shown in Figs. 5 and 6 respectively. Plots of heat of adsorption are shown in Figs. 7 and 8. Langmuir plots are given in Figs. 9-16 and BET plots in Figs. 17-24. Fig. 25 shows the variation of sorption of CPC and CTAB as a function of pH while Figs. 26 and 27 show the effect of salt present in the solution for CPC and CTAB respectively.

The values of heat of adsorption at various levels of adsorptions for the two cationic surfactants are given in Table 9. Values of Langmuir constants and BET constants for CPC and CTAB are listed in Tables 10 and 11 respectively. The results of effect of pH and particle size of adsorbent on adsorption of cationic surfactants are given in Tables 12 and 13, and Tables 14 and 15 respectively.

The results show (Figs. 5 and 6) a positive adsorption in all adsorption isotherms. These are regular and concave to equilibrium concentration axis. Although the extent of adsorption increases with increasing concentrations of adsorbate, the percentage of removal is quite high at low adsorbate concentrations. The nature of isotherms in Figs. 5 and 6 also reveal a relatively rapid initial rate of adsorption at low adsorbate concentrations which markedly decreases, at high adsorbate concentration with a slow approach to saturation. At low surfactant concentration, about 60-90% of the surfactant gets adsorbed showing that lignin is quite suitable for the removal of trace quantities of cationic surfactants. The results indicate that lignin possess better sorption capacity for the two cationic surfactants in comparison to activated carbon.

Among the two cationic surfactants, the uptake of CPC is much higher than CTAB. As the carbon hydrogen chain length is same in both the molecules the hydrophobicity of the two compounds would be similar. Hence the difference in the extent of adsorption of CPC and CTAB is due to the spatial geometry of their molecular structure. CPC is a planer molecule and possess positive charge at nitrogen which is more accessible to adsorbents thus causing a large amount of adsorption of this compound while substituents in CTAB are oriented tetrahedrally so that bulky groups sterically hinder the positively charged nitrogen which provides a positive site for the adsorbate molecule to get interact effectively with the adsorbent resulting in a lower uptake of this compound in comparison to CPC.

The adsorption isotherms of two cationic surfactants, CPC and CTAB at different temperatures are shown in Figs. 5 and 6. It is observed that adsorption increases with temperature in both cases and the process is exothermic. The heat of adsorption as calculated from equation 7 for the same amount of adsorption are given in Table 9. The values being higher for CTAB than CPC. Figs. 7 and 8 show the isosteric heats of adsorption for lignin surfactant system plotted against the amount of surfactant adsorbed. The curve is linear in both the cases. The complications in actual systems and the heterogeneity of the surface causes a progressive dimunition in the heat of adsorption as the surface coverage increases, long before the monolayer is complete. The attraction between the surfactant molecules tends to increase the heat of adsorption as surface coverage approaches unity and the average separation of the adsorbate molecules becomes small. However, the multilayer may begin to form on some parts of surface before the monolayer is complete and the increase in the heat of adsorption due to intermolecular attractions may be marked by the reduction in the same due to adsorption in higher layers.

The adsorption data have been correlated with Langmuir (Figs. 9-16) and BET adsorption models (Figs. 17-24). It can be seen that a good linearization of data is not observed if plotted for BET model. The linear BET plots limited only to low concentration range of surfactant are observed. The value of Q^o, the amount of surfactant adsorbed for forming a complete monolayer on the surface of lignin as calculated from BET plots (Table 11) are lower than one obtained from Langmuir plots (Table 10). Moreover, with the exception of CPC at 35°C the Q^o values are in the same order in which these are adsorbed on the lignin. The values of constant 'A' reflect the energy of interaction with the surface are higher for CTAB in comparison to CPC.

The entire adsorption data fits Langmuir model. This is shown by the linear curves (Figs. 9-16). The values of Q^o and 'b' as obtained from Langmuir model are listed in Table 10. Q^o values as obtained from Langmuir models are higher than those obtained from BET model. The values for CPC are also higher than in comparison to CTAB. The value of 'b' is the reciprocal of the concentration at which half saturation of the adsorbent is obtained. It can be seen from Table 10 that the values of 'b' are higher for CPC, indicating a greater tendency towards adsorption.

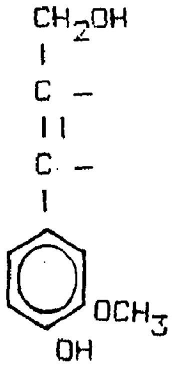
The adsorption of two cationic surfactants on lignin increases with increase of pH (Tables 12 and 13, Fig. 25). Vinogradova et al. (32) also observed and increase in sorption of Ca^{2+}

ions from solution by hydrolytic lignin due to dissociation of phenolic -OH and carboxylic groups. Wieber et al. (33) also observed similar behaviour for the sorption of Cu and Zn on lignin. Lignin carries a negative charge on its surface. Lignin is an aromatic complex polymeric product arising from the enzyme initiated dehydrogenative polymerisation of three primary precursors —

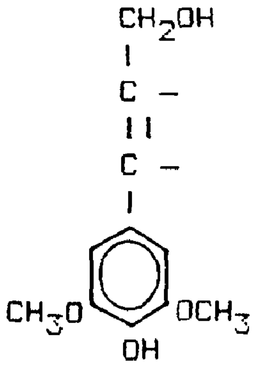
(a) Trans-coniferyl

(b) Trans-sinapyl and

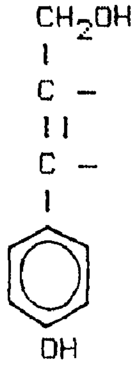
(c) Trans p-coumaryl alcohols.



(a)



(b)



(c)

The negative charge on the surface of lignin arises from the dissociation of phenolic -OH groups. At low pH, the dissociation of -OH group is suppressed and this results in a negative surface charge density of smaller magnitude in comparison to the dissociation of -OH group at high pH which provides an increased negative charge on the lignin surface. The negatively charged points, balanced by counter ions of opposite charge on lignin surface, provide the adsorption sites. As the number of adsorption sites increase with increasing pH of the surfactant solution, the uptake of solute also increases.

Adsorption results from Tables 14 and 15 show that the adsorption capacity of lignin for two cationic surfactants increases as the particle size of adsorbent decreases. This indicates that the surface area associated with the pores inside the particle is being freed at least partially and that the effective adsorption regime is confined to the external surface and a narrow layer just below the surface.

Many times dissolved salts are also present in waste water. Hence effect of salt concentrations on the sorption of fixed concentration of these two cationic surfactants have also been studied. The results are shown in Figs. 26 and 27. These results indicate that adsorption of both CPC and CTAB decrease with increasing salt concentration and decrease in adsorption follows the sequence —

$$Al^{3+} > Ca^{2+} > Na^{+}$$

Weiber et al. (33) also observed that the addition of NaCl reduces the Zn adsorption on lignin.

Table-1

Adsorption of Cetyl pyridinium chloride (CPC) on lignin at 20°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	1.0	0.11	0.44
2.	2.0	0.24	0.88
3.	3.0	0.41	1.30
4.	4.0	0.62	1.70
5.	5.0	0.90	2.05
6.	6.0	1.21	2.40
7.	7.0	1.50	2.75
8.	8.0	1.78	3.10
9.	9.0	2.10	3.45
10.	10.0	2.64	3.68
11.	11.0	3.27	3.87
12.	12.0	4.26	3.87

Table-2

Adsorption of Cetyl pyridinium chloride (CPC) on lignin at 25°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	1.0	0.05	0.47
2.	2.0	0.13	0.94
3.	3.0	0.23	1.39
4.	4.0	0.33	1.83
5.	5.0	0.46	2.27
6.	6.0	0.59	2.70
7.	7.0	0.96	3.07
8.	8.0	1.02	3.49
9.	9.0	1.24	3.89
10.	10.0	1.86	4.07
11.	11.0	2.46	4.17
12.	12.0	3.02	4.19

Table-3

Adsorption of Cetyl pyridinium chloride (CPC) on lignin at 30°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	1.0	0.05	0.48
2.	2.0	0.09	0.95
3.	3.0	0.17	1.42
4.	4.0	0.24	1.88
5.	5.0	0.31	2.34
6.	6.0	0.39	2.81
7.	7.0	0.53	3.23
8.	8.0	0.66	3.67
9.	9.0	0.85	4.08
10.	10.0	1.12	4.44
11.	11.0	1.93	4.54
12.	12.0	2.94	4.53

Table-4

Adsorption of Cetyl pyridinium chloride (CPC) on lignin at 35°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	1.0	0.01	0.50
2.	2.0	0.03	0.98
3.	3.0	0.05	1.47
4.	4.0	0.06	1.97
5.	5.0	0.10	2.45
6.	6.0	0.13	2.94
7.	7.0	0.17	3.41
8.	8.0	0.21	3.89
9.	9.0	0.27	4.37
10.	10.0	0.37	4.82
11.	11.0	0.50	5.25
12.	12.0	1.18	5.41
13.	13.0	1.99	5.50
14.	14.0	3.00	5.50

Table-5

Adsorption of Cetyl trimethyl ammonium bromide (CTAB) on lignin at 20^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	1.0	0.30	0.35
2.	2.0	0.65	0.67
3.	3.0	1.09	0.95
4.	4.0	1.50	1.25
5.	5.0	2.15	1.43
6.	6.0	2.90	1.55
7.	7.0	3.55	1.73
8.	8.0	4.15	1.93
9.	9.0	5.01	2.00
10.	10.0	5.75	2.13
11.	11.0	6.65	2.18
12.	12.0	7.66	2.17

Table-6

Adsorption of Cetyl trimethyl ammonium bromide (CTAB) on lignin at 25^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	1.0	0.29	0.36
2.	2.0	0.62	0.69
3.	3.0	1.00	1.00
4.	4.0	1.34	1.33
5.	5.0	1.75	1.63
6.	6.0	2.41	1.80
7.	7.0	3.22	1.89
8.	8.0	3.75	2.13
9.	9.0	4.50	2.25
10.	10.0	5.18	2.41
11.	11.0	5.98	2.51
12.	12.0	7.01	2.50

Table-7

Adsorption of Cetyl trimethyl ammonium bromide (CTAB) on lignin at 30^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	1.0	0.06	0.47
2.	2.0	0.13	0.94
3.	3.0	0.24	1.38
4.	4.0	0.41	1.80
5.	5.0	0.64	2.18
6.	6.0	0.80	2.60
7.	7.0	1.21	2.90
8.	8.0	1.56	3.22
9.	9.0	1.89	3.56
10.	10.0	2.51	3.74
11.	11.0	3.37	3.81
12.	12.0	4.35	3.82

Table-8

Adsorption of Cetyl trimethyl ammonium bromide (CTAB) on lignin at 35°C.

Total volume = 50 ml.
Particle size = 100-200 mesh.
Lignin added = 0.1 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	1.0	0.05	0.48
2.	2.0	0.10	0.95
3.	3.0	0.21	1.40
4.	4.0	0.31	1.84
5.	5.0	0.42	2.29
6.	6.0	0.64	2.68
7.	7.0	0.83	3.08
8.	8.0	1.25	3.38
9.	9.0	1.65	3.68
10.	10.0	1.91	4.04
11.	11.0	2.11	4.44
12.	12.0	3.10	4.45

Table-9

Values of Heat of adsorption at various amounts of adsorption for cationic surfactants.

	Sl. No.	Adsorption mg.g^{-1} lignin	Heat of adsorption K.cal.mole^{-1}
CPC	1.	0.98	-11.29
	2.	1.47	-12.79
	3.	1.97	-13.70
	4.	2.27	-13.93
	5.	2.70	-14.43
	6.	3.42	-16.11
CTAB	1.	0.38	-16.64
	2.	0.62	-16.74
	3.	1.34	-17.92
	4.	2.41	-17.97
	5.	2.64	-18.96

Table-10

Values of Langmuir constants for cationic surfactants.

Temperature ^{o}C	CPC		CTAB	
	b mg^{-1}	Q^{o} $mg.g^{-1}$ lignin	b mg^{-1}	Q^{o} $mg.g^{-1}$ lignin
20	1.04	4.54	0.49	2.78
25	1.97	4.93	0.44	3.40
30	2.74	5.29	1.87	4.39
35	8.70	5.75	1.82	5.18

Table-11

Values of BET constants for cationic surfactants.

Temperature °C	CPC		CTAB	
	A mg^{-1}	Q^o $mg.g^{-1}$ lignin	A mg^{-1}	Q^o $mg.g^{-1}$ lignin
20	11.80	3.03	6.32	1.06
25	19.29	4.21	4.79	1.48
30	14.17	6.79	26.45	2.82
35	123.10	4.28	32.15	3.24

Table-12

Effect of pH on the adsorption of Cetyl pyridinium chloride (CPC) on lignin at 30°C

Total volume = 50 ml.
Initial concentration = 10 $mg.l^{-1}$
Particle size = 100–200 mesh.
Lignin added = 0.1 g.

pH	Adsorption $mg.g^{-1}$ lignin
1	3.27
2	3.61
3	3.73
4	4.09
5	4.21
6	4.33
7	4.51
8	4.59
9	4.85
10	4.87

Table-13

Effect of pH on the adsorption of Cetyl trimethyl ammonium Bromide (CTAB) on lignin at 30°C

Total volume = 50 ml.

Initial concentration = 10 $mg.l^{-1}$

Particle size = 100-200 mesh.

Lignin added = 0.1 g.

pH	Adsorption $mg.g^{-1}$ lignin
1	1.98
2	2.25
3	2.59
4	2.80
5	3.40
6	3.57
7	3.75
8	3.89
9	3.98
10	4.11

Table-14

Effect of particle size on the adsorption of Cetyl pyridinium chloride (CPC) on lignin at 30^{o}C.

Total volume = 50 ml.

Initial concentration = 10 mg.l^{-1}

Lignin added = 0.1 g.

Sl. No.	Particle size Mesh	Adsorption mg.g^{-1} lignin
1.	100-200	4.40
2.	52-100	3.51
3.	<52	2.07

Table-15

Effect of particle size on the adsorption of Cetyl trimethyl ammonium bromide (CTAB) on Lignin at 25°C.

Total volume = 50 ml.

Initial concentration = 5.0 $mg.l^{-1}$

Lignin added = 0.1 g.

Sl. No.	Particle size Mesh	Adsorption $mg.g^{-1}$ lignin
1.	100-200	1.63
2.	50-100	0.65
3.	<52	0.47

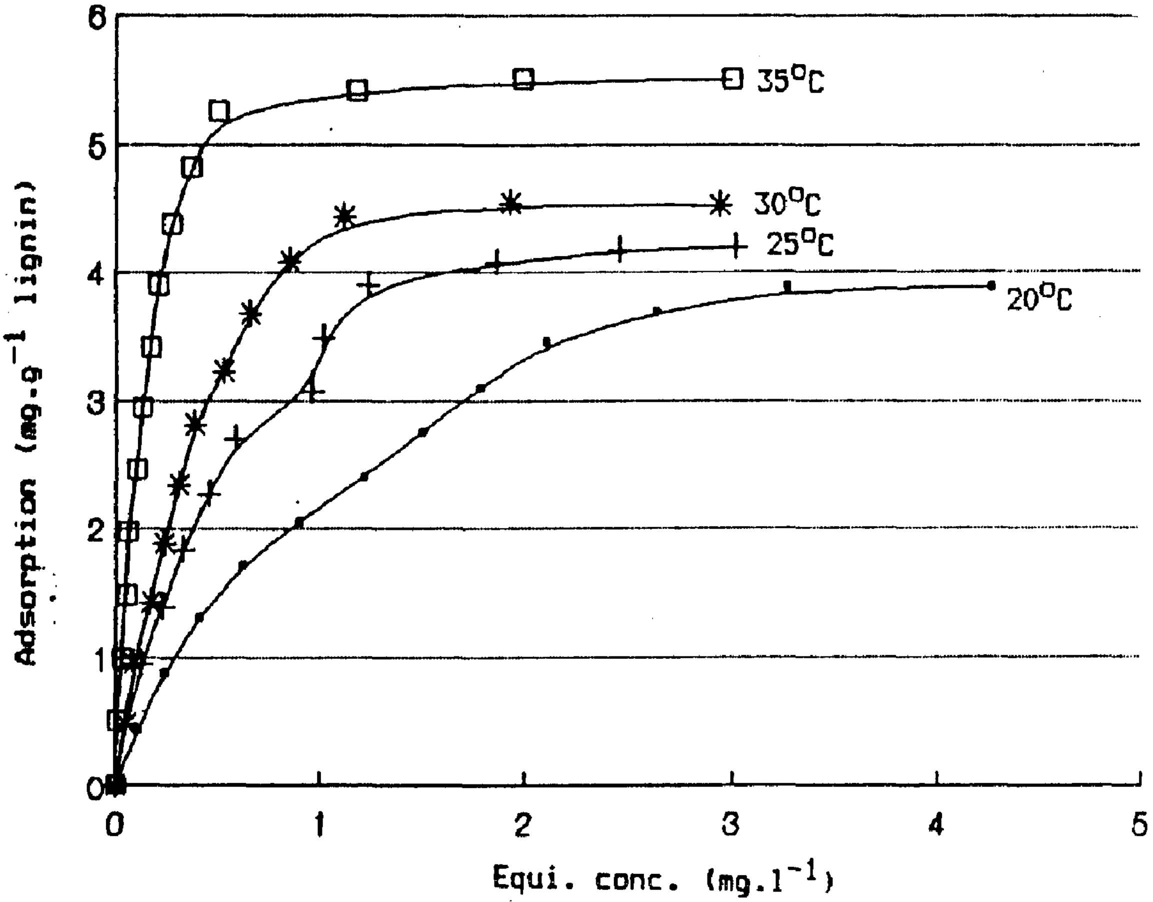


Fig. 5- Adsorption isotherms of CPC.

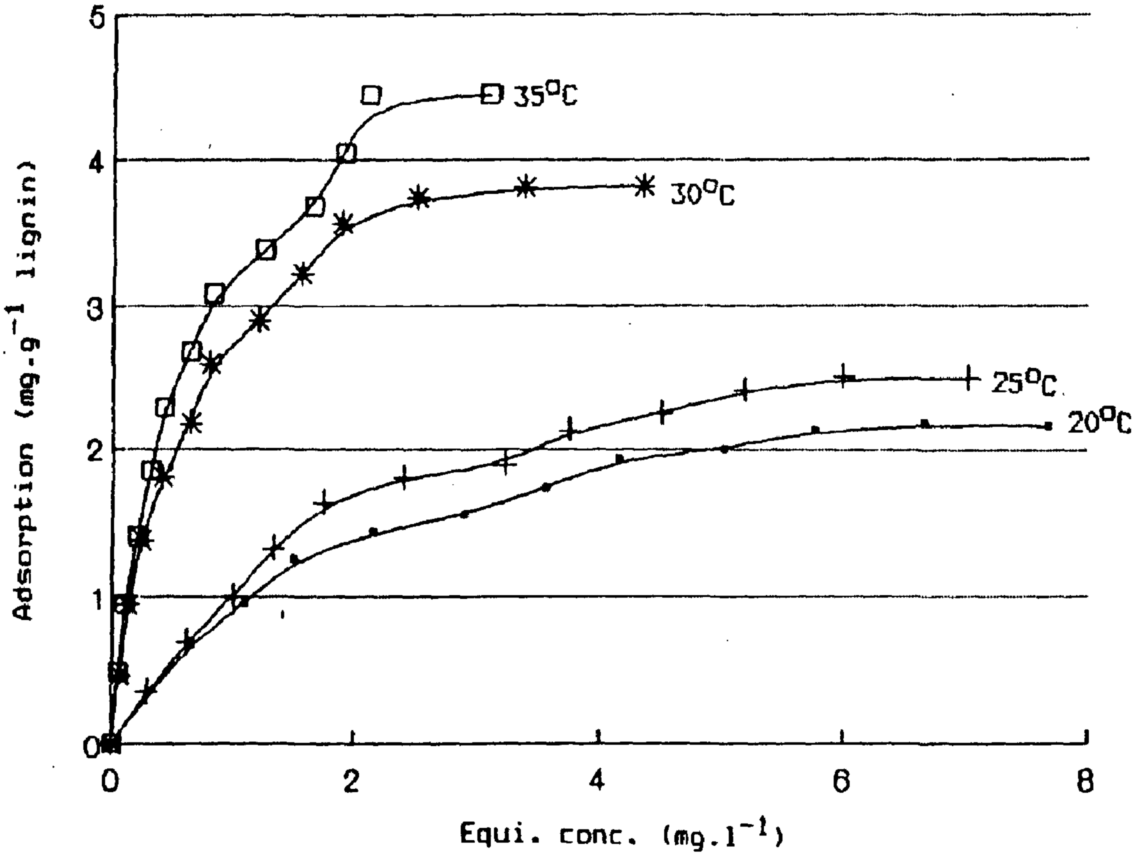


Fig. 6- Adsorption isotherms of CTAB.

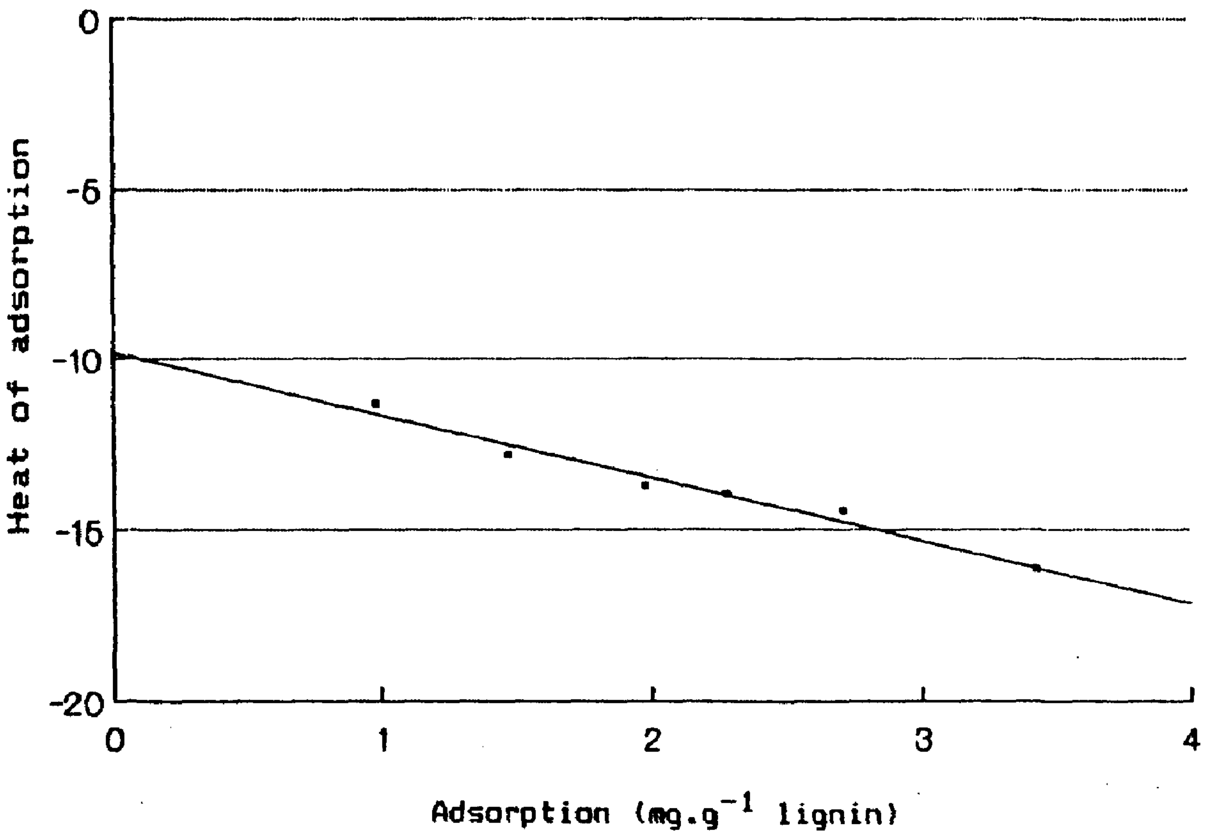


Fig. 7- Plots showing the adsorption of CPC vs heat of adsorption.

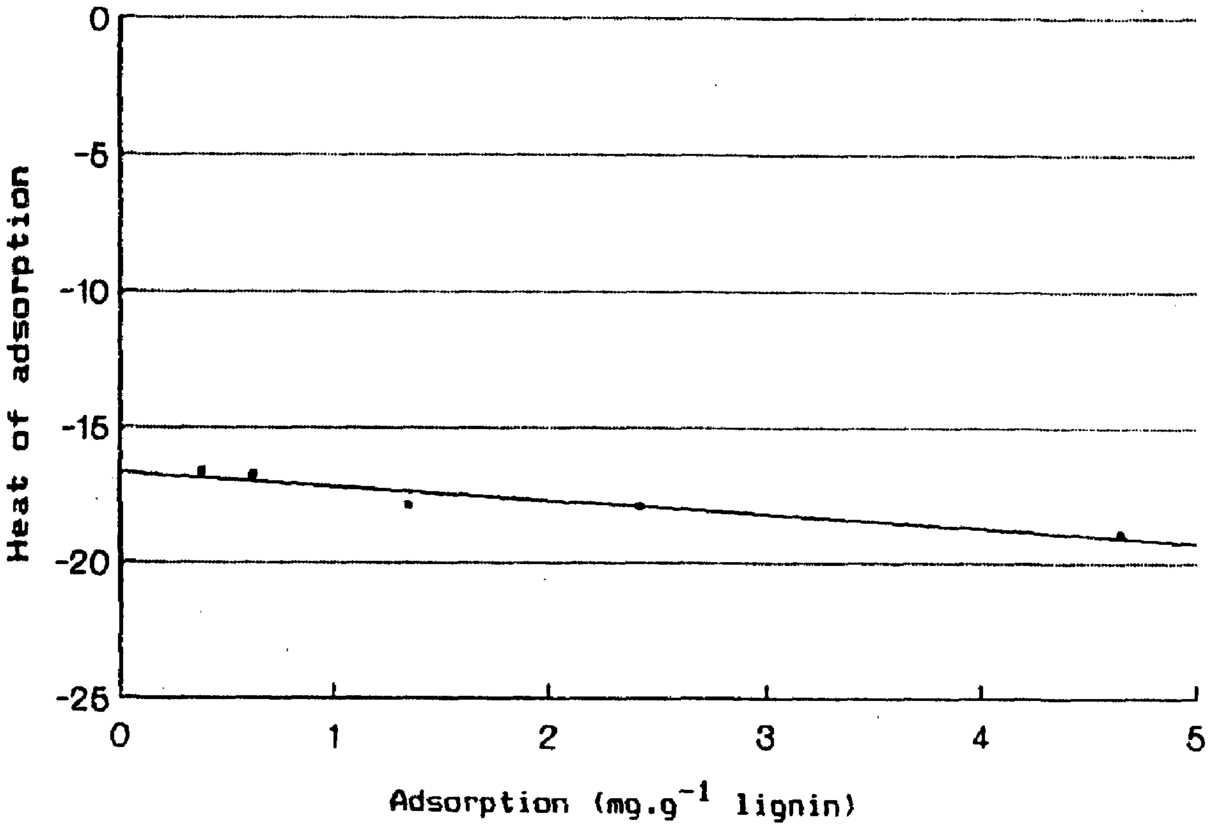


Fig. 8- Plots showing the adsorption of CTAB vs heat of adsorption.

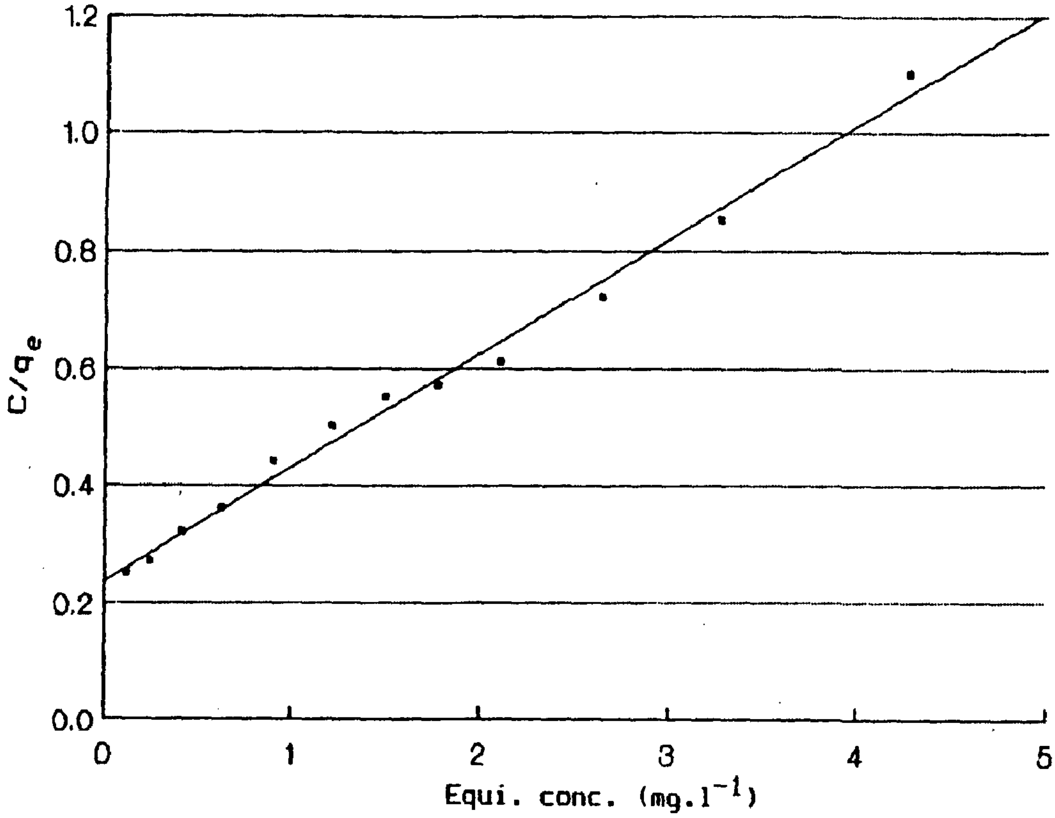


Fig. 9- Langmuir plot for CPC at 20°C.

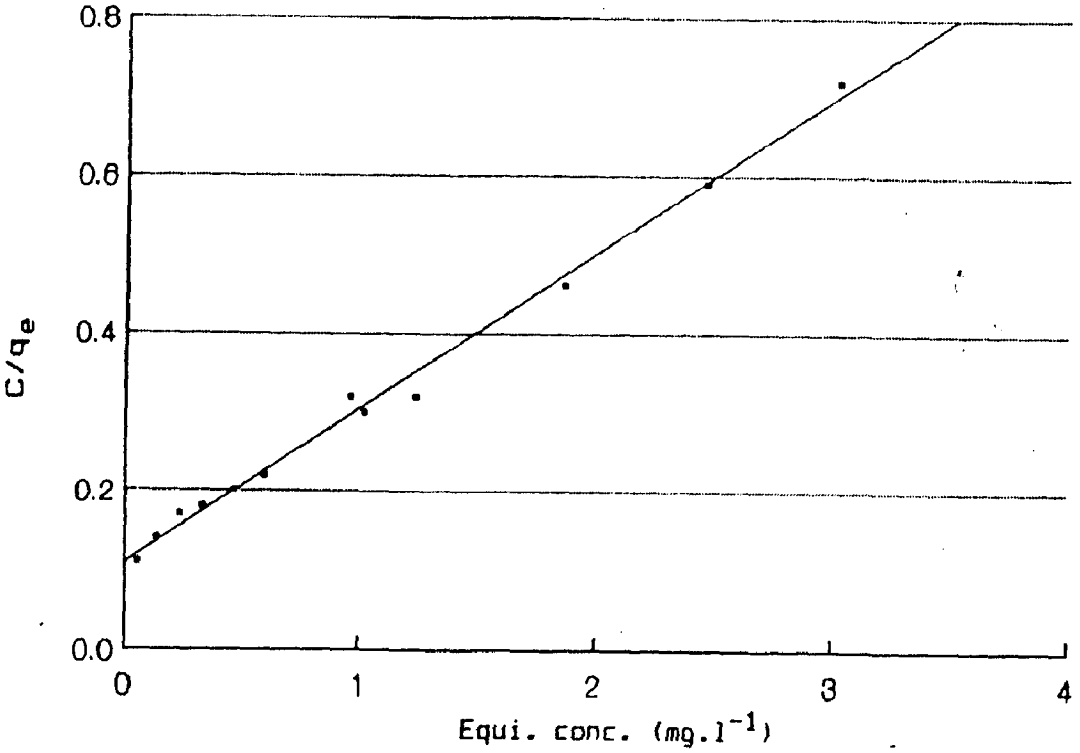


Fig. 10- Langmuir plot for CPC at 25°C.

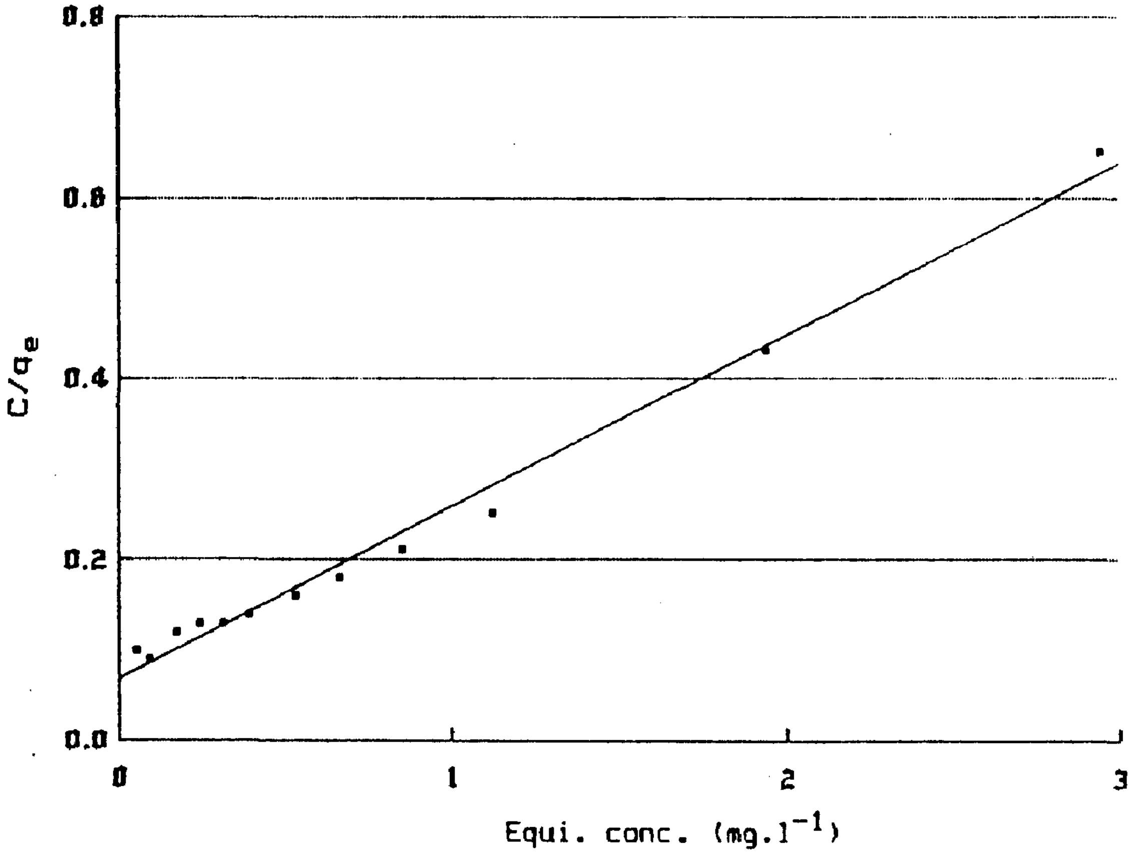


Fig. 11- Langmuir plot for CPC at 30°C.

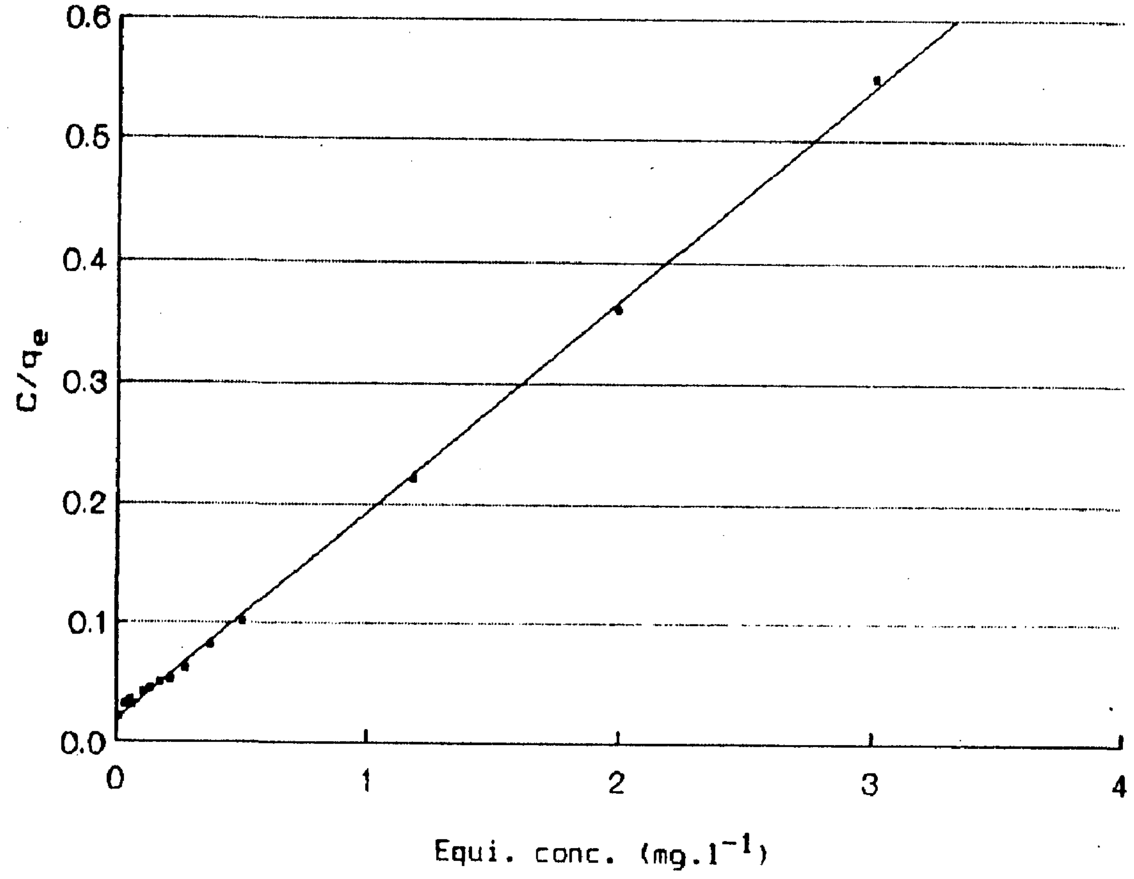


Fig. 12- Langmuir plot for CPC at 35°C.

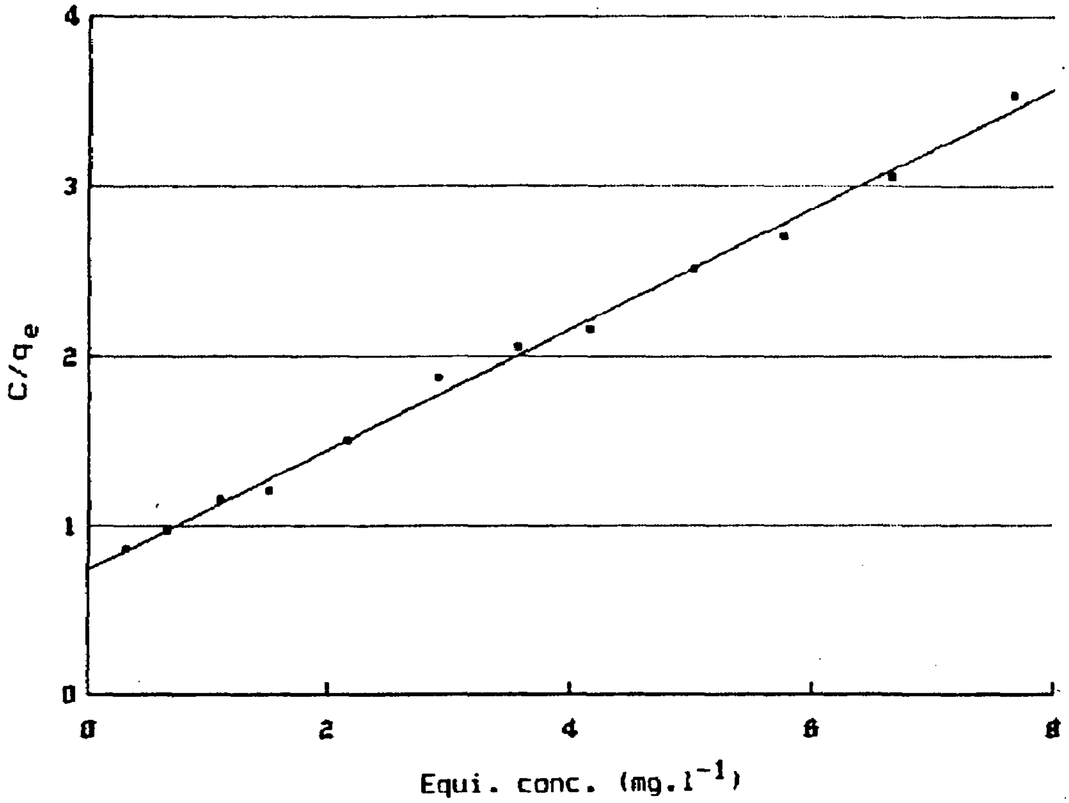


Fig. 13- Langmuir plot for CTAB at 20^{o}C.

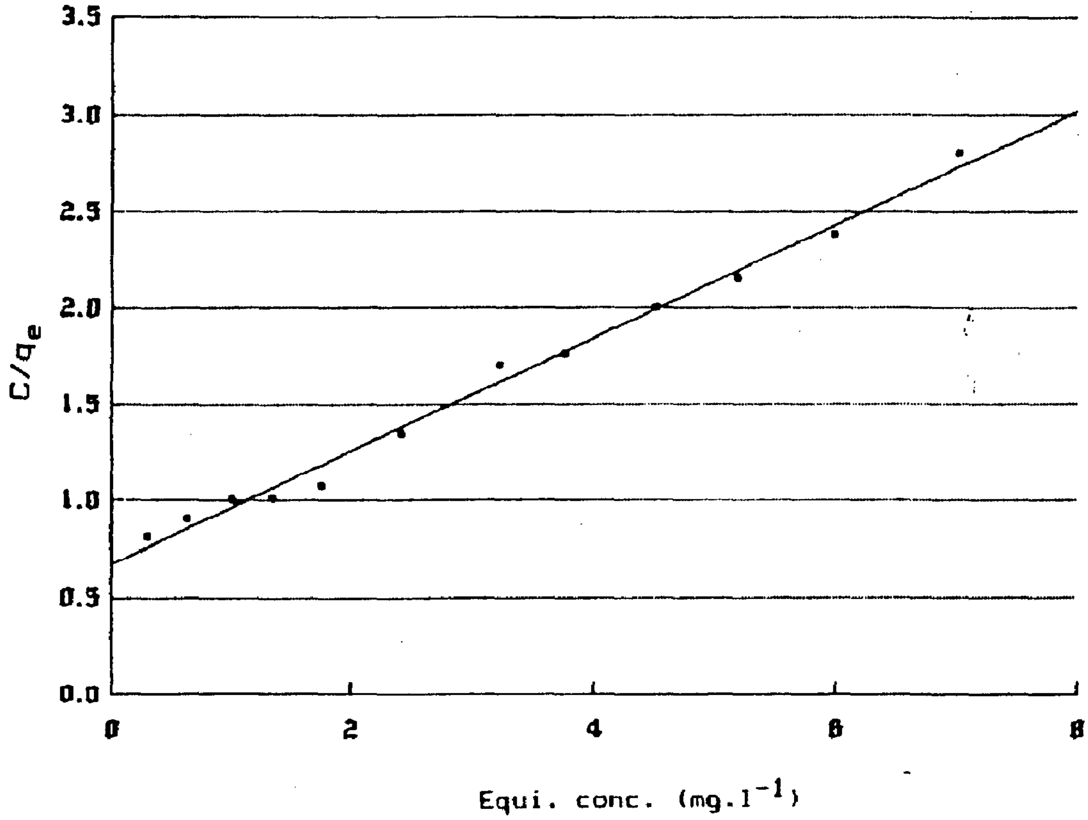


Fig. 14- Langmuir plot for CTAB at 25^{o}C.

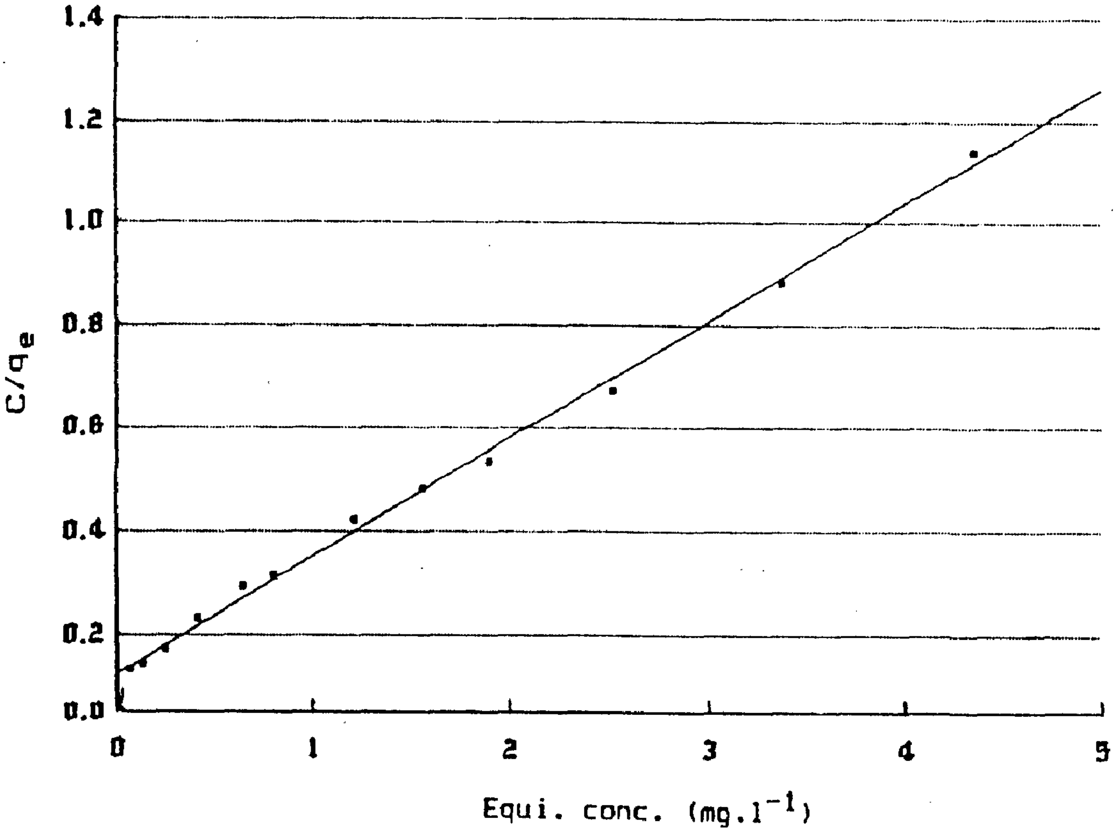


Fig. 15- Langmuir plot for CTAB at 30°C.

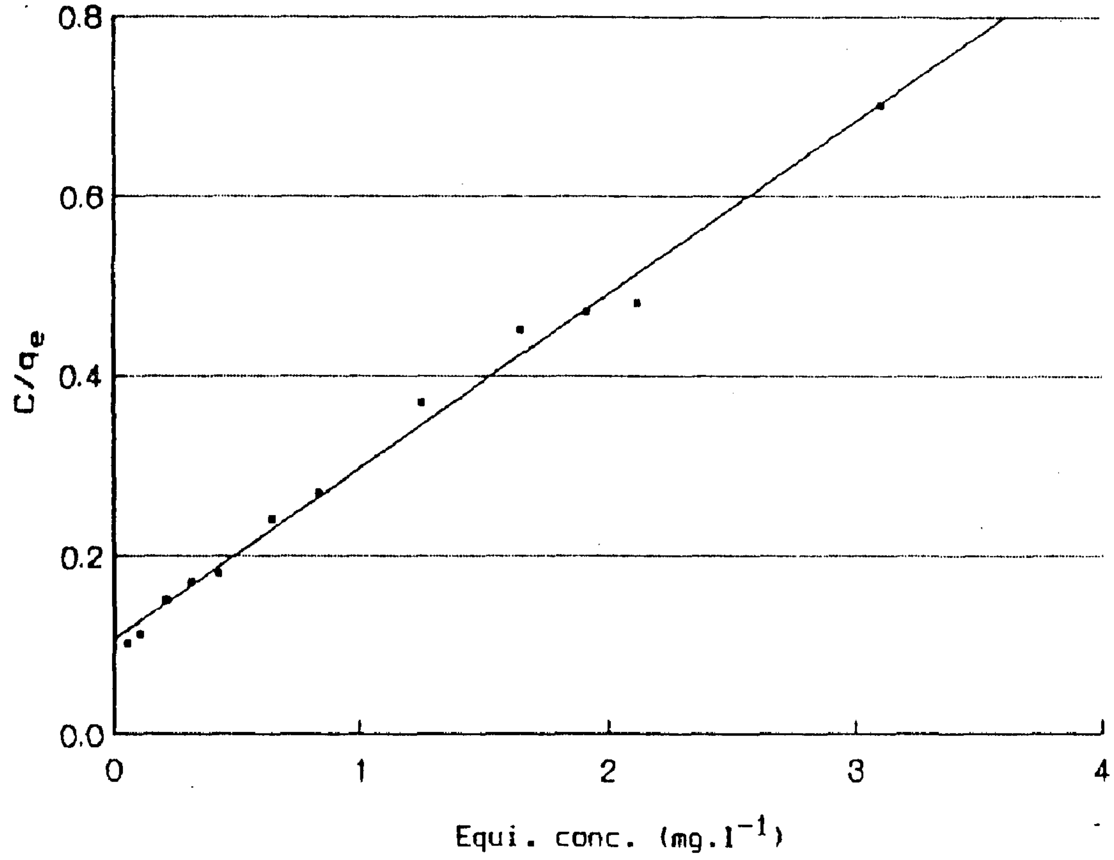


Fig. 16- Langmuir plot for CTAB at 35°C.

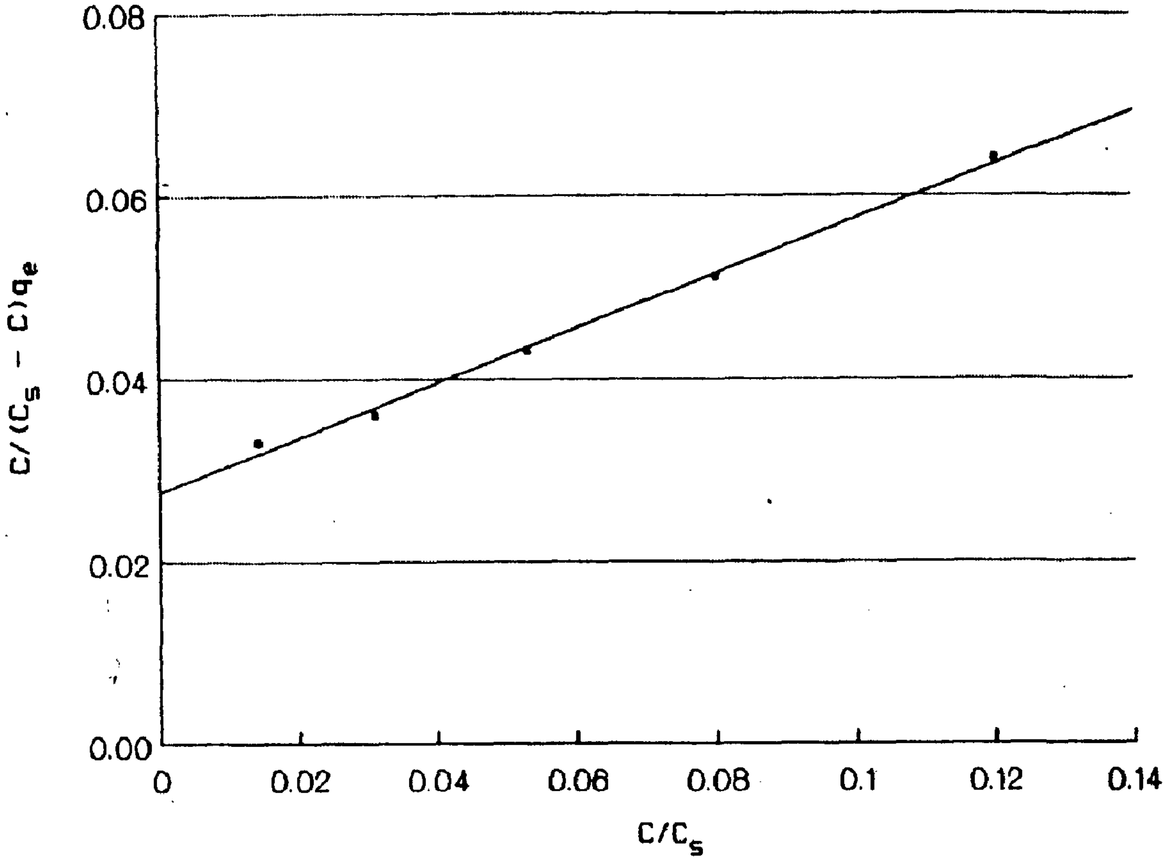


Fig. 17- B.E.T. plot for CPC at 20°C.

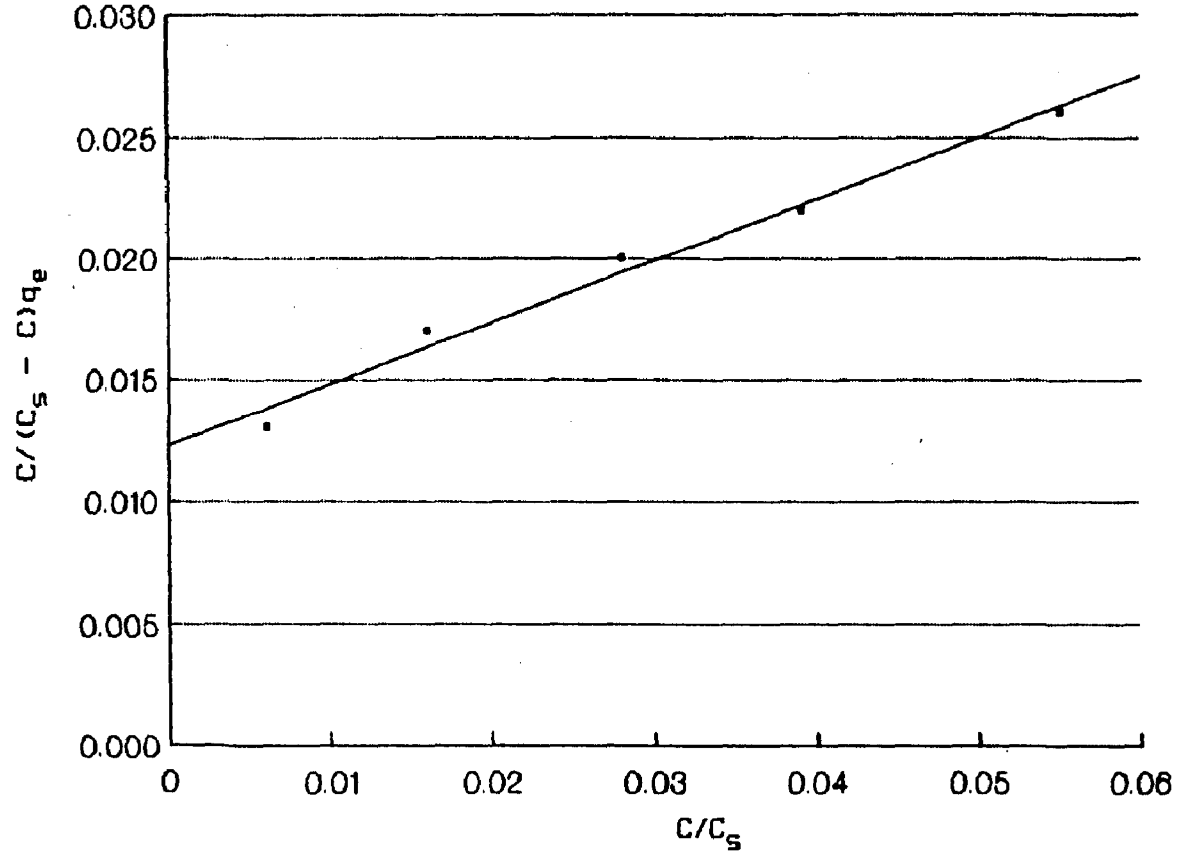


Fig. 18- B.E.T. plot for CPC at 25°C.

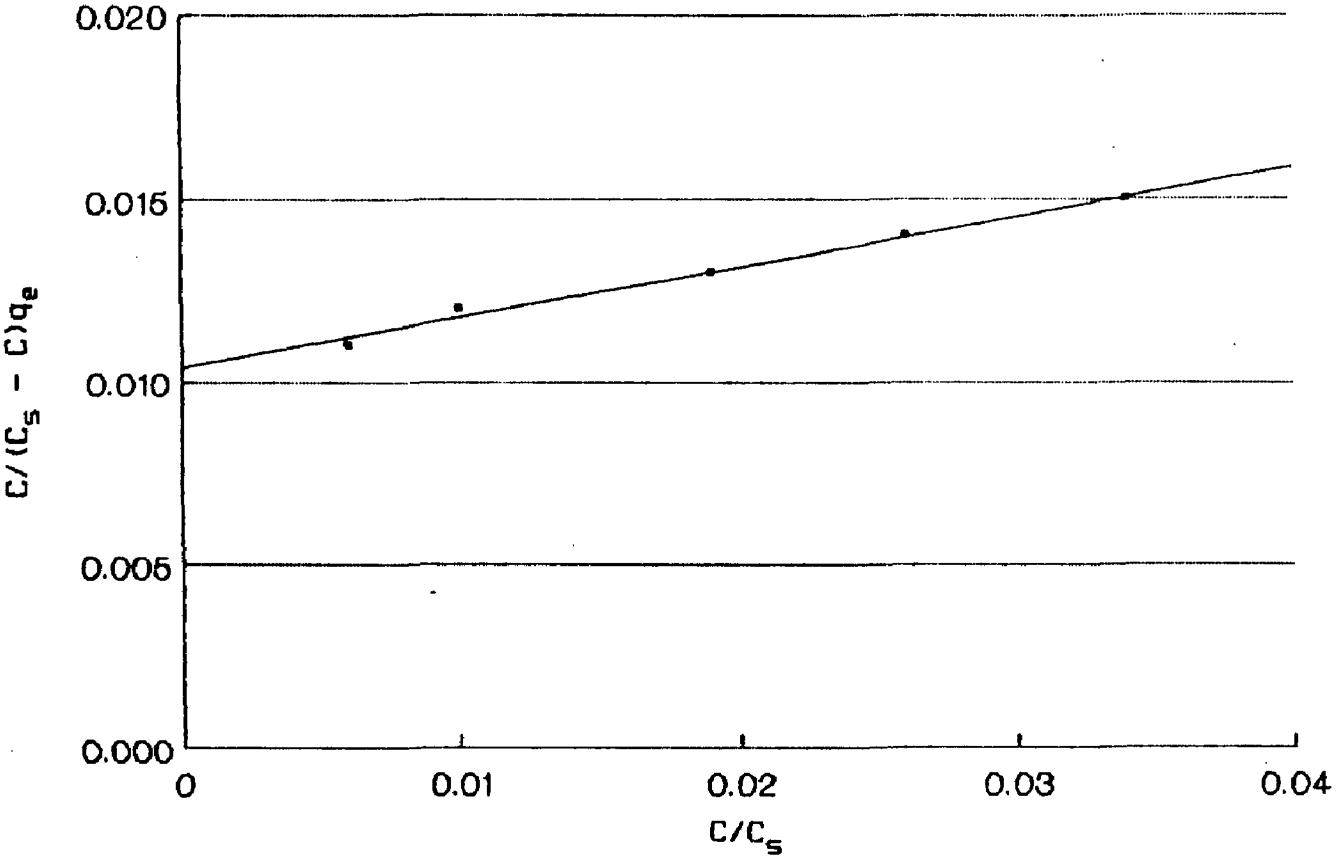


Fig. 19- B.E.T. plot for CPC at 30°C.

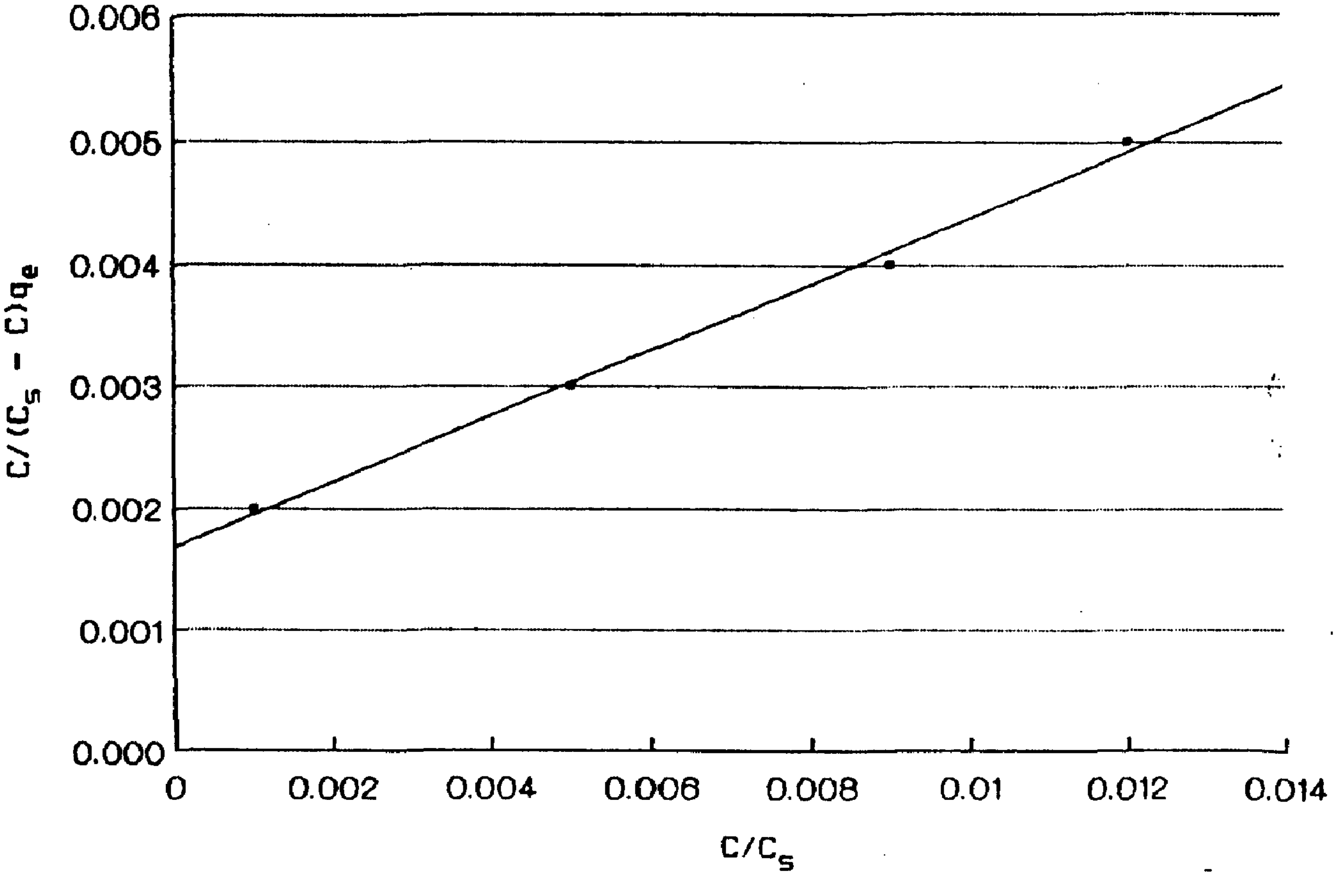


Fig. 20- B.E.T. plot for CPC at 35°C.

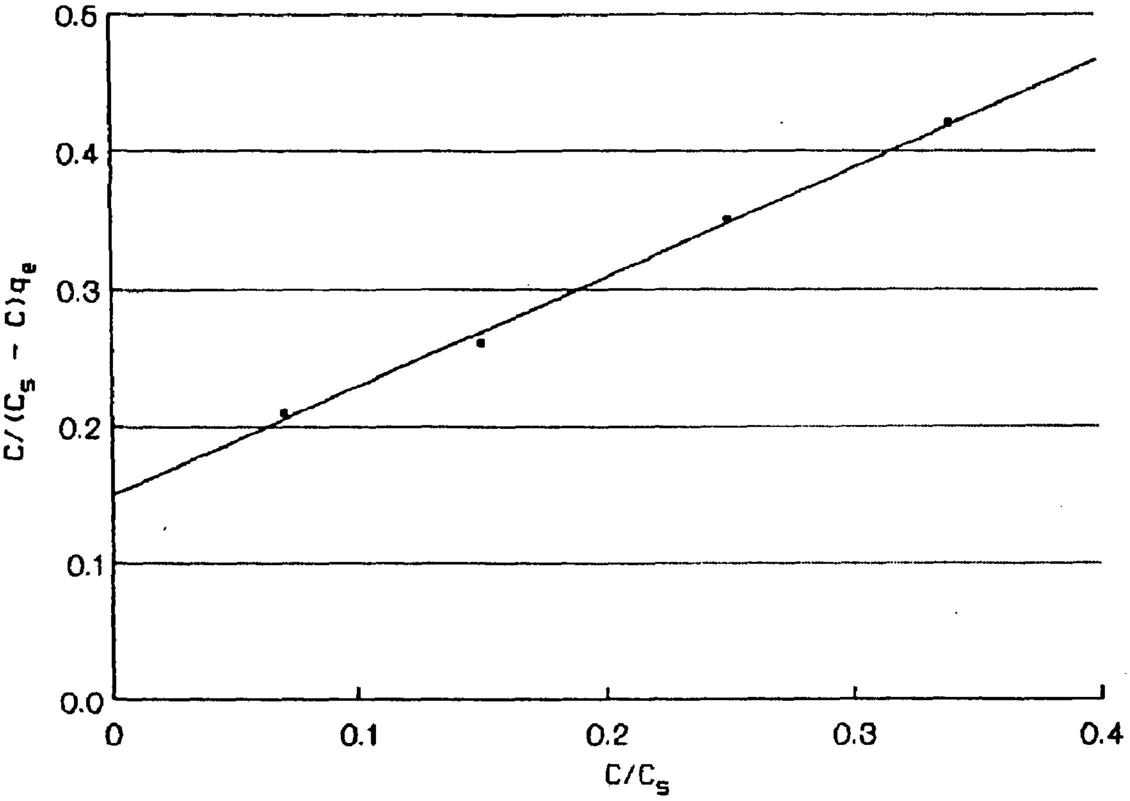


Fig. 21- B.E.T. plot for CTAB at 20°C.

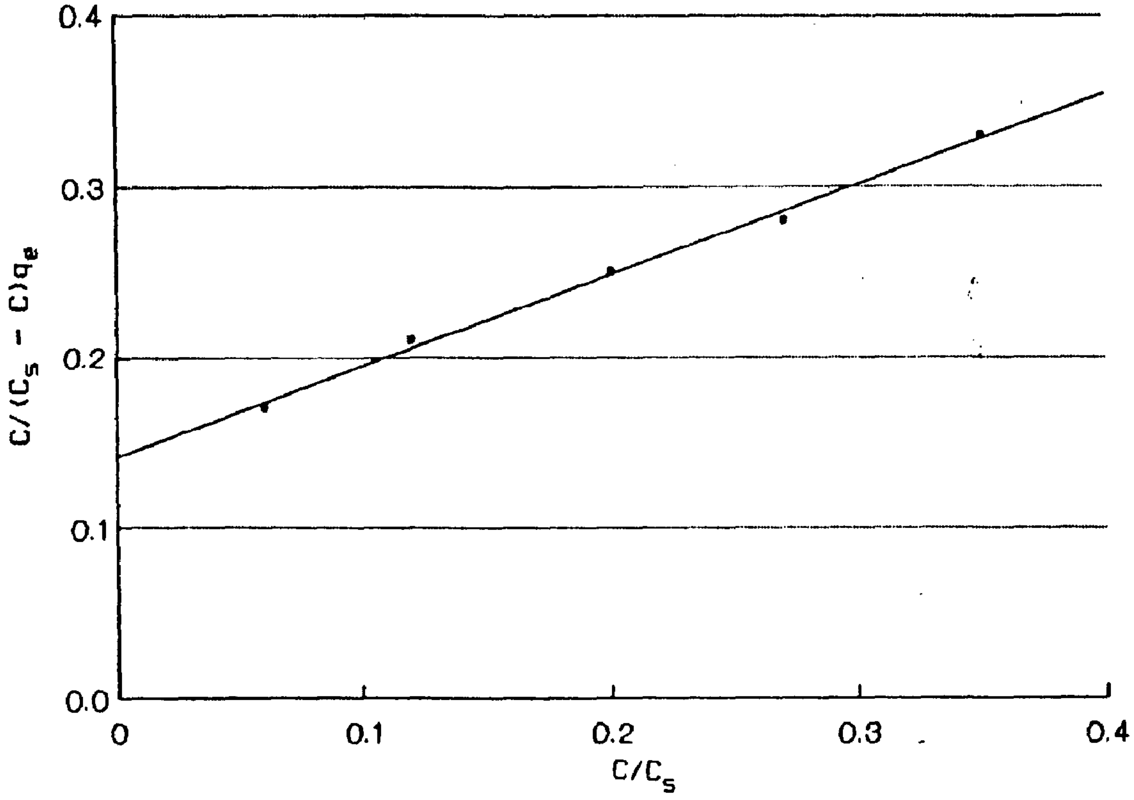


Fig. 22- B.E.T. plot for CTAB at 25°C.

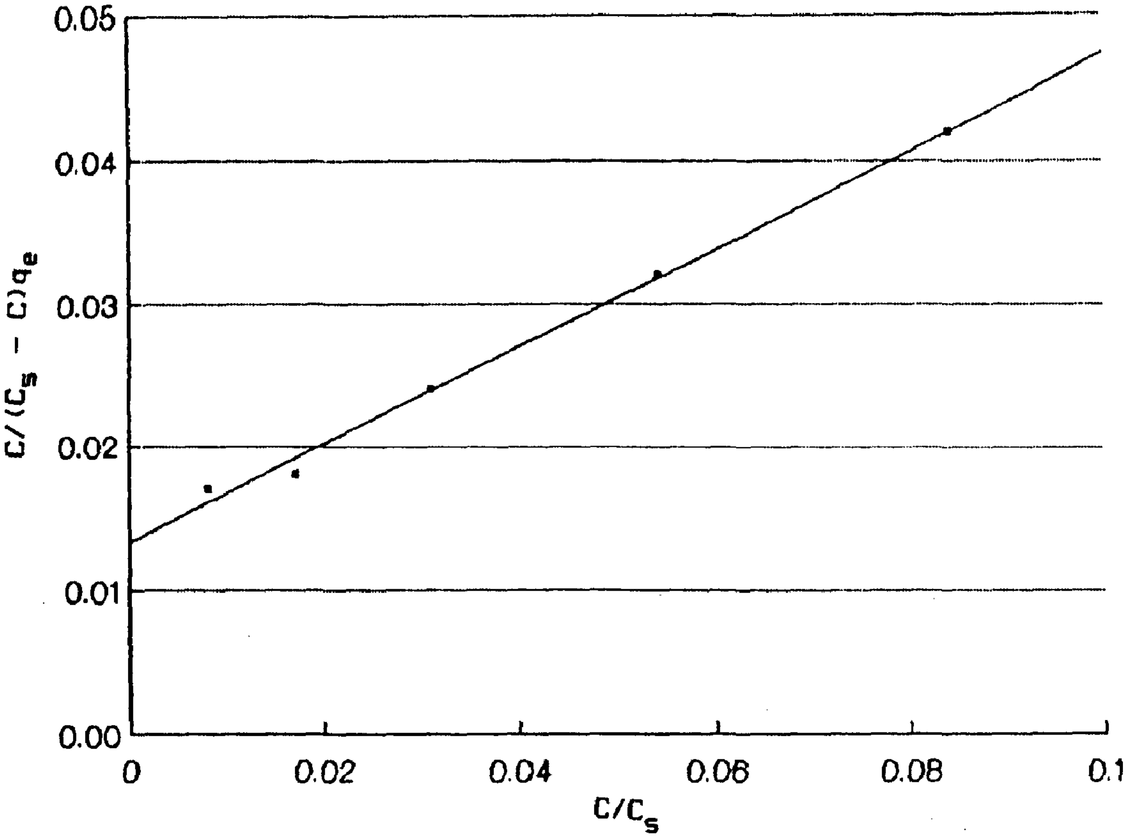


Fig. 23- B.E.T. plot for CTAB at 30°C.

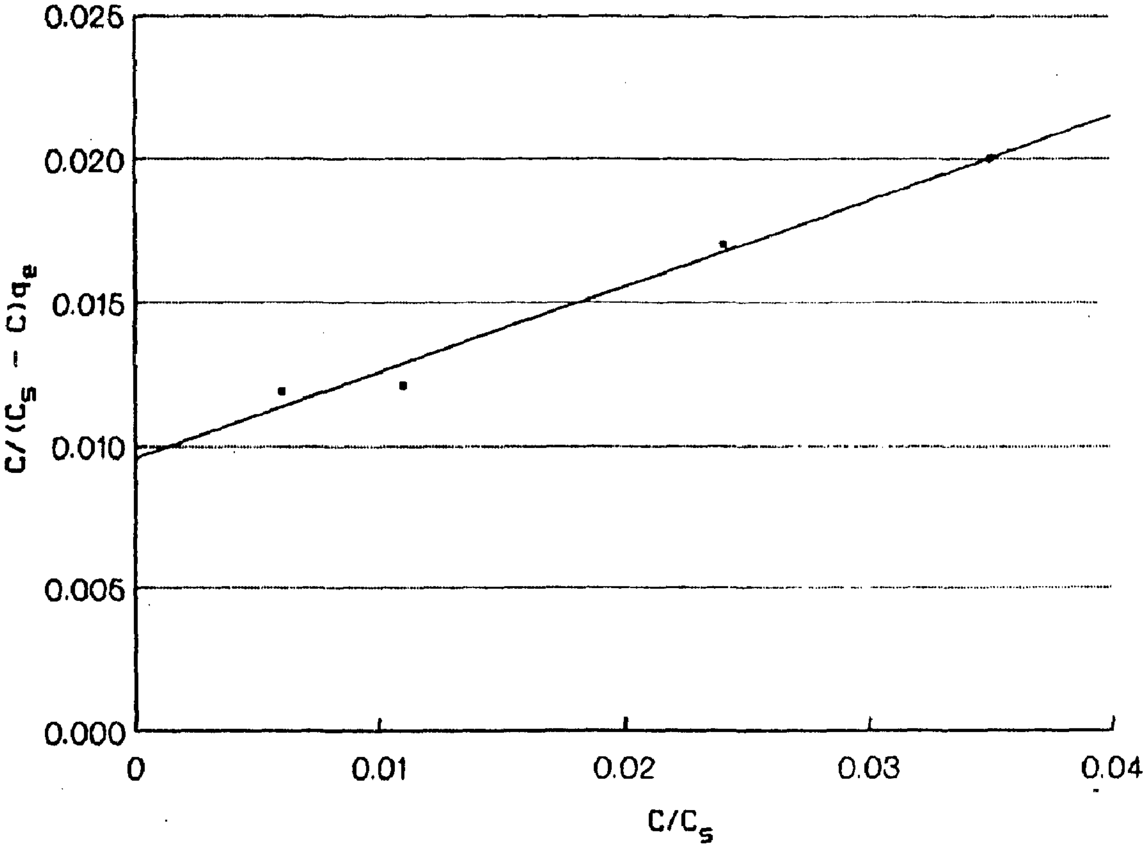


Fig. 24- B.E.T. plot for CTAB at 35°C.

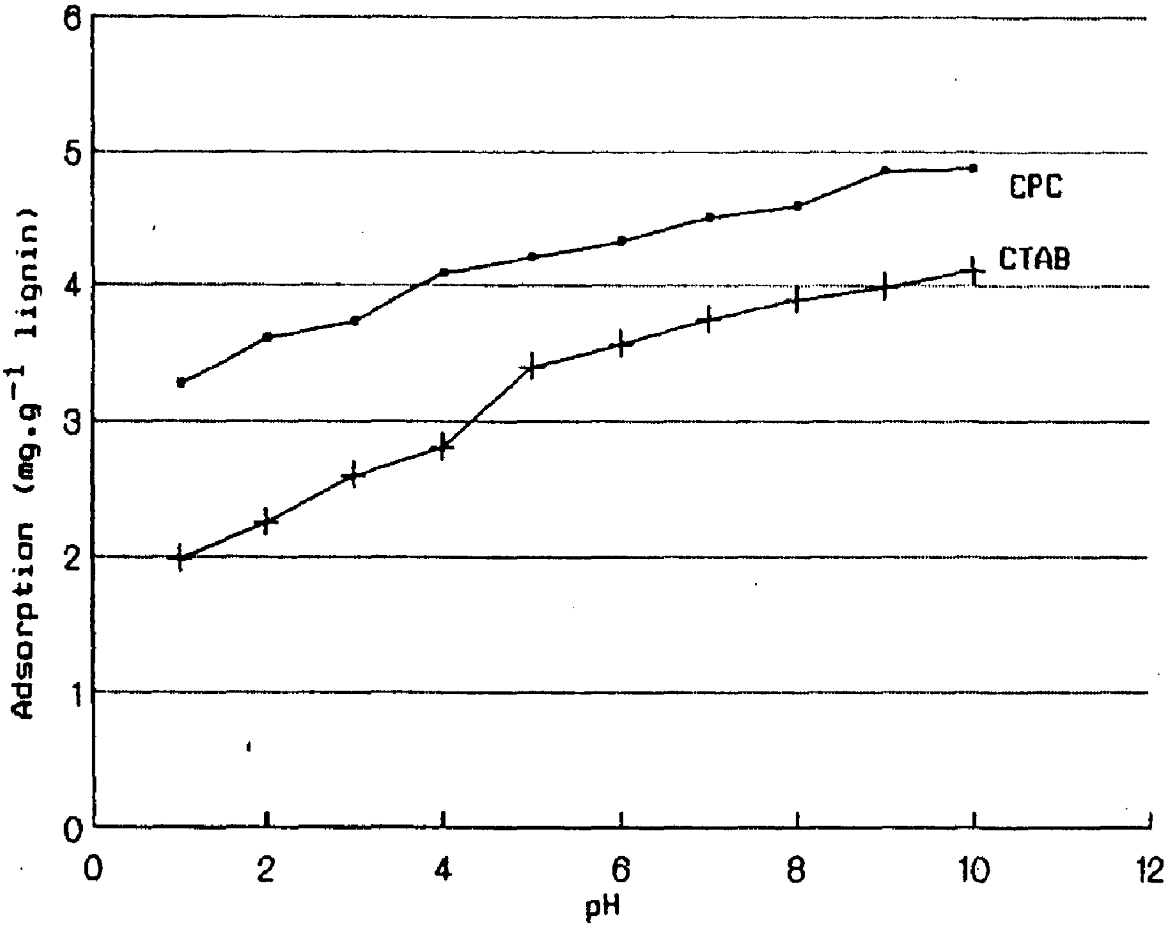


Fig. 25- Plots showing the effect of pH on the adsorption of cationic surfactants.

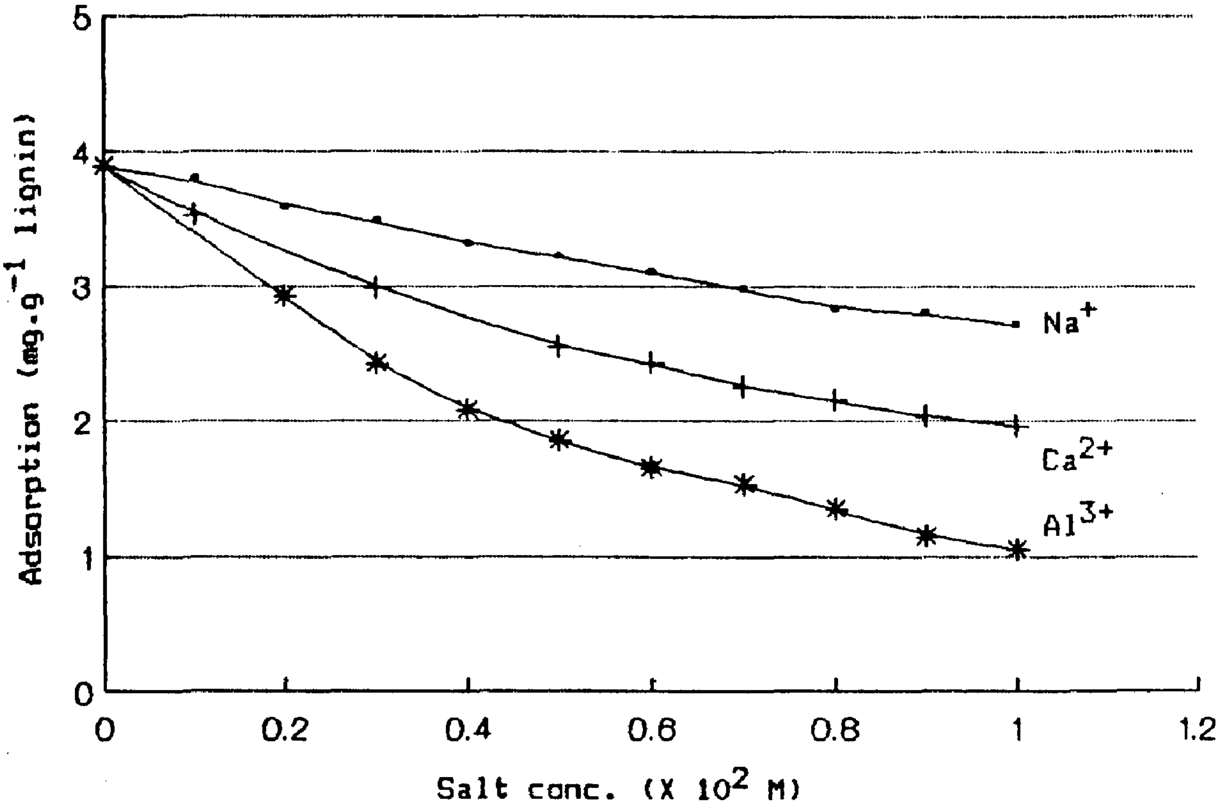


Fig. 26- Plots showing the effect of salt solutions on the uptake of CPC.

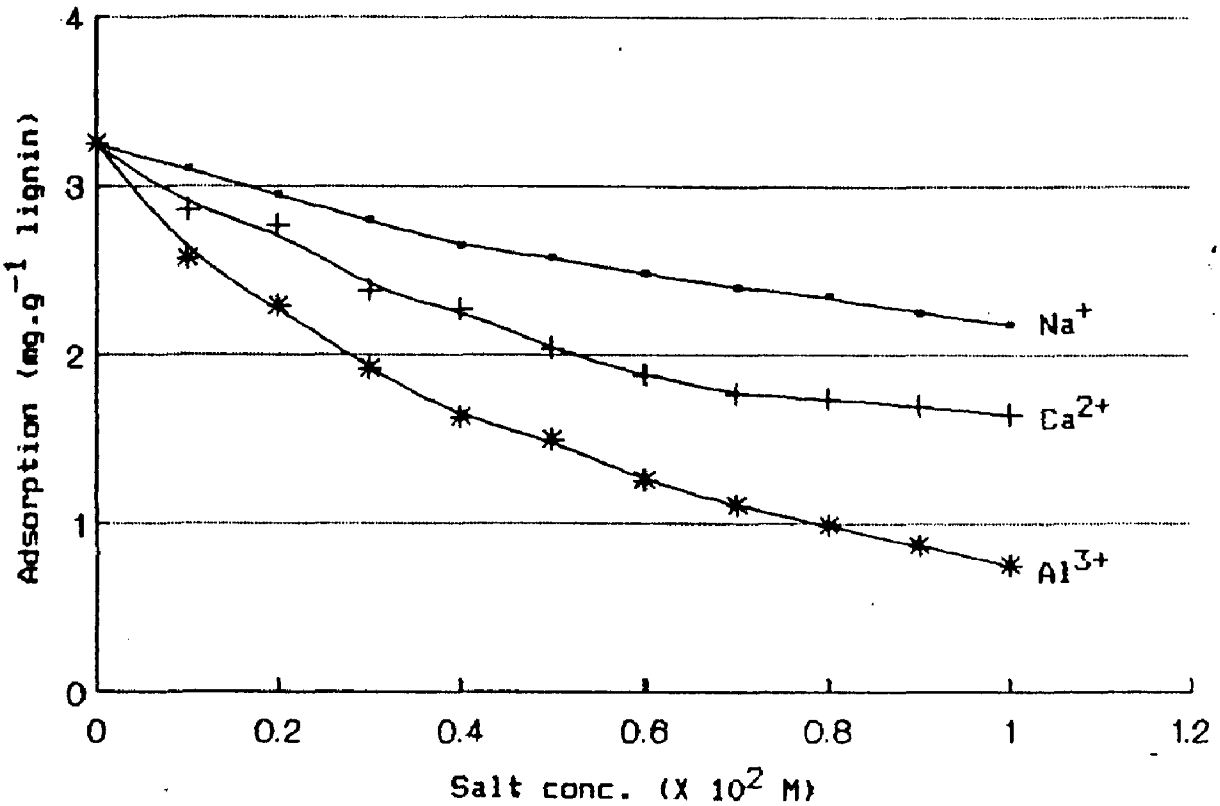


Fig. 27- Plots showing the effect of salt solutions on the uptake of CTAB.

3.7 ADSORPTION OF NONIONIC SURFACTANTS

Adsorption data of nonionic surfactants, Tween20 (T20) and Tween40 (T40) are listed in Tables 16-19 and Tables 20-23 respectively while adsorption isotherms are presented in Figs. 28 and 29. Plots of heat of adsorption are shown in Figs. 30 and 31. Langmuir plots are shown in Figs. 32-39 and BET plots are represented in Figs. 40-43. Fig. 44 indicates the effect of pH on the sorption of T20 and T40 while Figs. 45 and 46 show the effect of salt concentration on the sorption of T20 and T40 respectively.

The values of heats of adsorption at various levels of adsorption for T20 and T40 are listed in Table 24. Tables 25 and 26 give the values of Langmuir constants and BET constants for nonionic surfactants respectively. The results of effect of pH and particle size of adsorbent on the adsorption of both the nonionic surfactants are given in Tables 27-30.

Like cationic surfactants the adsorption isotherms of T20 (Fig. 28) and T40 (Fig. 29) are also regular and concave to equilibrium concentration axis, thus indicating positive adsorption. The extent of adsorption increases with the increasing surfactant concentration, but the percentage removal is higher at low adsorbate concentration. Further, the nature of isotherms, in both cases, reveal a rapid initial uptake of surfactants, followed by a slow approach to saturation condition at high adsorbate concentration. Thus, lignin can also act as a good adsorbent for removal of trace quantities of nonionic surfactants from their aqueous solutions.

The sorption of nonionic surfactants is much lower than cationic surfactants. The lignin particles are negatively charged which attracts more strongly the positively charged surfactants, thereby, giving a higher uptake of cationic surfactants.

Among the two nonionic surfactants, the uptake of T20 is higher than T40. The longer carbon hydrogen chain length in T40 molecules leads to higher hydrophobicity which results in lower uptake of T40.

The adsorption isotherms of the two nonionic surfactants T20 and T40 at different temperatures are shown in Figs. 28 and 29. It is observed that like cationic surfactants, the adsorption of nonionic surfactants also increase with increase in temperature and the process is exothermic. The heats of adsorption as calculated from equation 7 for the same amount of adsorption are given in Table 24. The values being higher for T20 and T40. Figs. 30 and 31 show the isosteric heat of adsorption for lignin-surfactant system plotted against the amount of surfactant adsorbed. The curve is linear in both the cases.

The adsorption data has also been correlated with Langmuir as well as BET adsorption models. Langmuir plots are shown in Figs. 32-39 and BET plots in Figs. 40-43. It is observed that linear relationship for BET plots in case of T20 is only observed at low concentration of adsorbates while the entire adsorption data is better represented by Langmuir model in case of both the surfactants and also it has not been possible to make BET plots of sorption data of T40. Langmuir as well as BET parameters are given in Tables 25 and 26. Q^0 values as calculated from BET models (Table 26) are much less as compared to those calculated from Langmuir plots (Table 25), since BET plot could only be drawn at lower concentration of adsorbate, the same would not give a correct value of the amount of surfactant necessary to form a monolayer on the adsorbent surface. Q^o values as obtained from Langmuir model (Table 25) are also in the same order in which these are adsorbed on lignin. The values of Langmuir parameter 'b' which reflect the steepness of approach to saturation, are in the same order in which both the cationic and nonionic surfactants are adsorbed on lignin. The values being higher for T20 and T40, thereby, indicating a greater tendency towards adsorption.

Like cationic surfactants the sorption of nonionic surfactants also increases with increase of pH (Tables 27 and 28, Fig. 44). The sorption of nonionic surfactants also has been found to increase with decrease of particle size of lignin (Tables 29 and 30).

The effect of salt concentration on the adsorption of nonionic surfactants has also been studied. The results are shown in Figs. 45 and 46. The results show that like cationic surfactants the adsorption of nonionic surfactants also decrease with increasing concentration of various salts. The decrease in adsorption follows the sequence —

$$Al^{+3} > Ca^{+2} > Na^{+}$$

Table-16

Adsorption of Tween20 (T20) on lignin at 20°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	16.0	4.97	11.03
2.	20.0	6.11	13.89
3.	24.0	9.06	14.94
4.	40.0	18.56	21.44
5.	48.0	24.54	23.46
6.	60.0	33.96	26.04
7.	64.0	37.11	26.89
8.	80.0	49.99	30.01
9.	88.0	58.93	29.07
10.	96.0	66.65	29.35
11.	100.0	71.13	28.87
12.	104.0	74.06	29.94

Table-17

Adsorption of Tween20 (T20) on lignin at 25^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	16.0	1.14	14.86
2.	24.0	2.70	21.30
3.	40.0	5.76	34.24
4.	48.0	8.09	39.91
5.	64.0	16.18	47.82
6.	80.0	24.46	55.54
7.	88.0	29.07	58.93
8.	96.0	37.64	58.36
9.	104.0	45.36	58.64

Table-18

Adsorption of Tween20 (T20) on lignin at 30^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	16.0	0.48	15.52
2.	24.0	0.90	23.10
3.	40.0	2.16	37.84
4.	48.0	2.91	45.09
5.	64.0	4.91	59.09
6.	80.0	10.99	69.01
7.	88.0	17.70	70.30
8.	96.0	25.14	70.86
9.	104.0	34.00	70.00

Table-19

Adsorption of Tween20 (T20) on lignin at 35^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	24.0	0.44	23.56
2.	40.0	1.13	38.86
3.	48.0	1.64	46.36
4.	64.0	3.08	60.92
5.	80.0	4.41	75.59
6.	88.0	9.15	78.85
7.	96.0	16.86	79.14
8.	104.0	23.13	80.87

Table-20

Adsorption of Tween40 (T40) on lignin at 20°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	24.0	12.69	11.31
2.	40.0	24.14	15.86
3.	48.0	30.42	17.58
4.	56.0	37.00	19.00
5.	64.0	43.99	20.01
6.	72.0	51.33	20.67
7.	80.0	58.51	21.49
8.	88.0	66.22	21.78
9.	96.0	74.23	21.77
10.	104.0	82.35	21.65

Table-21

Adsorption of Tween40 (T40) on lignin at 25^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	24.0	9.86	14.14
2.	40.0	17.99	22.01
3.	56.0	30.88	25.12
4.	64.0	37.22	26.78
5.	72.0	44.38	27.62
6.	80.0	51.16	28.84
7.	88.0	57.12	30.88
8.	96.0	64.56	31.44
9.	104.0	72.56	31.44

Table-22

Adsorption of Tween40 (T40) on lignin at 30^{o}C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration mg.l^{-1}	Equilibrium concentration mg.l^{-1}	Adsorption mg.g^{-1} lignin
1.	24.0	5.39	18.61
2.	40.0	12.49	27.51
3.	56.0	22.58	33.42
4.	64.0	27.50	36.50
5.	72.0	34.49	37.51
6.	80.0	40.53	39.47
7.	88.0	46.78	41.22
8.	96.0	54.77	41.23
9.	104.0	62.49	41.51

Table-23

Adsorption of Tween40 (T40) on lignin at 35°C.

Total volume = 50 ml.

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

Sl. No.	Initial concentration $mg.l^{-1}$	Equilibrium concentration $mg.l^{-1}$	Adsorption $mg.g^{-1}$ lignin
1.	24.0	4.50	19.50
2.	40.0	8.28	31.72
3.	56.0	16.54	39.46
4.	64.0	20.61	43.39
5.	72.0	26.07	45.93
6.	80.0	31.79	48.21
7.	88.0	37.75	50.25
8.	96.0	45.95	50.05
9.	104.0	53.83	50.17

Table-24

Values of Heat of adsorption at various amounts of adsorption for nonionic surfactants.

	Sl. No.	Adsorption mg.g^{-1} lignin	Heat of adsorption K.cal.mole^{-1}
	1.	14.86	-12.04
	2.	23.56	-13.22
	3.	34.24	-14.28
T20	4.	39.91	-14.81
	5.	46.40	-16.03
	6.	56.84	-17.24
	1.	5.00	- 7.66
	2.	10.00	- 8.38
T40	3.	14.14	- 9.05
	4.	21.01	-10.08
	5.	26.22	-11.10

Table-25

Values of Langmuir constants for nonionic surfactants.

Temperature °C	T20		T40	
	b mg^{-1}	Q^o $mg.g^{-1}$ lignin	b mg^{-1}	Q^o $mg.g^{-1}$ lignin
20	0.10	33.90	0.07	26.39
25	0.19	66.23	0.06	38.46
30	0.59	74.63	0.11	47.62
35	0.75	86.96	0.13	58.48

Table-26

Values of BET constants for nonionic surfactants.

Temperature °C	T20		T40	
	A mg^{-1}	Q^o $mg.g^{-1}$ lignin	A mg^{-1}	Q^o $mg.g^{-1}$ lignin
20	39.48	10.92	_	_
25	33.44	13.00	_	_
30	44.71	63.90	_	_
35	70.44	78.87	_	_

Table-27

Effect of pH on the adsorption of Tween20 (T20) on lignin at 35^{o}C

Total volume = 50 ml.

Initial concentration = 80 mg.l^{-1}

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

pH	Adsorption mg.g^{-1} lignin
1	65.36
2	68.36
3	72.31
4	73.08
5	74.55
6	75.24
7	77.32
8	78.51
9	79.23
10	79.93

Table-28

Effect of pH on the adsorption of Tween40 (T40) on lignin at 35°C

Total volume = 50 ml.

Initial concentration = 80 $mg.l^{-1}$

Particle size = 100-200 mesh.

Lignin added = 0.05 g.

pH	Adsorption $mg.g^{-1}$ lignin
1	36.82
2	40.78
3	43.37
4	44.56
5	45.22
6	46.47
7	48.89
8	50.23
9	52.67
10	55.37

Table-29

Effect of particle size on the adsorption of Tween20 (T20) on lignin at $30^{o}C$.

Total volume = 50 ml.

Initial concentration = 80 $mg.l^{-1}$

Lignin added = 0.05 g.

Sl. No.	Particle size Mesh	Adsorption $mg.g^{-1}$ lignin
1.	100-200	69.01
2.	52-100	66.53
3.	<52	65.77

Table-30

Effect of particle size on the adsorption of Tween40 (T40) on lignin at 30°C.

Total volume = 50 ml.

Initial concentration = 80 $mg.l^{-1}$

Lignin added = 0.05 g.

Sl. No.	Particle size Mesh	Adsorption $mg.g^{-1}$ lignin
1.	100-200	39.47
2.	52-100	28.84
3.	<52	17.83

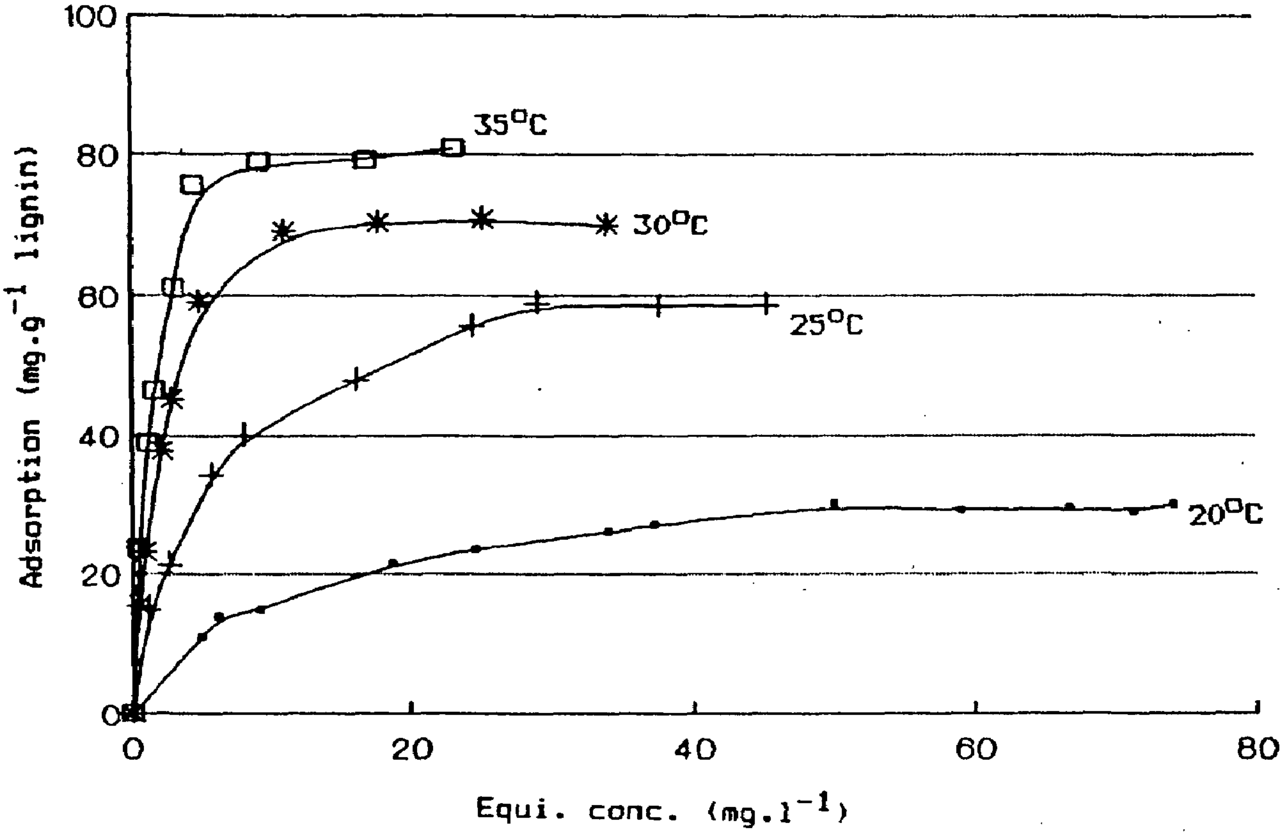


Fig. 28- Adsorption isotherms of T20.

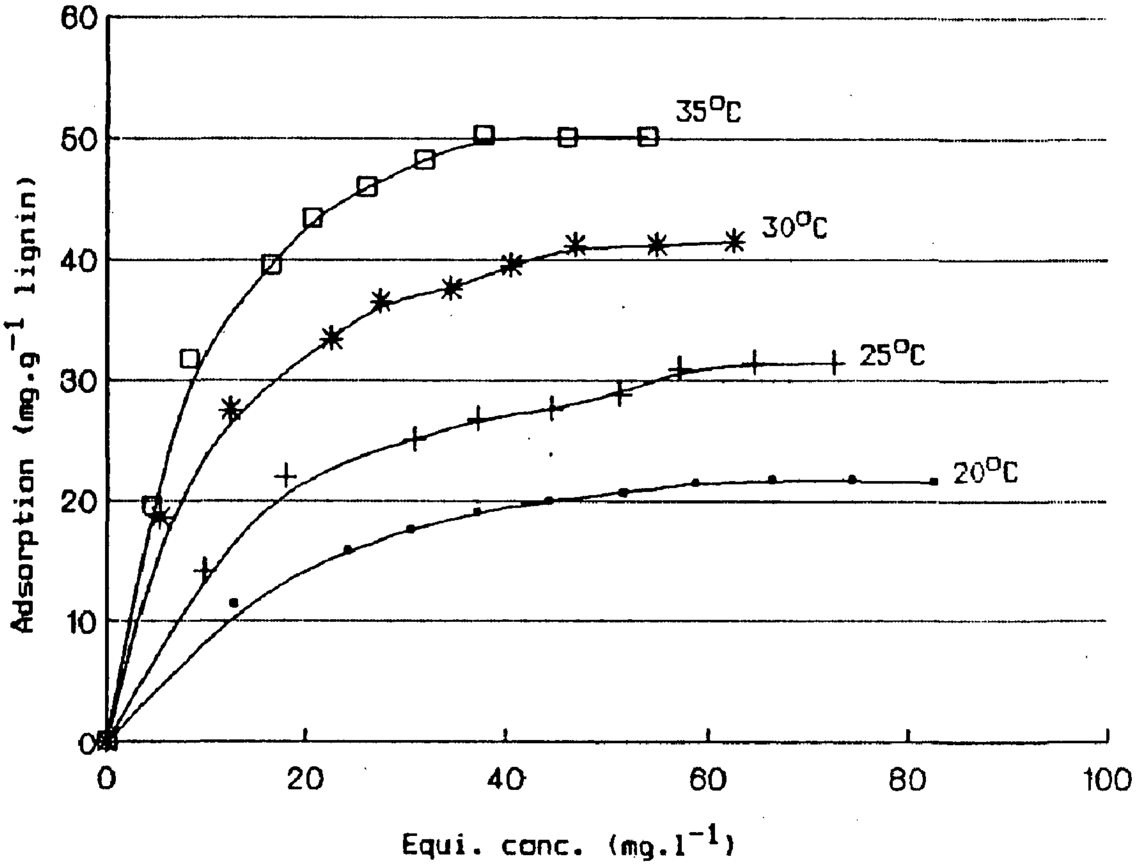


Fig. 29- Adsorption isotherms of T40.

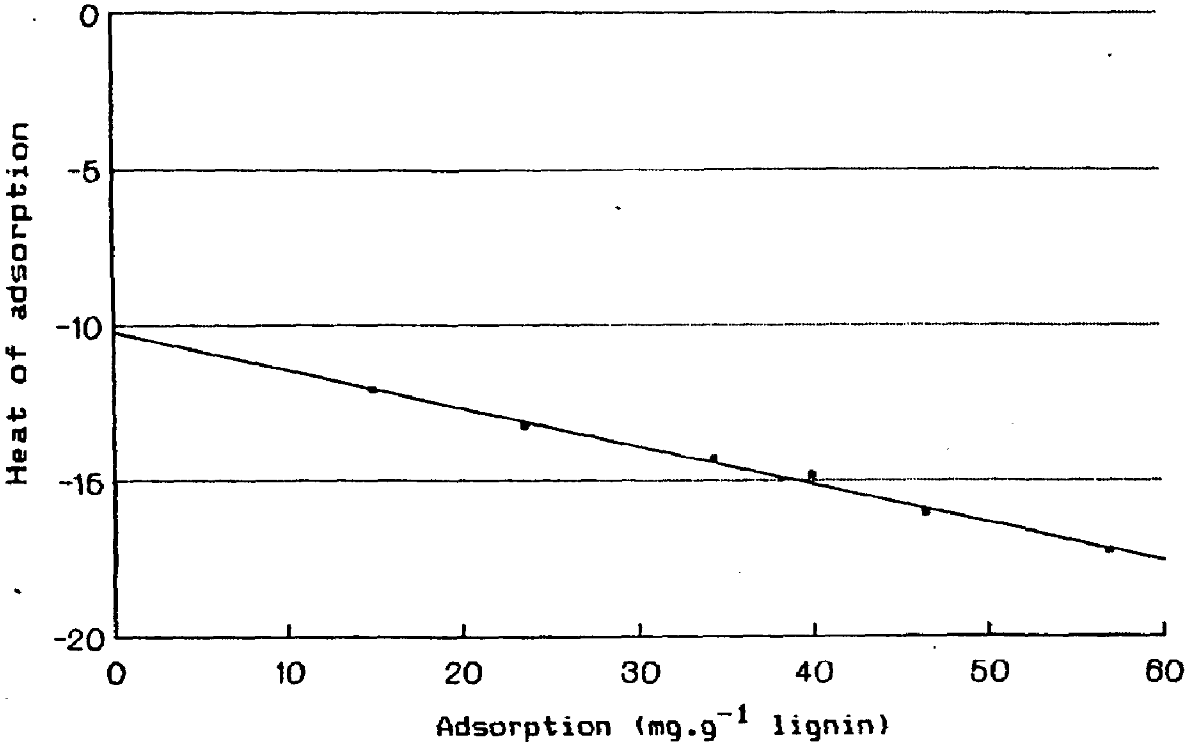


Fig. 30- Plots showing the adsorption of T20 vs heat of adsorption.

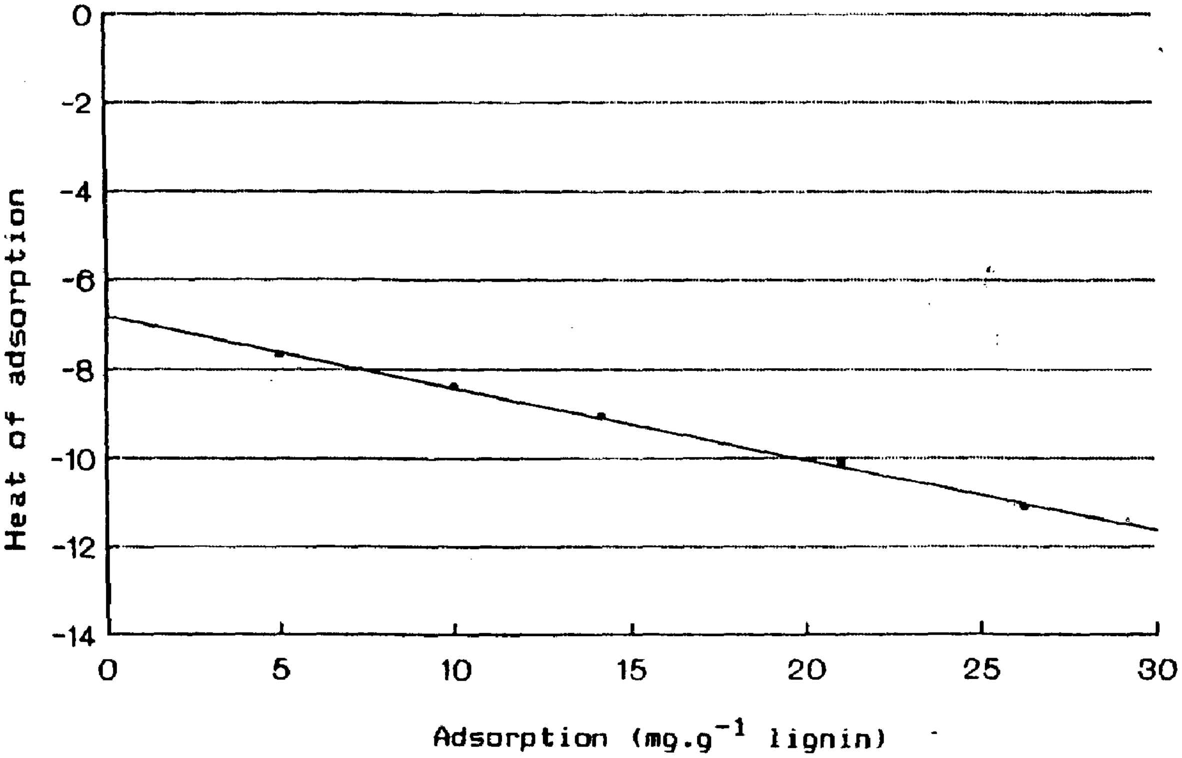


Fig. 31- Plots showing the adsorption of T40 vs heat of adsorption.

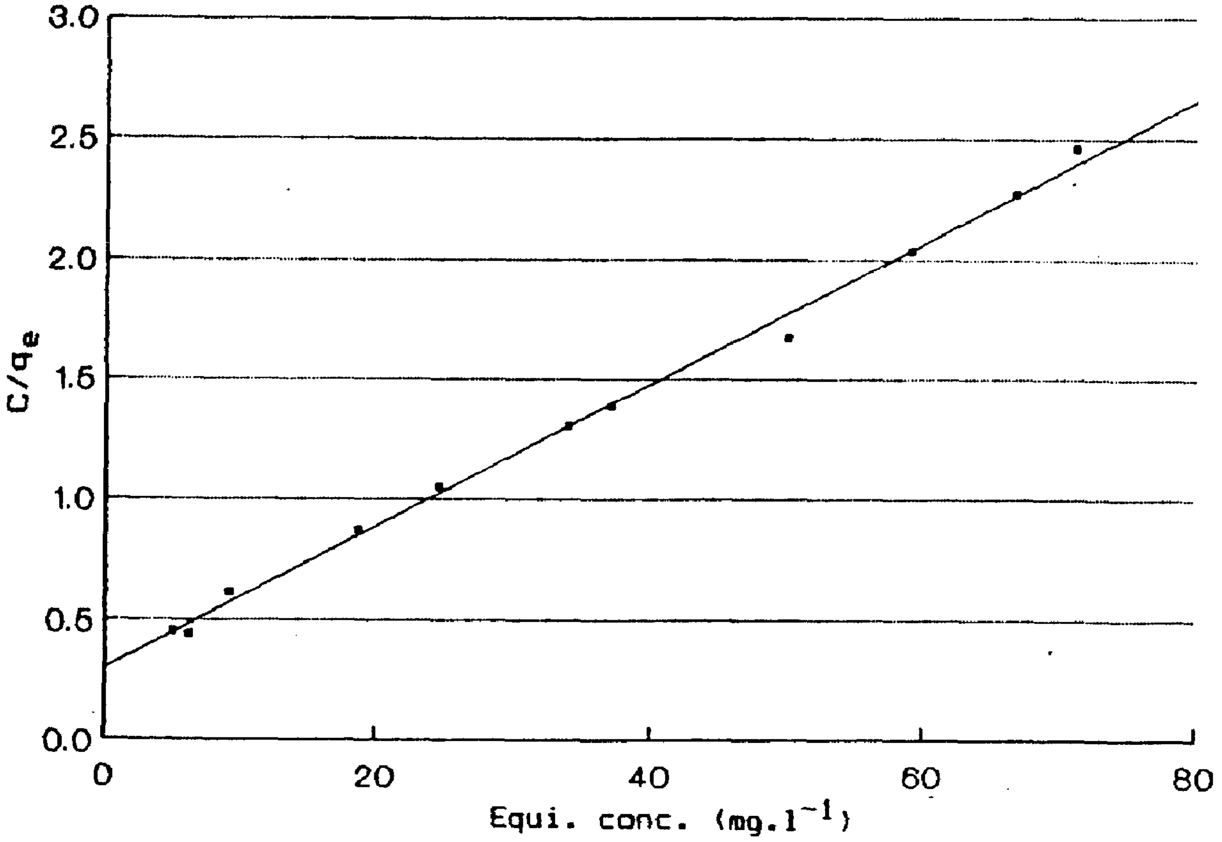


Fig. 32- Langmuir plot for T20 at 20°C.

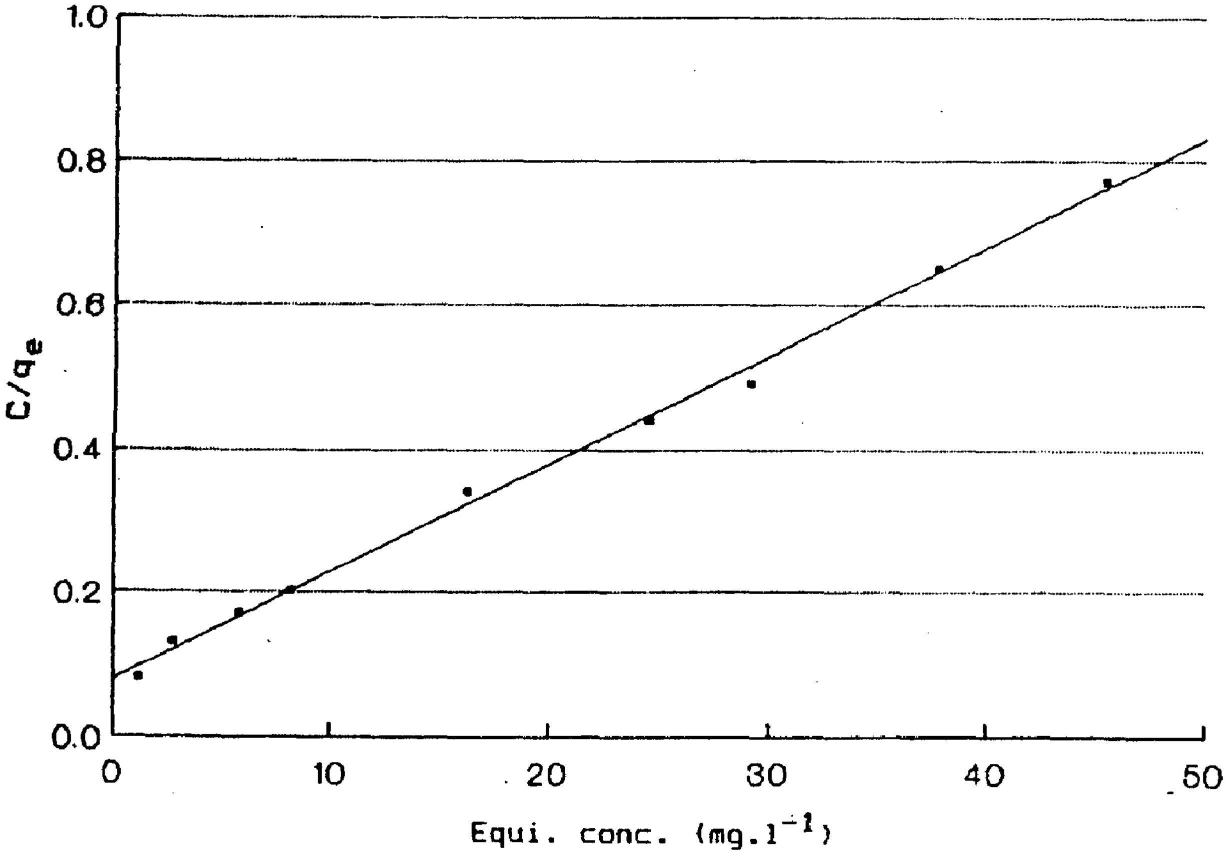


Fig. 33- Langmuir plot for T20 at 25°C.

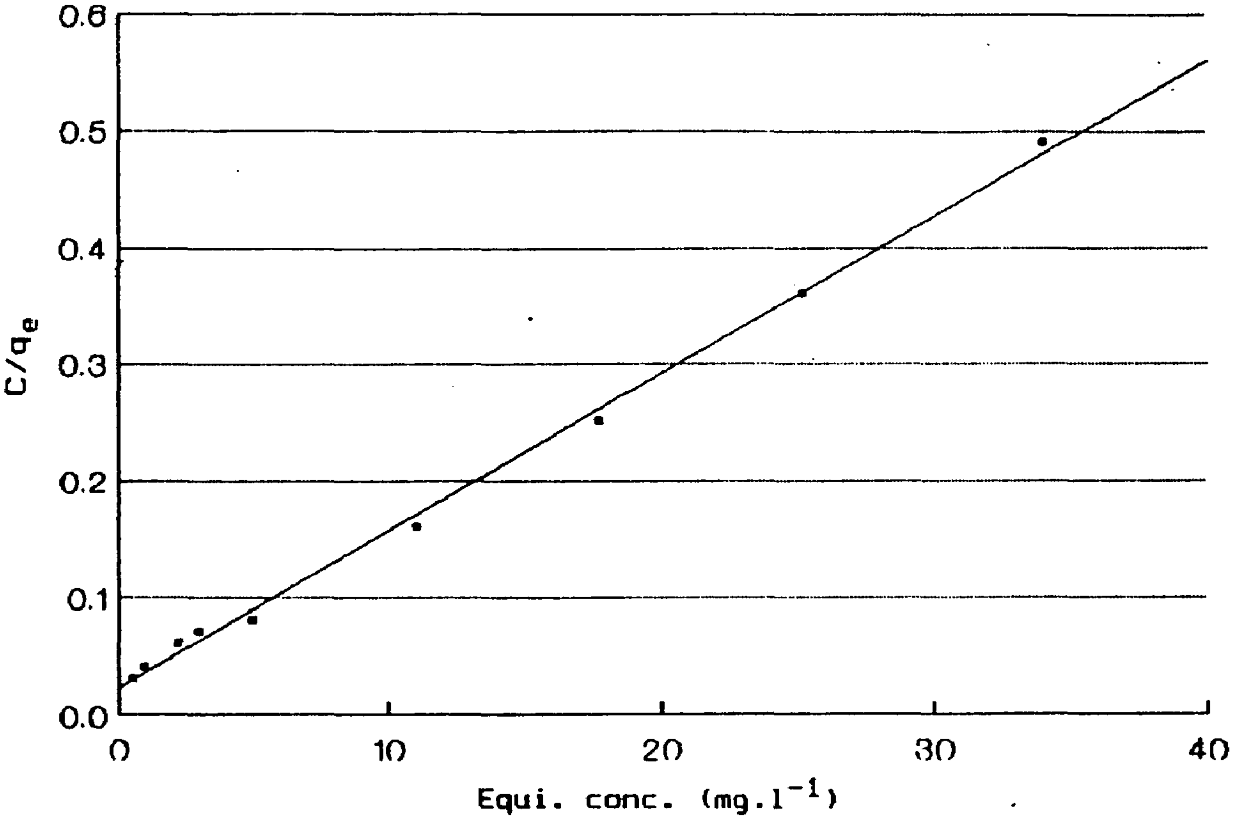


Fig. 34– Langmuir plot for T20 at 30°C.

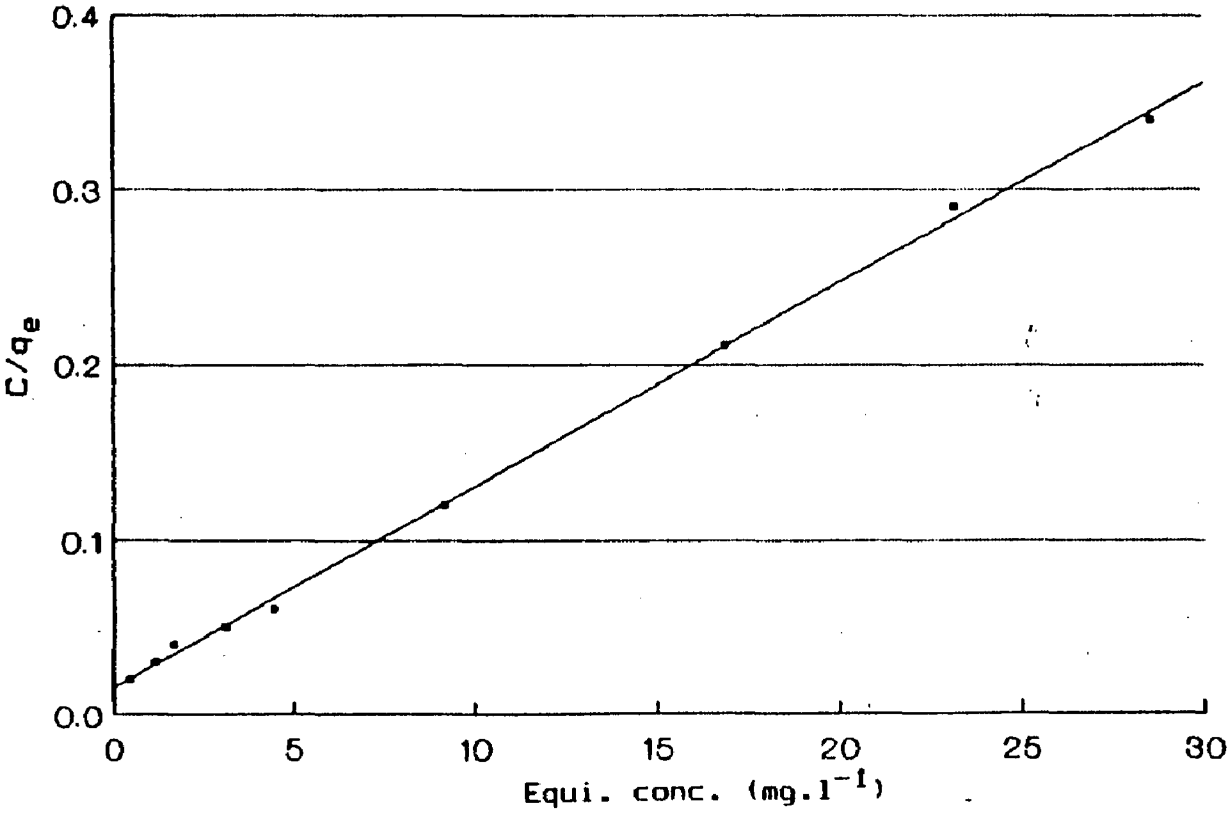


Fig. 35– Langmuir plot for T20 at 35°C.

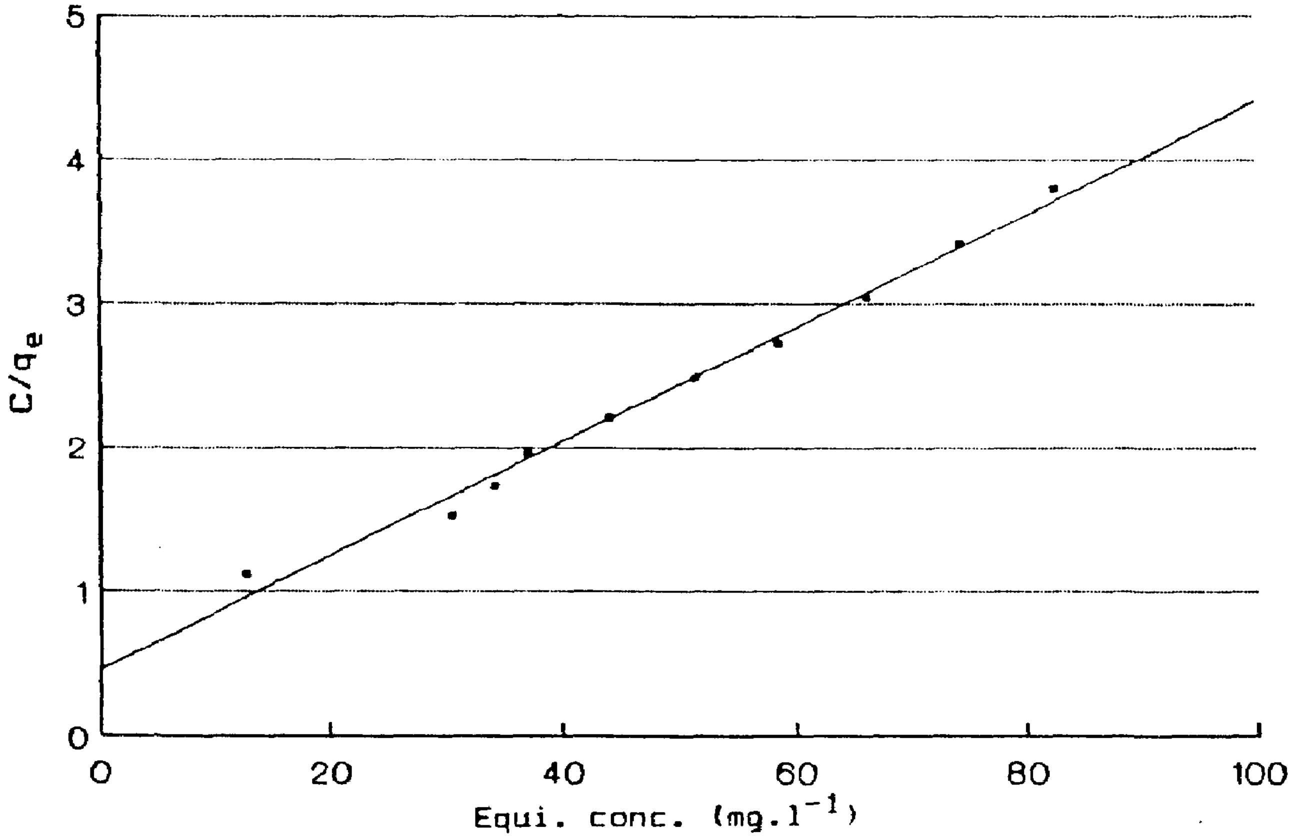


Fig. 36- Langmuir plot for T40 at 20°C.

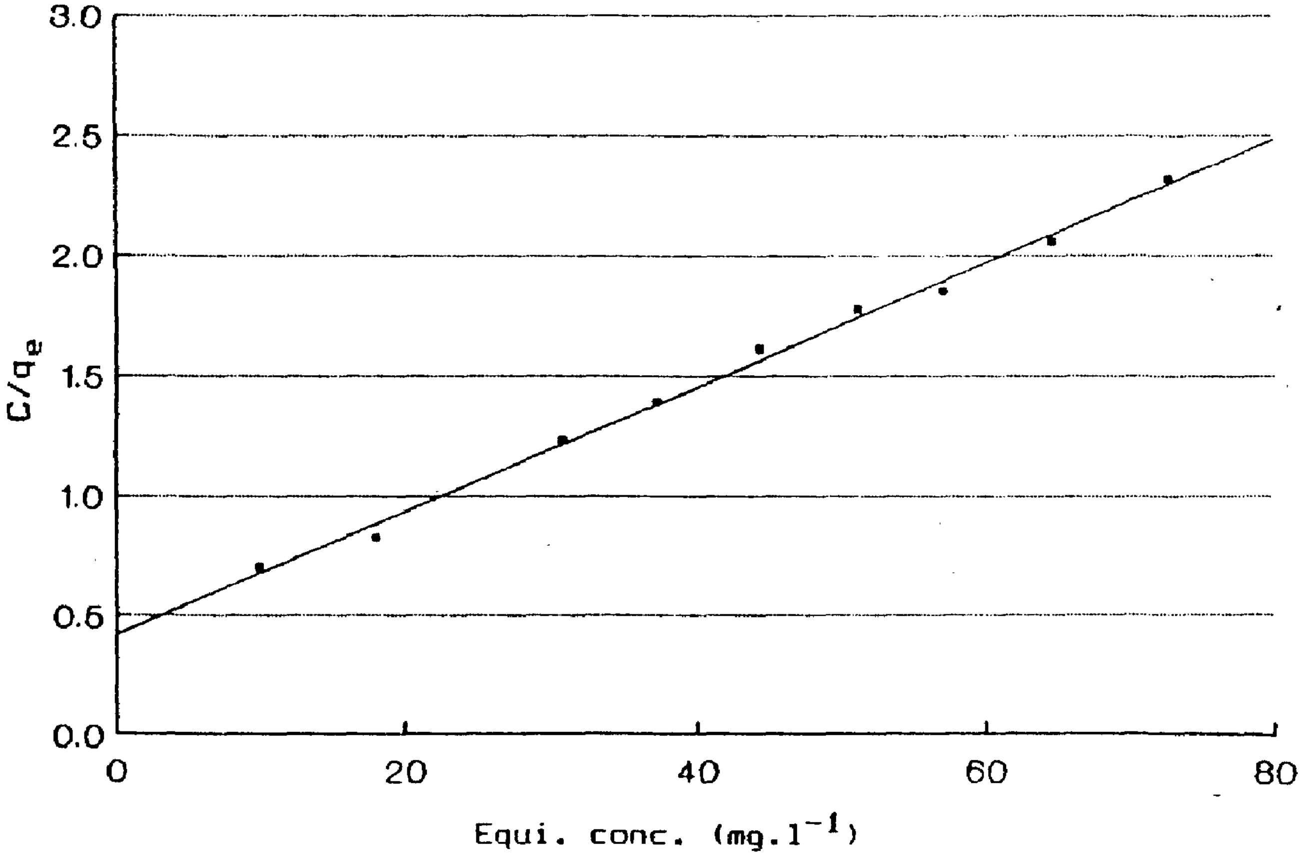


Fig. 37- Langmuir plot for T40 at 25°C.

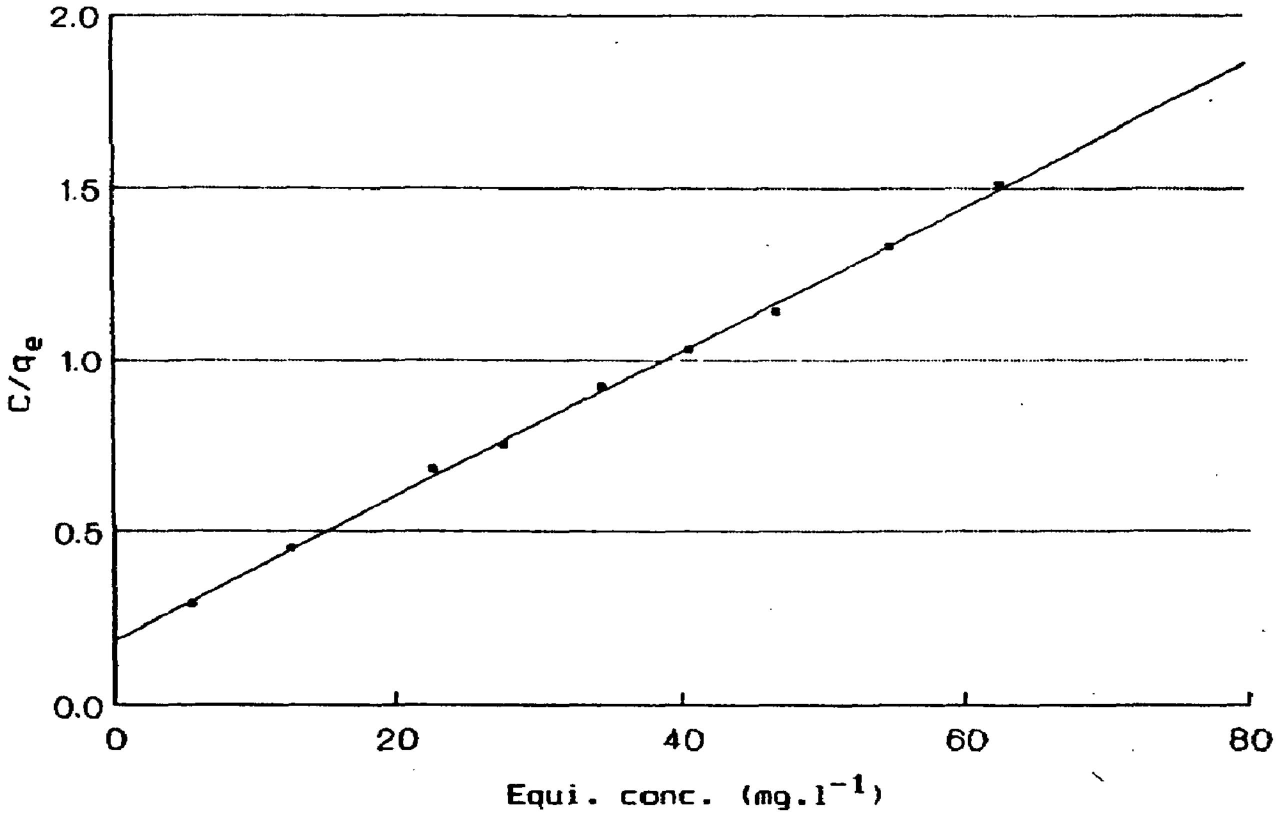


Fig. 38- Langmuir plot for T40 at 30°C.

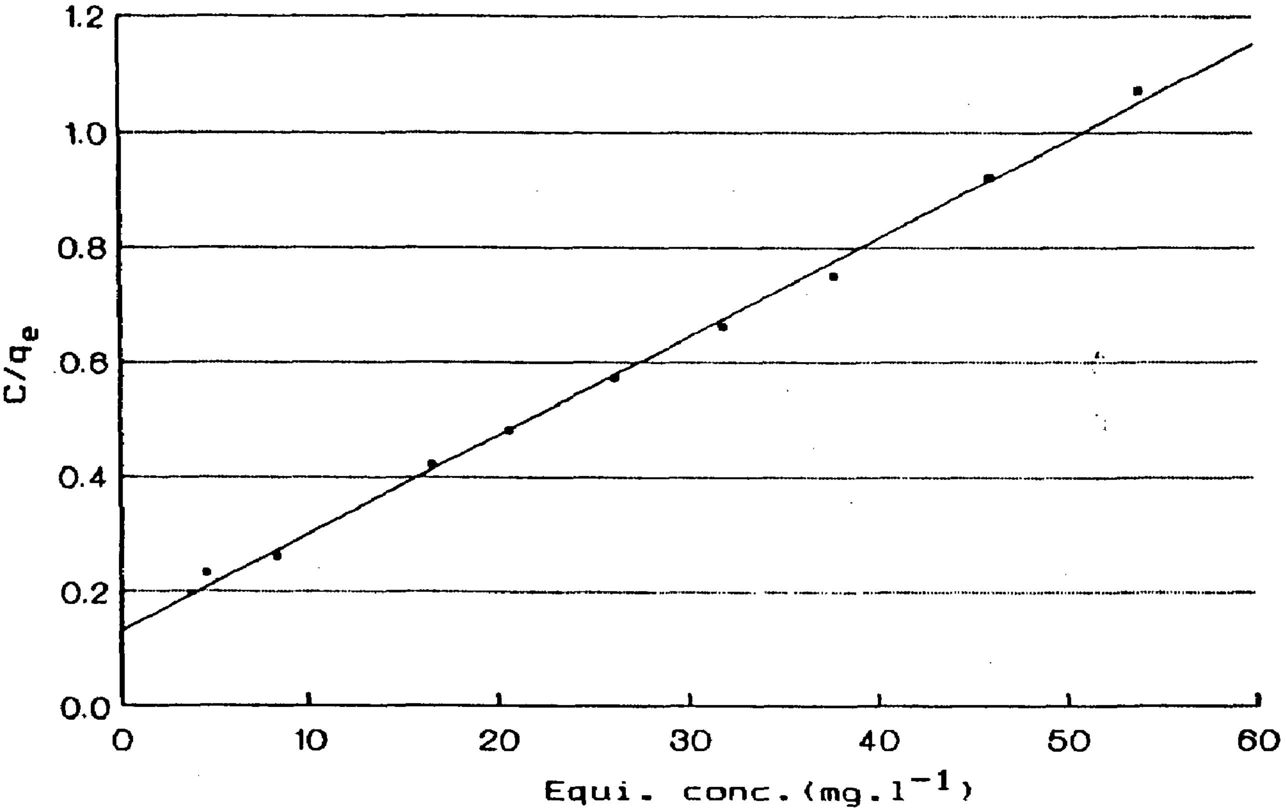


Fig. 39- Langmuir plot for T40 at 35°C.

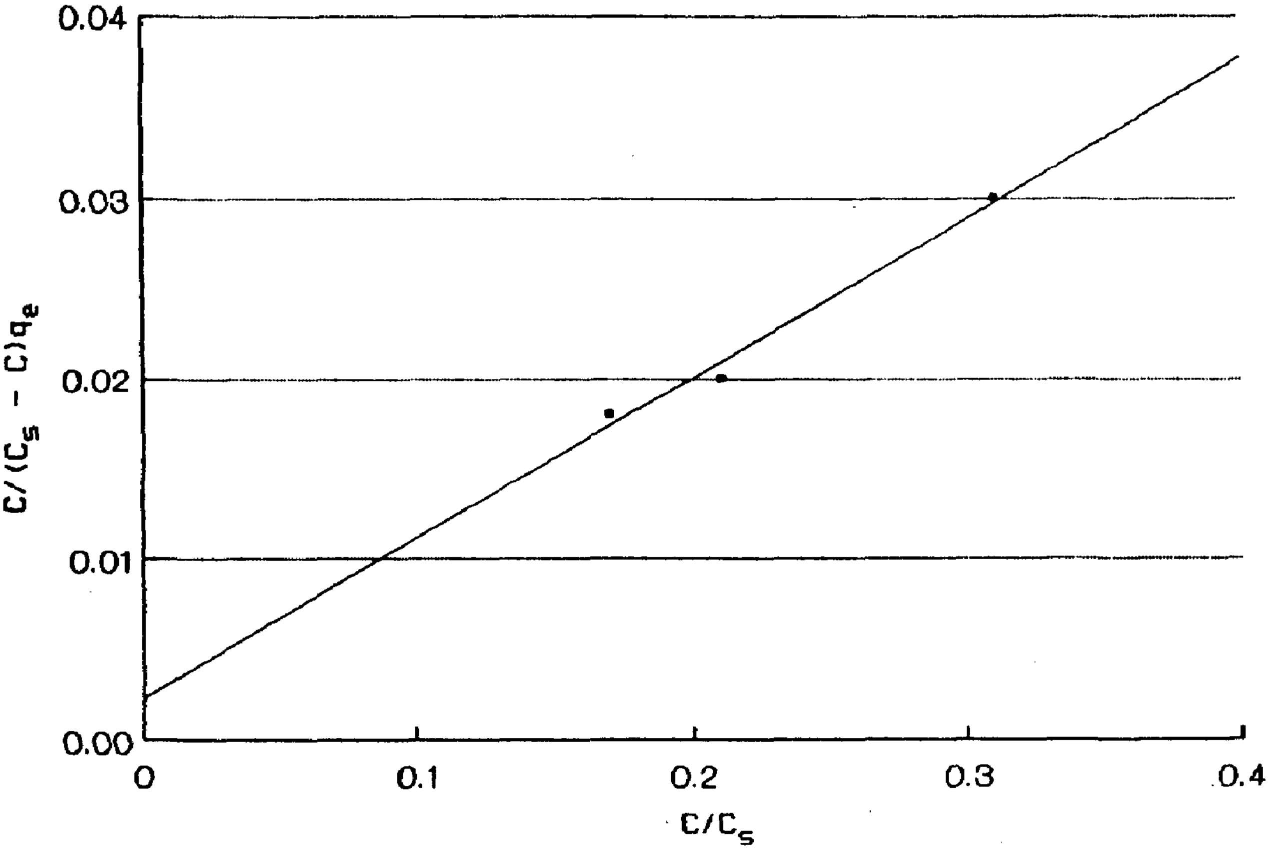


Fig. 40- B.E.T. plot for T20 at 20°C.

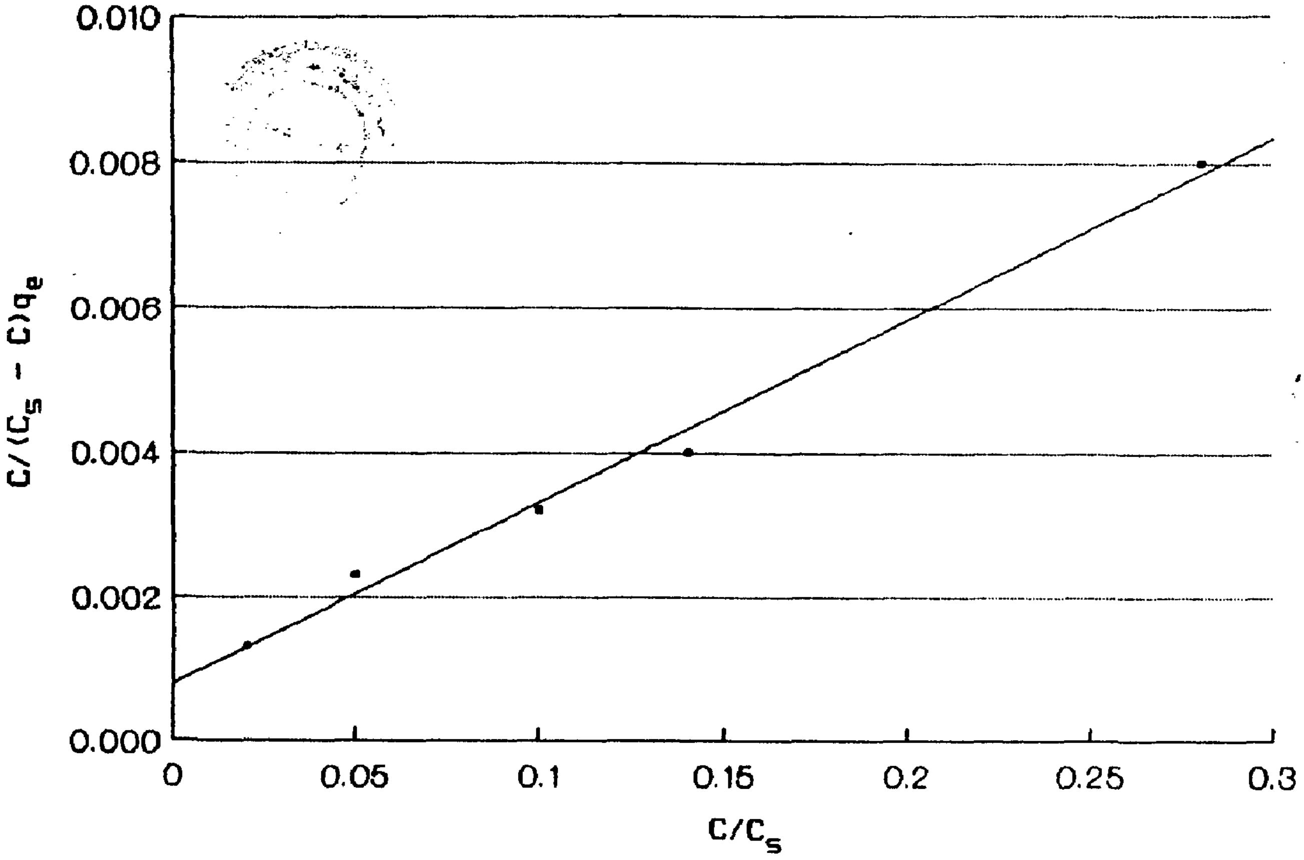


Fig. 41- B.E.T. plot for T20 at 25°C.

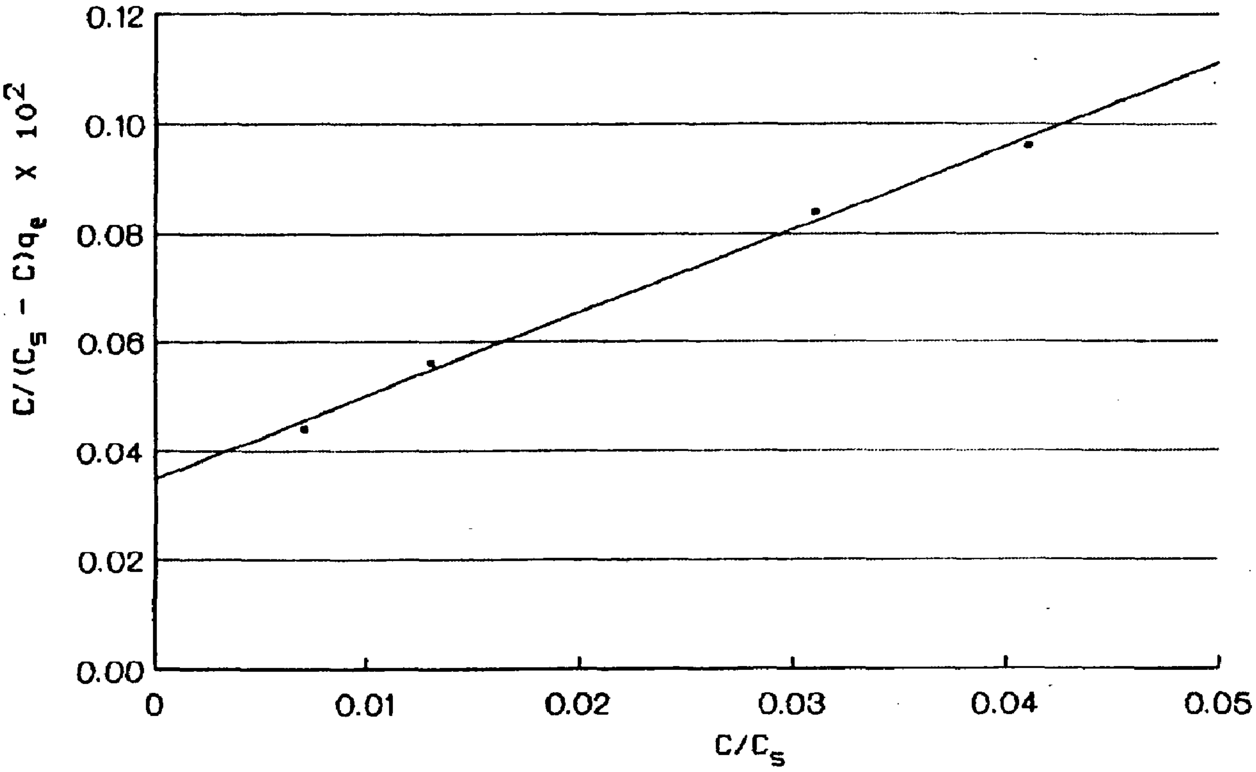


Fig. 42- B.E.T. plot for T20 at 30°C.

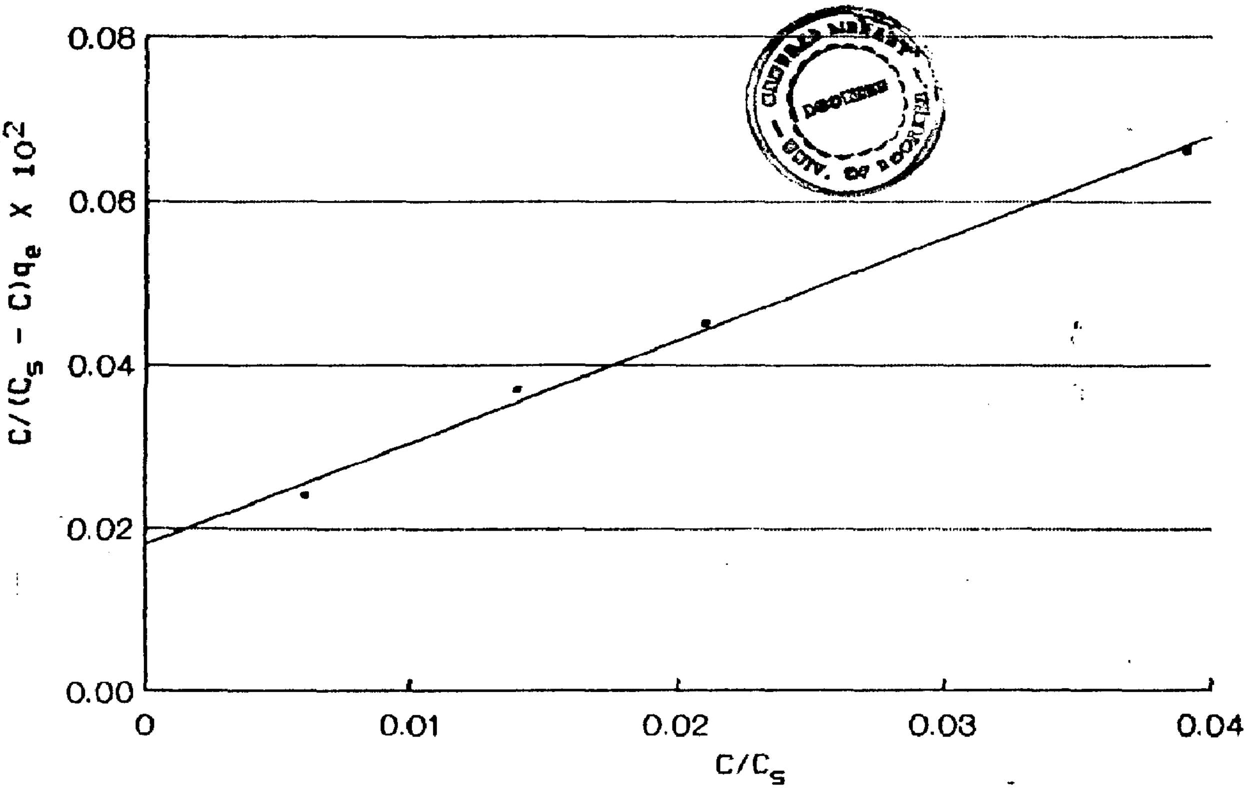


Fig. 43- B.E.T. plot for T20 at 35°C.

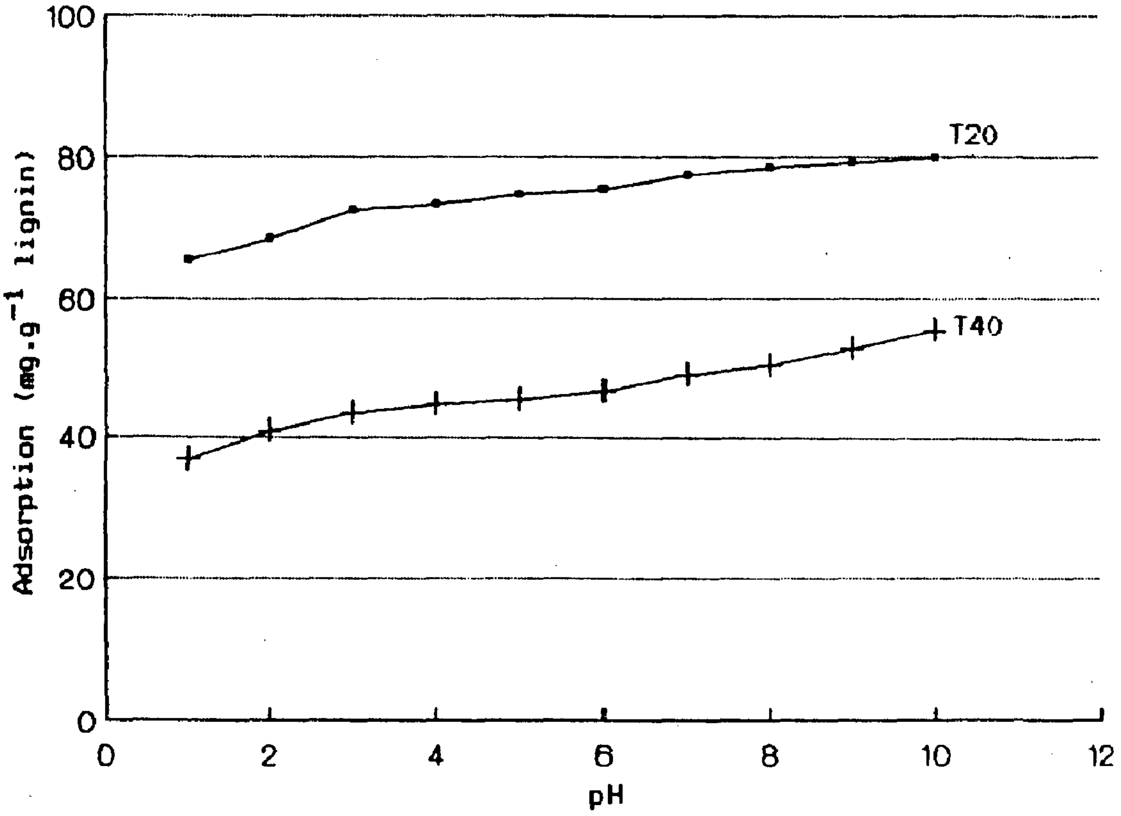


Fig. 44- Plots showing the effect of pH on the adsorption of nonionic surfactants.

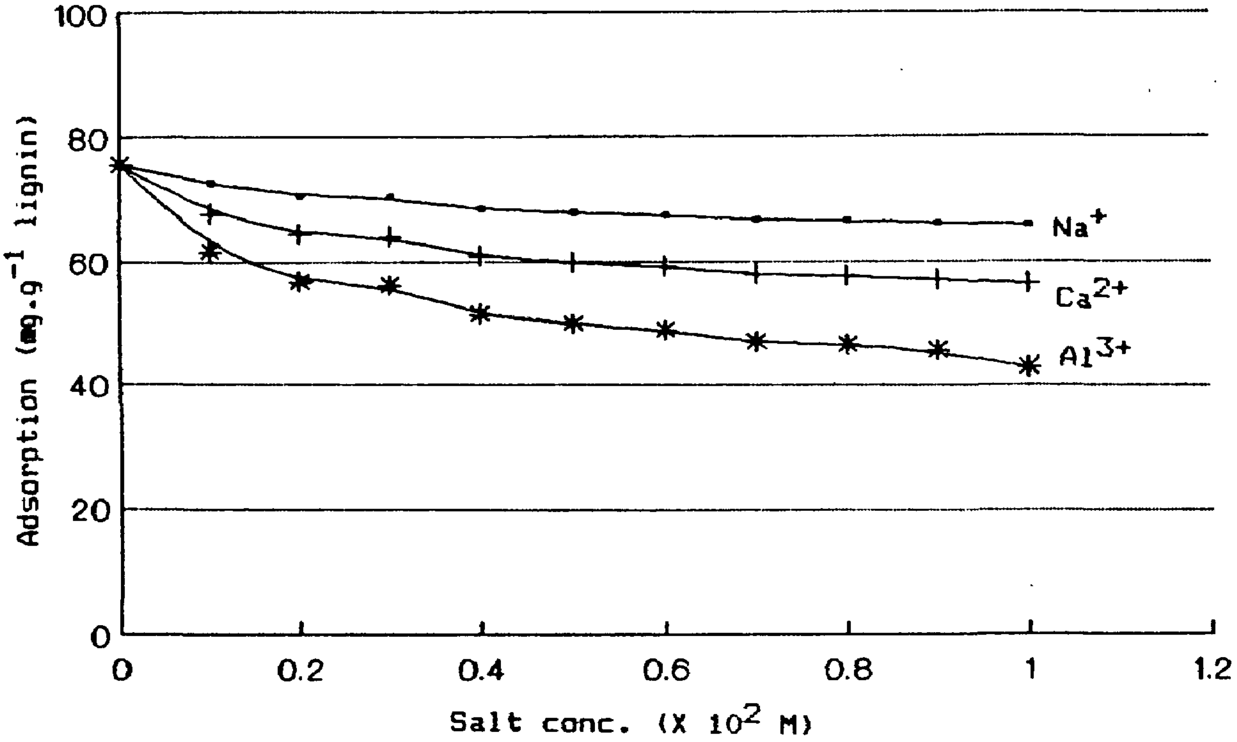


Fig. 45- Plots showing the effect of salt solutions on the uptake of T20.

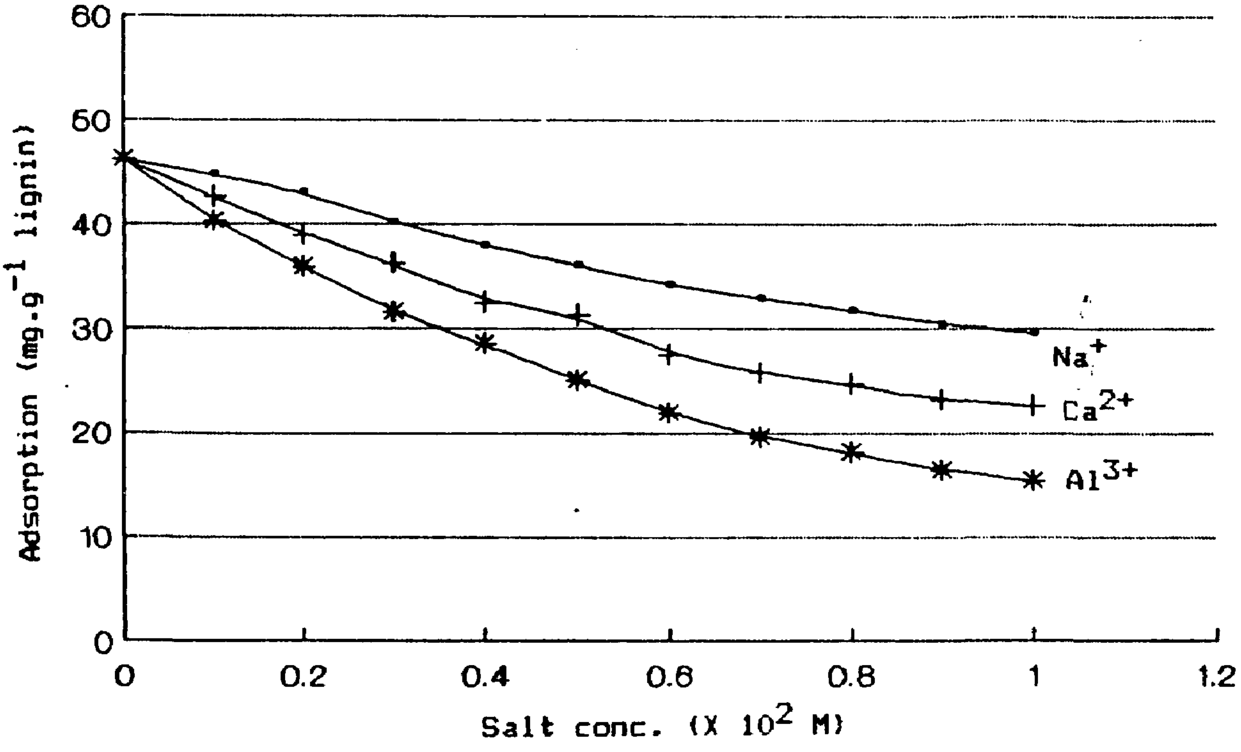


Fig. 46- Plots showing the effect of salt solutions on the uptake of T40.

3.8 Desorption studies

The desorption studies indicate that about 5-15% of the total surfactant adsorbed could only be desorbed with different desorbing solutions. Thus we may conclude that desorption of lignin does not take place with the various desorbing solutions used. Hence no further desorption experiments were performed.

REFERENCES

1. L. Adelson and I. Sunshine, J. Clinical Path., 22, 656 (1952).

2. E.F.W. Mackenzie, J. Brit. Water Works Assocn., 35, 75 (1953).

3. H.J. Heinz and W.K. Fischer, Public Health Engg. Abs., 58, 1531 (1963).

4. Orsanco Comitte Report, J. Amer. Water Works Assocn., 55(3), 369 (1963).

5. F.M. Middleton, W. Grant, and A.A. Rosen, Ind. Engg. Chem., 48, 268 (1956).

6. F.M. Middleton and A.A. Rosen, Pub. Health Reps. 71, 1125 (1956).

7. R.S. Joyce, J.B. Allen, and V.A. Sukenik, J. Water Polln. Control Fedn., 38, 5, 813 (1966).

8. J.S. Mattson, H.B. Mark, M.D. Malbin, J. Colloid Sci., 31, 116 (1969).

9. W.J. Weber, Jr., J.C. Morris, J. San. Engg. Div., 90, 79 (1964).

10. W.J. Weber, Jr., J.C. Morris, J. Amer. Water Works Assocn., 56, 4, 447 (1964).

11. D.W. Sundstrom, H.E. Klei and T. Tsui, Water Research, 13, 1225 (1979).

12. G. Belfort, Environ. Sci. Tech., 13, 1939 (1979).

13. K.H. Maney, W.E. Gates, J.D. Eye, and P.K. Deb, 19th Ind. Waste Conf., Purdue, (1964).

14. C.E. Renn and M.F. Barada, Sewage and Ind. Wastes, 31, 850 (1959).

15. J.N. William Son, A.H. Heit, and C. Calman, Final Tech. Report, Ionac Chemical Co., Birmingham, N.J. (1962).

16. H.G. Page and C.H. Wayman, Ground Water, 3, 10 (1966).

17. M.L. Jackson and V.V. Volk, Soil Sci. Soc., Amer. Proc., 30, 685 (1966).

18. M.L. Jackson and V.V. Volk, J. Water Polln. Control Fedn., 40, 205 (1968).

19. Chander Kishore, Ph.D. Thesis, University of Roorkee, Roorkee, India (1980).

20. R.L. Gustafson and J. Paleos, 'Organic Compounds in Aquatic Environment', Marcel Dekker Inc. N.Y. (1971).

21. I.M. Abrams and S.M. Lewon, J. Amer. Water Works Assocn., 54, 537 (1962).

22. V. Vesely and V. Pekarek, Talanta, 19, 219 (1972).

23. E. V. Kazakov and I. F. Karpova, Yestn. Leningard Univ., Ser. Fiz. Khim., 21, 139 (1966).

24. E. Wedekind, and G. Garre, Kolloid-Z., 44, 202 (1928).

25. Verkhanovskii et al. Khim. Tekhnol Vody 4, 1, 29-31 (1982).

26. Verkhanovskii et al. Soviet J. Water Chem. Technol. 4, 1, 37, (1982).

27. Nikiforov A. F. et al. Zh. Prikl. Khim, 58, 2, 306-312 (1985).

28. Tsolova et al. God Vissh. Khim. Technol. Instt. Sofia 29(3) 139-429 (1984).

29. Ponkina, N.A., Ioileva, K.A., Gardin 44 f, Lafrides, J.L. and Komshlov, N.F., Tr. Karel S.K. Filiala, Akad, Nauk SSR. 38, 26 (1963).

30. Yang J. Larkdisch et al., Biotechnol, Bio Engg., 35(3), 268-78 (1990).

31. Kay R.M. et al.,Dietary Fibers Chem. and Nutrition 57-65 (1979).

32. A.F. Kiprianova et al., Zh. Prikl. Khim., 63(2), 473 (1990)

33. J. Wieber et al., Colloids Surfaces 33, 1/2, 141 (1988).

CHAPTER -4

ADSORPTION KINETICS OF SURFACTANTS ON LIGNIN

4.1 Introduction

4.2 Results and Disscussion

- — Mechanism of sorption
- — Rate determination
- — Adsorption kinetics of cationic surfactants
- — Adsorption kinetics of nonionic surfactants

ADSORPTION KINETICS OF SURFACTANTS ON LIGNIN

4.1 INTRODUCTION

Adsorption is an effective process for the removal of dissolved organic substances from waters and waste waters. Successful application of this technique would, however, demand adsorbents of known kinetic parameters and sorption characteristics. A ~~prehand knowledge~~ pre-knowledge of optimal conditions would herald a better design and modelling of the process. A thorough study of sorption kinetics reveals the mechanism of the rate controlling step and in some cases, sheds significant light on the internal physical structure of adsorbent material.

In the early stages of development of exchange kinetics, one encounters quantitative statements, like reaction proceeds rapidly at first and then slows down as the equilibrium is approached (1) etc. etc. Nachod and Wood (2,3) were the first to start systematic investigations on ion exchange kinetics. The concept of diffusion was also first introduced by G. Schulze (4) who pointed out that the rate determining step in the exchange kinetics is the inter diffusion of counter ions.

Several characteristics of adsorbent, adsorbate and solution phase are of importance, in determining the rate limiting step. These factors include the particle size, amount of adsorbent, concentration of adsorbate, degree of mixing, affinity of adsorbate for adsorbent and diffusion coefficient of the solute molecules in bulk solution as well as with in the pores of the adsorbent material. Certain properties of the adsorbate and adsorbent can be useful in indirectly determining the nature of the rate limiting step and these are described in detail by Helfferich (5) and Weber and Morris (6).

It is now well established that the rate determining step in the exchange sorption is the inter diffusion of counter ions. The rates of exchange adsorption is controlled by diffusion either through a hydrostatic boundary layer called "film diffusion control" or through the pores of resin matrix called "particle diffusion control". The rate of ion exchange adsorption is mainly controlled by film diffusion under conditions of small resin particle, dilute solution and mild stirring. It is controlled by particle diffusion under conditions of large resin particle, high concentration of solution and vigorous stirring. Otherwise, it is controlled by both processes. Many workers treat more of the cases as those involving both the film as well as particle diffusion mechanism.

A survey of literature reveals that lignin exhibits sorption properties. This material has so far not been exploited for waste water treatment. Since we have studied the sorption characteristics of lignin for the removal of cationic and nonionic surfactants (chapter 3), it becomes imperative to study the sorption rate of these surfactants on lignin as a function of adsorbate concentration, temperature. This chapter describes the results of kinetic studies and value of diffusion coefficients as well as some thermodynamic parameters have been evaluated and used to determine the mechanistic aspects of the process.

4.2 RESULTS AND DISCUSSION

4.21 Mechanism of sorption

In order to determine the rate at which dissolved organic substances are removed from dilute aqueous solutions by solid adsorbents, it is necessary to determine the step which controls the overall mechanism of sorption. These are essentially three consecutive steps in the adsorption of organic material on porous adsorbent (5,7). These are —

(a) transport of the adsorbate to the external surface of the adsorbent,

(b) transport of the adsorbate within the pores of the adsorbent (except for a small amount of adsorption that occurs on the surface of the adsorbent), and

(c) adsorption of the adsorbate on the interior surface of the adsorbent.

It is generally accepted that the process (c) is very rapid and does not represent the rate limiting step in uptake of organic compounds (6). For the remaining two steps, if external transport is rapid as compared to the internal transport, the rate of adsorption is governed by the process (b) i.e., particle diffusion, while if the internal transport is more rapid than the external one, the rate is governed by the step (a). In latter case, the transport of adsorbate to the boundary may not be possible at a significant rate, thereby leading to the formation of a liquid film with a concentration gradient surrounding the sorbent particle and the overall rate is governed by the diffusion of adsorbate through this film i.e., film diffusion.

A number of methods have been devised to find out the nature of rate limiting step which depends upon the characteristics of adsorbent (particle size) and adsorbate (Concentration) and the rate of mixing. These characteristics have been described in detail by Boyd et al. (8), Helfferich (5) and others (6,9,10).

The distinction between external and intraparticle diffusion controlled processes can be made by performing the interruption test (5) suggested by Kressman and Kitchener (11) and Smith and co-workers (12). It yields good results particularly if a large concentration gradient exists within the pores of the adsorbent.

The theories developed on the basis of ion exchange phenomenon have conveniently been used (7) for the sorption of surfactants for determining the kinetic and thermodynamic parameters of the sorption processes.

4.22 Rate determination

At time t, the extent of sorption has been expressed as —

$$F = \frac{Q_t}{Q_\alpha} = \frac{\text{Amount of exchange after time t}}{\text{Amount of exchange after infinite time or at equilibrium}} \qquad (1)$$

As the batch technique is used, the ingenious equations developed by Boyd et al. (8) and later improved by Reichenberg (13) have been used to distinguish between the film diffusion and particle diffusion controlled mechanisms. According to Boyd at al. (8) if rate controlling step is particle diffusion, "F" is related to time "t" and particle radius "r" as —

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\alpha} \frac{\exp(-n^2 Bt)}{n^2} \qquad (2)$$

where n is the number of exchanger particles and "B", the time coordinate, is given by the expression —

$$B = \frac{\pi^2}{r^2} D_i \qquad (3)$$

where D_i is called the effective diffusion coefficent of the ingoing particles. Thus, knowing the value of "B" and mean particle radius "r" the value of D_i can be evaluated.

It can be noticed from equation 2 that "F" is calculable mathematical function of Bt and vice versa, and depends only upon D_i/r^2, i.e., it will be independent of the adsorbate concentration. The plots of Bt vs t must be a straight line passing through the origin, if the particle diffusion is the rate determining step.

In these studies, for every observed value of "F" corresponding Bt value has been obtained from Reichenberg's Table (13). The linearity test of Bt vs t plots has been employed to distinguish between the particle and film diffusion mechanisms. The experimental conditions were set for particle diffusion as the sole rate determining step to study the thermodynamics of the sorption process. The energy of activation "E_a" has been determined by applying the Arrhenius type expression (14-20) —.

$$D_i = D_o \exp (- E_a/RT) \qquad (4)$$

The pre exponential constant "D_o" (analogous to Arrhenius frequency factor) gives the entropy of activation ΔS^* as (14-21)

$$D_o = 2.72\ d^2\ \frac{k\ T}{h}\ \exp(\Delta S^*/R) \qquad (5)$$

Where "k", "h" and "R" are the Boltzmann, planck and gas constants respectively, "d" is the average distance between the successive exchange sites and is taken as 5 A (14-20), T (= 273 K) is the temperature in kelvin scale.

The method of least squares has been applied to all linear plots and standard deviations are less than 5 percent on all reported values.

4.23 Adsorption kinetics of cationic surfactants

The effect of adsorbate concentration on the sorption rate of the two cationic surfactants on lignin is shown in Figs. 1-4. The variation in sorption rate with temperature has been graphically represented in Figs. 5-8 along with the respective B values in Figs. 7 and 8. McKay (22) plots [log(1-F) vs t] for sorption process are depicted in Figs. 9 and 10. Fig. 11 indicates a linear relationship between the logarithm of effective diffusion coefficient (D_i) and the reciprocal of temperature (K^{-1}) for the sorption of CPC and CTAB. Kinetic and thermodynamic parameters of the diffusion process are listed in Tables 1 and 2.

Figs. 1 and 2 show F vs t plots for CPC and CTAB respectively at different sorbate concentrations. These curves indicate that the adsorption process is quite rapid and about 50-80% of the adsorption occurs within first twenty minutes of contact. This initial rapid adsorption subsequently gives a slow approach to equilibrium. These curves also indicate that the amount of solute removed during the first ten minutes of contact increases with increase in the concentration of adsorbate. However, the required for fifty percent adsorption is more or less unaffected by the initial adsorbate concentration. This suggeststhat particle diffusion may be the rate controlling step. These findings are in agreement with the results reported by Zogorski, Faust and Haus (7).

Figs. 3 and 4 are obtained by replacing F values by the corresponding values of Bt. In both the cases Bt vs t plots are linear and passing through origin and also independent of initial solution concentration at and above 11 mg/l. However, at lower concentration (9 mg/l), the plots deviate from the linear behaviour and also depend on the initial adsorbate concentration. This shows that sorption of CPC and CTAB is particle diffusion controlled at and above 11 mg/l while at low solution concentration (9 mg/l), the film diffusion also affects the adsorption (8,13,18-20).

The increase in sorption rate with increase in temperature (Figs. 5-8) further support particle diffusion mechanism as the rate controlling process (8,13,18-20). The none linear behaviour of log (1-F) vs t plots (McKay plots) drawn for adsorption process (Figs. 9 and 10) under investigation, is also an evidence in favour of particle diffusion mechanism (18-20,23) as the rate controlling step.

The concentrations of CTAB and CPC required for particle diffusion mechanism, in the investigation, are considerable less than those reported for the ion exchange sorption of some simple as well as complex cations on various adsorbents (14-17,20,23-

26). It is quite certain that the sorption rate and mobility of ions in solution determine the characteristics of liquid film surrounding the sorbent particle. Here, the bigger size of CTA^+ and CP^+ ions and their relatively slow rate of sorption, as compared to simple metal ions, reduce the possibility of the formation of a liquid film of significant concentration gradient around the sorbent particles, and consequently, even at such lower solution concentrations i.e., 11 mg/l the sorption rate is governed by the particle diffusion mechanism (18,19).

The sorption rates for the two surfactants have been found to increase with temperature. Increase in mobility of CPC and CTAB ions at higher temperature results in the increased sorption rate. Similar behaviour has also been noted by Saraswat and co workers for the sorption of heavy alkali metal ions (20) and complex cations (18,19) on chromium ferrocyanide gel, Heitner et al. (23) and Rawat et al. (14) for the exchange of metal ions on the H^+ form of chelating resin, Bio-chelex-100 and tantalum arsenate respectively.

The shapes of the McKay plots (22) (Figs. 9 and 10) for both the cationic surfactants are similar to those obtained for independently decaying radioactivities (27). The initial portion of these plots are convex to log (1-F) axis while the later portion lies on a straight line. It indicates that in the sorption of CPC and CTAB surfactants, mainly two inter diffusion processes, contribute to the overall rate of sorption.

(i) a faster process, corresponding to the residual curve,

(ii) a slower process, corresponding to later straight line portion of the plot.

As the system tends towards equilibrium, process (i) becomes less significant and the (ii) dominates. It may be argued that the effective diffusion coefficient, D_i, here is mainly comprised of two components, which are due to the simultaneous diffusion of the ingoing surfactant ions through the pores of different mesh widths and different electric fields along the diffusion path. The diffusion within the pores of wider mesh widths and weaker retarding forces of electrostatic interaction (particularly at the surface of the sorbent) accounts for the faster one, and that within the pores of narrower mesh widths and stronger retarding forces accounts for the slower component of D_i. As the temperature increases, the contribution of faster component to D_i increases (Figs. 9 and 10). It is because of the increasing mobility of ingoing species at higher temperature which overcomes, to some extent, the influence of retarding forces. Helfferich et al. (28-31) have observed a similar behaviour and explained the variable interdiffusion coefficients on the basis of electric field gradient along the diffusion path. Saraswat, Srivastava et al. (20) have also observed identical results for the exchange sorption of heavy alkali metal ions on chromium ferrocyanide gel and for the exchange sorption of bigger complex cations of Cobalt(III) on the same sorbent.

A perusual of data in Table 1 indicates that the values of effective diffusion coefficient D_i, are higher for CPC in comparison to CTAB. The geometry and bigger size of CTAB as compared to CPC, causes more hinderance to its mobility within the pores of the sorbent.

It can be seen from Table 1 and 2 that the order of pre exponential constant (D_o) is reverse to that of effective diffusion coefficient (D_i) and this may be attributed to higher activation energy value associated with the higher values of D_o. These values are analogous to those observed for the exchange sorption of complex cations on chromium ferrocyanide gel where higher D_o value observed for $[Co(en)_3]^{+3}$ ion was found to be associated with higher E_a value thereby resulting in a lower value of D_i as compared to that of $[Co(NH_3)_6]^{+3}$ ion (18,19). Similar behaviour was also observed for ion exchange in felsphathoids by Barrer et al. (32) who found small D_o value associated with a small value of E_a and vice versa.

A comparison for the sorption of cations may be worthwhile in determining the efficiency of the sorbent, under study, for the removal of surfactants. The values of effective diffusion coefficients observed in present case are comparable to those observed for the exchange of sorption of Rb^+ and Cs^+ on chromium ferrocyanide gel (20) (of the order of 10^{-8} cm^2/sec). However, these values are higher as compared to those observed for the self diffusion of alkali metal ions in analcite (33) and for the exchange sorption of complex cations of Cobalt(III) on chromium ferrocyanide gel (18,19) (of the order of 10^{-14} to 10^{-20} and 10^{-12} cm^2/sec respectively). These values are also higher as compared to those observed for the exchange of Rb^+ and Cs^+ on the H^+ form of tin and zirconium antimonate (16,17) (of the order of 10^{-9} to 10^{-10} $cm^2/sec.$).

The $\log D_i$ vs $1/T$ plots drawn for the sorption of two surfactants (Fig. 11) are linear in nature. This permits use of the Arrhenius equation (Equation 4) for the determination of D_0 and E_a from the intercepts and slopes of the linear plot. D_0 values are further used to evaluate the entropy of activation (Equation 5) for the sorption of CP^+ and CTA^+ on lignin. The values of D_0, E_a and ΔS^* for both surfactants are listed in Table 2. It can be concluded from Table 2 that the value of activation energy (E_a) is higher for CTAB as compared to CPC. This may be attributed to the bigger size of the former adsorbate, which causes more steric hinderence (18,19) to its mobility through the pores of sorbent material and thus need more energy to undergo diffusion.

The entropy of activation value is negative for the sorption of CP^+ and positive for the sorption of relatively bigger CTA^+ ion. Several workers have observed a negative value of ΔS^* for various sorption systems (14-17,20,34). However, positive values of ΔS^* have also been observed by some workers (18,19,21). Dyer and Fawcett (21) have obtained positive ΔS^* for the migration of ca^{+2}, Sr^{+2} and Ba^{+2} ions in Linde Molecular Sieve 13X. Saraswat et al. (18,19) have also obtained a positive values of ΔS^* for the sorption of some complex cations on chromium ferrocyanide gel. A positive value of ΔS^* has also found out by Kaishava et al. (35) for the sorption of sodium lauryl sulphate on murcury. Negative values of entropy of activation obtained ion diffusion of alkaline earth metal ions (36) in zeolites, are indicative of a comparatively higher degree of mobility and the lack of orientational effect which the ingoing ion influences upon its water environment (36). Conversely, the positive value associated with CTA^+ sorption would thus be a reflection of its restricted diffusion path and large orientation effect upon the water environment of ingoing cation (36). Further, the negative value of ΔS^* also indicates that as a result of sorption of CPC, no significant change occurs in the internal structure of the sorbent material (16,17,20). Saraswat et al (18,19) have explained the positive ΔS^* value observed for the exchange of trivalent complex cation of cobalt(III) on chromium ferrocyanide gel (18,19) on the basis of deformation in the exchanger matrix resulting form bending or coiling of the frame work. In the present process of investigation where the surfactants yields univalent cations, such type of changes are not possible. As such a positive value of ΔS^* observed for CTA^+ sorption indicates a greater disorder produced in the structure of the sorbent as a result of the uptake of surfactant cation.

Table-1

Effective diffusion coefficient (D_i) values for cationic surfactants.

Temperature ^oC	$D_i \times 10^9$ ($cm^2.sec^{-1}$) CPC	$D_i \times 10^9$ ($cm^2.sec^{-1}$) CTAB
20	6.83	2.68
25	9.46	4.15
30	11.81	5.76
35	14.02	7.67

Table-2

D_o values and thermodynamic Parameters for cationic surfactants.

Surfactants	$D_o \times 10^2$ ($cm^2.sec^{-1}$)	E_a ($Kcal.mole^{-1}$)	ΔS^* ($cal.deg^{-1}.mole^{-1}$)
CPC	2.35	3.80	- 0.99
CTAB	984	5.57	11.02

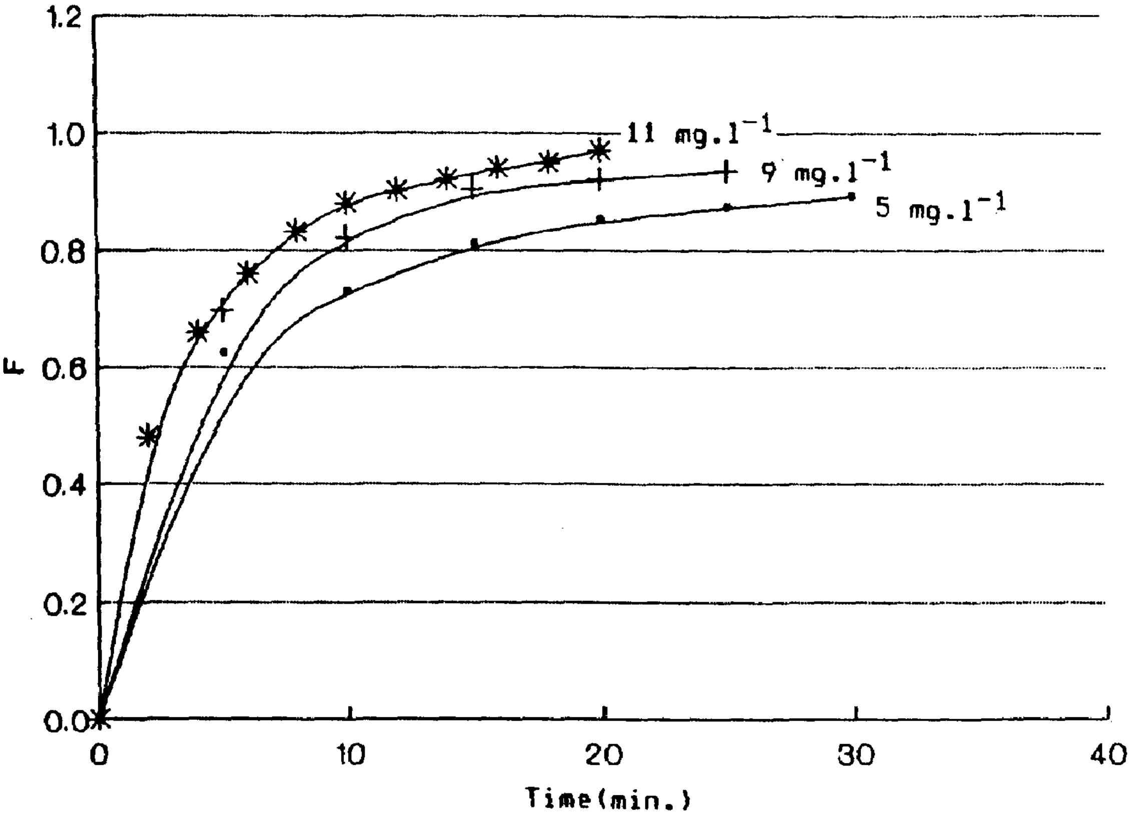
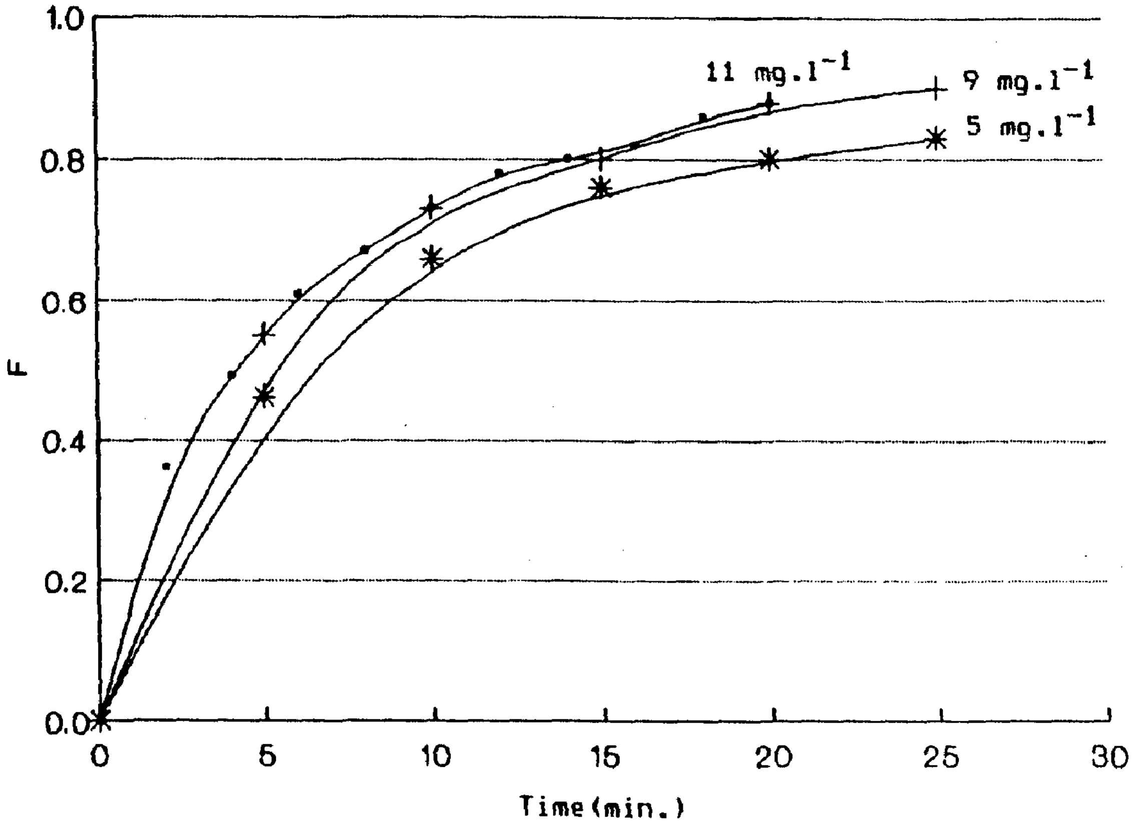


Fig. 1- Plots of F vs t for CPC, using different solution concentrations.



(Fig. 2- Plots of F vs t for CTAB, using different solution concentrations.

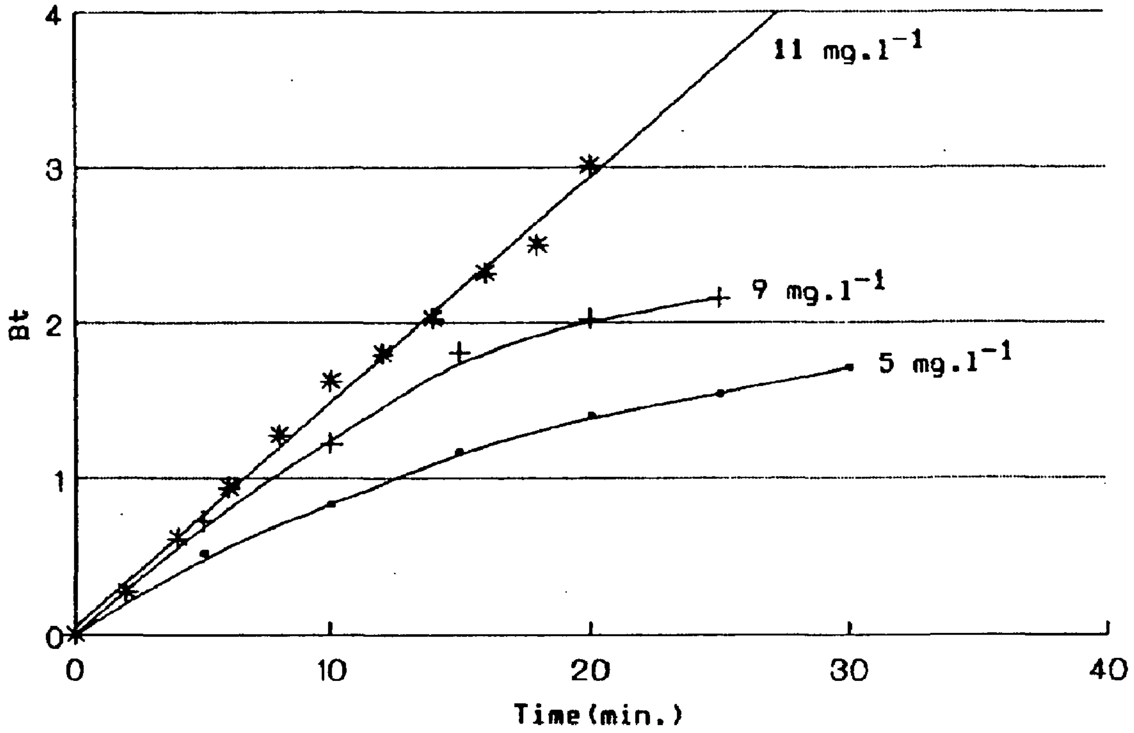


Fig. 3- Plots of Bt vs t for CPC, using different solution concentrations.

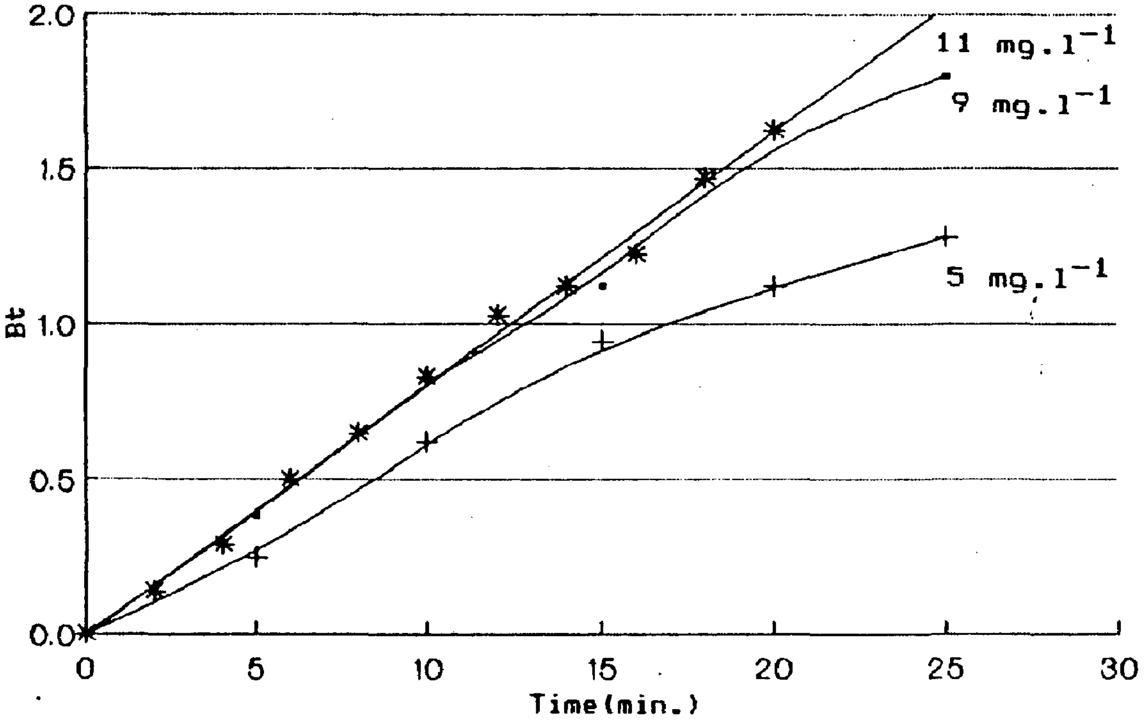


Fig. 4- Plots of Bt vs t for CTAB, using different solution concentrations.

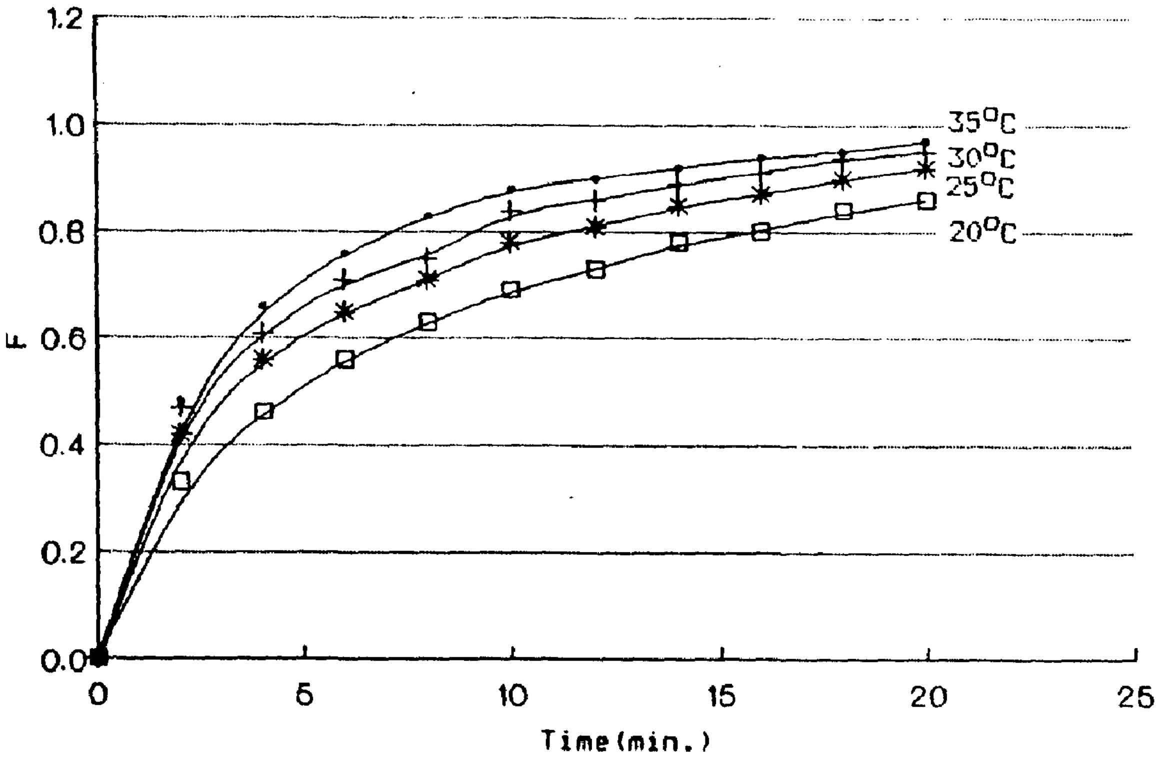


Fig. 5- Plots of F vs t for CPC, at different temperatures and solution concentrations 11 mg.l^{-1}.

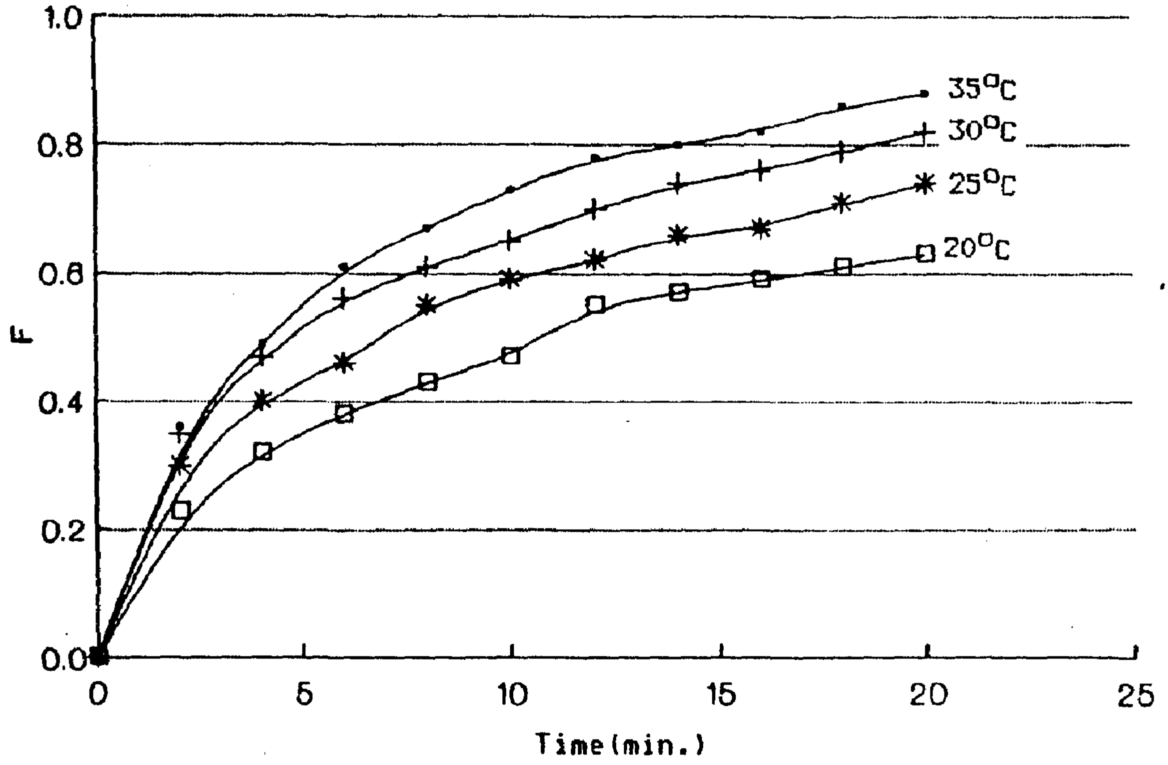


Fig. 6- Plots of F vs t for CTAB, at different temperatures and solution concentration 11 mg.l^{-1}.

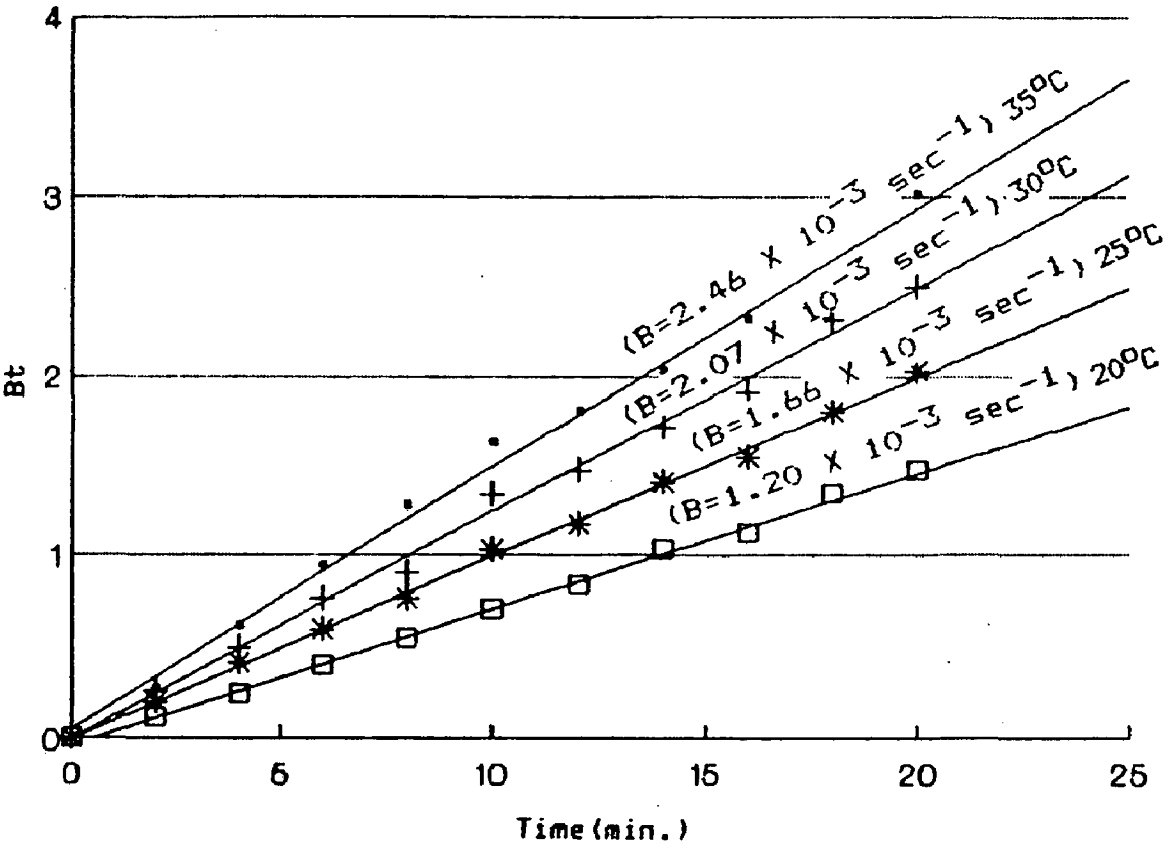


Fig. 7- Plots of Bt vs t for CPC, at different temperatures and solution concentration 11 $mg.l^{-1}$.

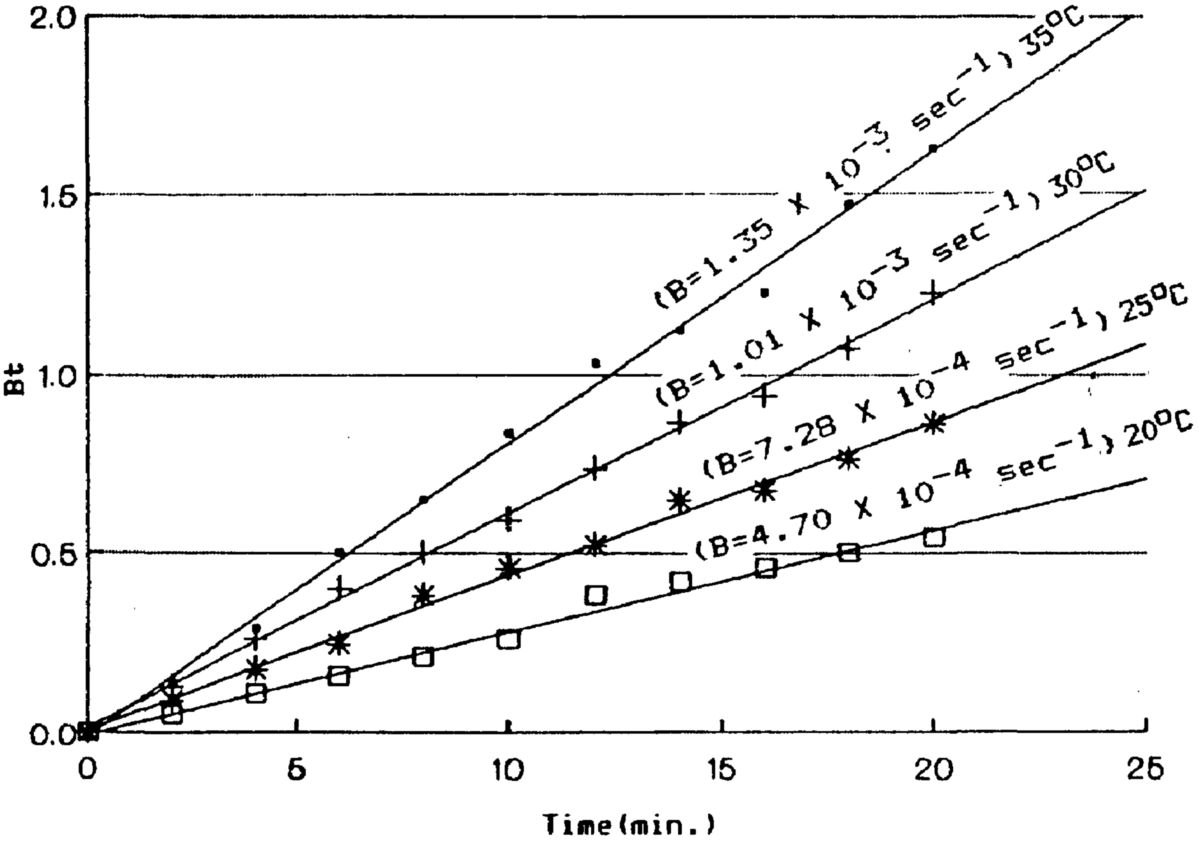


Fig. 8- Plots of Bt vs t for CTAB, at different temperatures and solution concentrations 11 $mg.l^{-1}$.

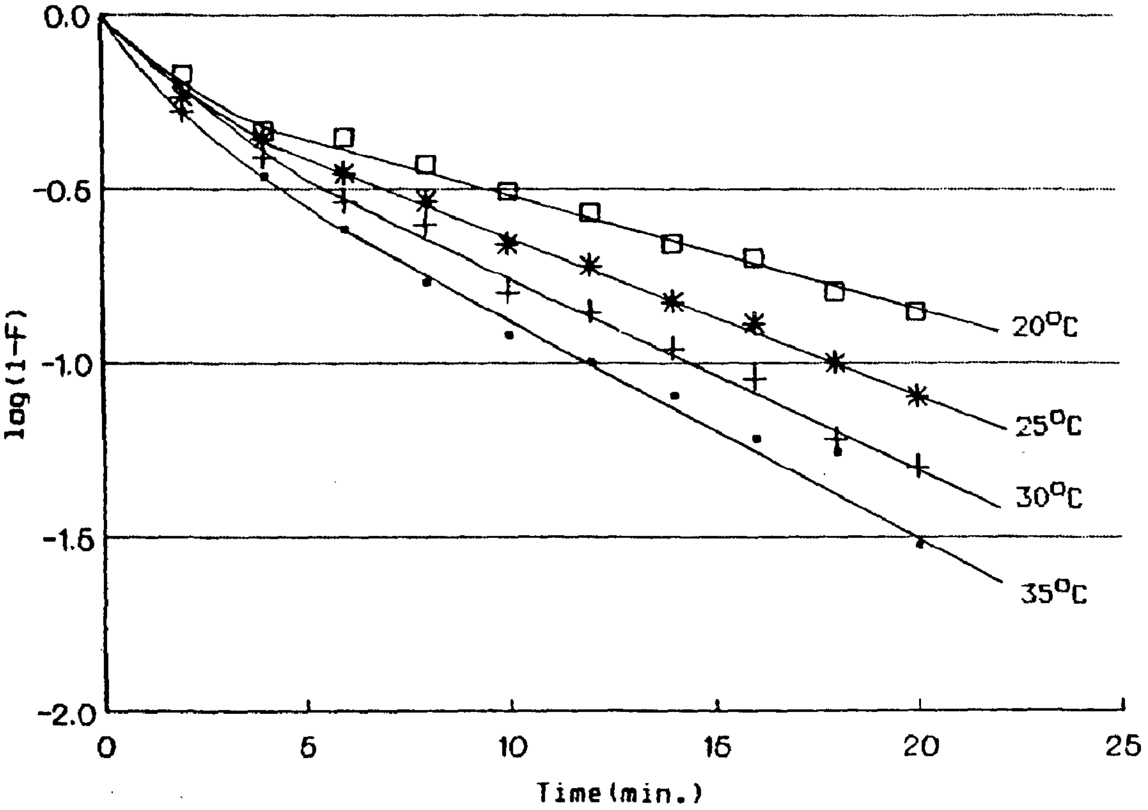


Fig. 9- McKay plots for the sorption of CPC.

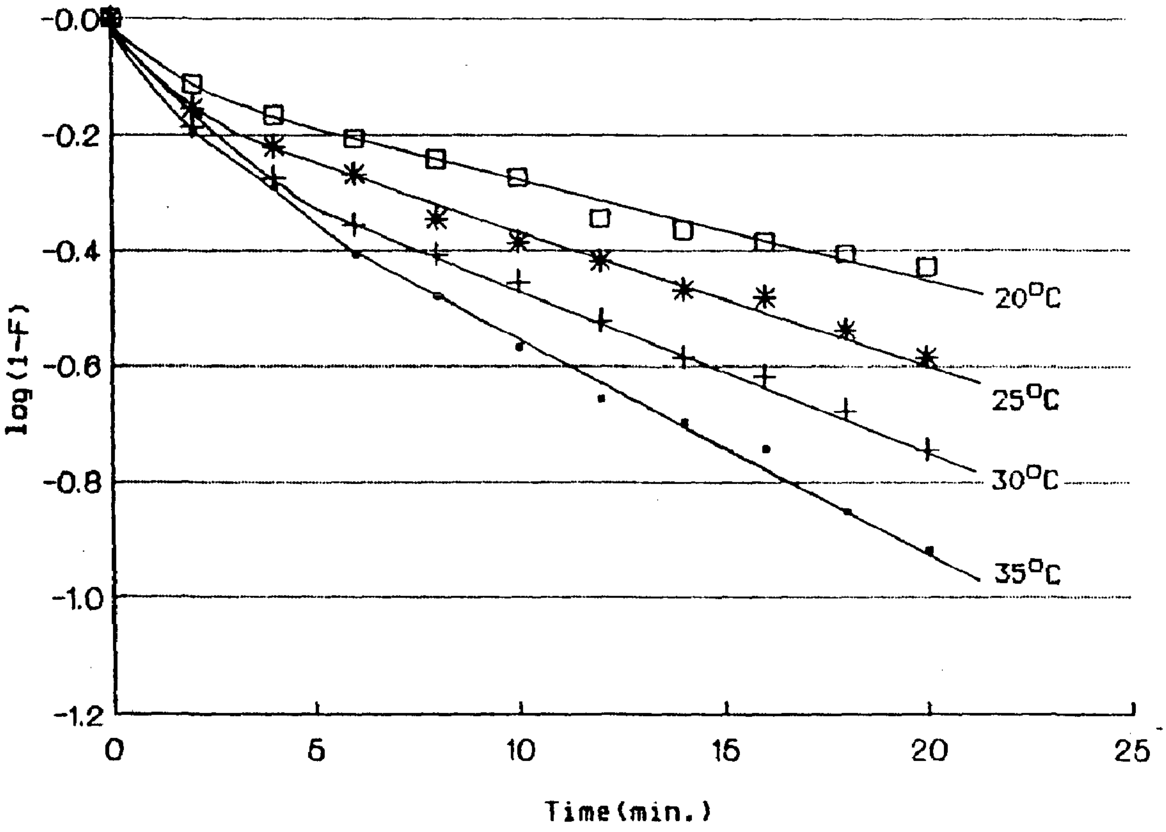


Fig. 10- McKay plots for the sorption of CTAB.

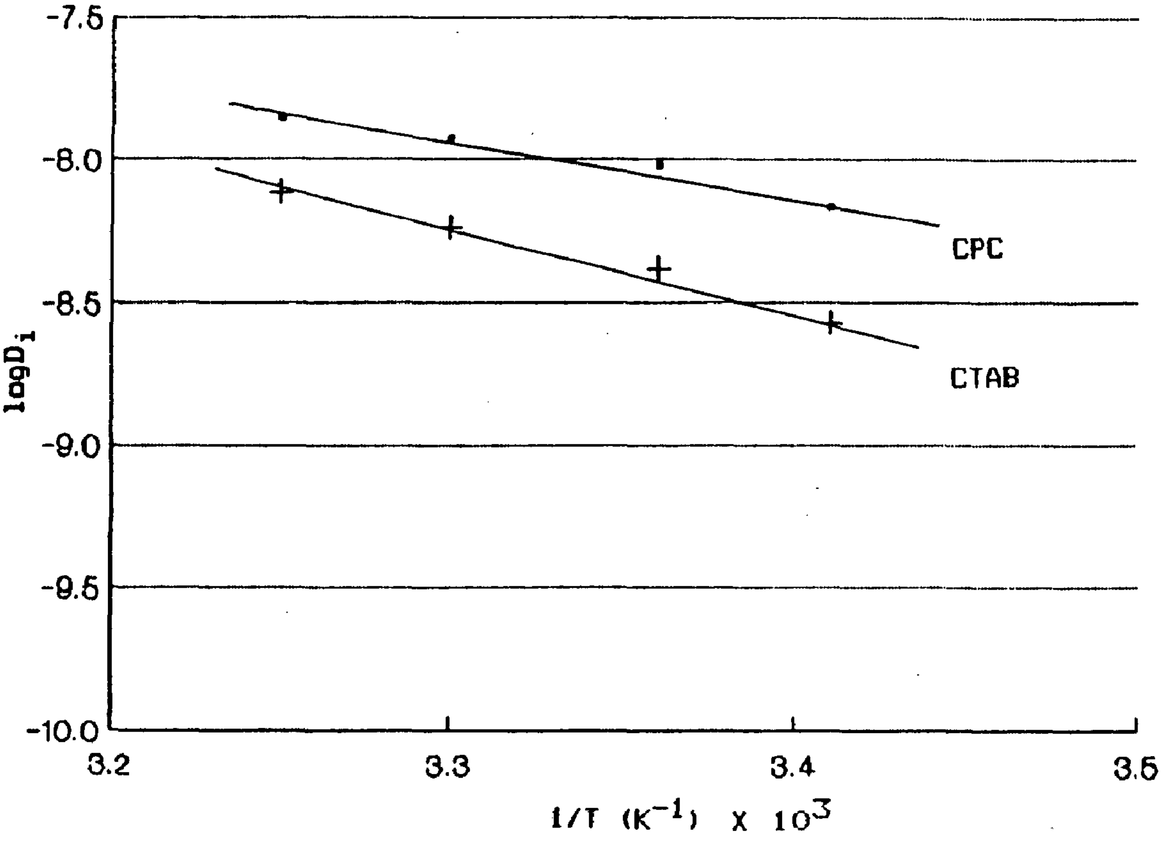


Fig. 11- Plots of log D_i vs 1/T for cationic surfactants.

4.24 Adsorption kinetics of nonionic surfactants

The kinetics of sorption of nonionic surfactants on lignin has been studied as a function of concentration (Figs. 12-15) and temperature (Figs. 16-19). The McKay plots [log(1-F) vs t] for the sorption of T20 and T40 have been shown in Figs 20 and 21. The linear plots drawn between $\log D_i$ and $1/T$ are depicted in Fig. 22. Tables 3 and 4 record the kinetic and thermodynamic parameters for the sorption.

Figs. 12 and 13 (F vs t plots) shows the effect of concentration of T20 and T40 on the extent of adsorption. These curves indicate a rapid initial adsorption and with a subsequent slow approach to equilibrium. The results suggest that ~~Like~~ cationic surfactants particle diffusion may be the rate controlling step in case of two nonionic surfactants also.

It is evident from Figs. 14 and 15 that Bt vs t plots are linear passing through origin and concentration independent at and above certain adsorbate concentration value. This shows the validity of Boyd's Equation (8) and Reichenberg's test (13) for particle diffusion controlled kinetics. The increase in sorption rate with increase in temperature (Figs. 16-19) further support that the sorption kinetics of the two nonionic surfactants (T20 and T40) is governed by the diffusion of adsorbing species inside the sorbate material (8). An indirect evidence in favour of/the particle diffusion mechanism also comes from the non linear nature of log(1-F) vs t plots (Figs 20 and 21). These plots reveal that sorption is neither controlled by film diffusion nor by mass action law (20,23).

The sorption of T20 and T40 is concentration independent and linear at and above 80 mg/l concentration however, at concentration of 40 mg/l the Bt vs t plots deviate from linear behaviour. This observation is indicative of the fact that the sorption kinetics is controlled by particle diffusion at 80 mg/l concentration and above and at lower concentrations some other processes like film diffusion also does influence the rate. The concentration of nonionic surfactants required for the particle diffusion controlled kinetics are more in comparison to cationic adsorbents. This is because of considerably higher rate (8,20) of sorption of cationic surfactants as compared to nonionic surfactants.

Figs. 16-19 show an increase in the sorption rate of nonionic surfactants with increase in temperature. The increased sorption rate at higher temperature is probably due to an increase in the mobility of sorbing species (14,18-20). It is evident from the F vs t plots (Figs 16 and 17) that in both the cases, the rate of uptake is rapid initially which slows down with time. This may be due to the tendency of surfactant molecule to get sorbed first at the easily available sites on the surfaces of sorbent resulting in a faster initial uptake. Similar behaviour has been observed for the sorption of cationic surfactants. Similar results have also been reported for the sorption of complex cations on chromium ferrocyanide gel (18,19). Heitner et al. (23), Rawat et al. (14) and others (16,17,20) have also observed similar behaviour for sorption of metals on sorbents.

The McKay plots for T20 and T40 are shown in Figs. 20 and 21 respectively. These plots are quite similar to the one obtained in case of cationic surfactants and comparable to those reported for independently decaying radioactive processes (27). The curves have been resolved (27) and it is found that analogous to CTAB and CPC the effective diffusion coefficient (D_i) values in the nonionic surfactants are also comparable of two components. The one corresponds to residual curve (faster component) and the later portion of the plot (lying on the straight line) corresponds to the slower component.

It is evident from Table 3 that the D_i values are higher for the sorption of T20 as compared to that of T40. This is because of restricted mobility of surfactant T40, in the sorbent material. Further D_i are less for nonionic surfactants in comparison to cationic surfactants which may be due to low capacity of nonionic surfactant to adsorb on lignin in comparison to that of cationic surfactant.

The linear behaviour of $\log D_i$ vs 1/T plots (Fig. 22) permits the use of expression 4 for evaluating the energy of activation and D_o values. The D_o in turn are used to evaluate the entropy of activation ΔS^* (Equation 5). The parameters D_o, E_a and ΔS^* are listed in Table 4. It can be concluded that the E_a values observed for the sorption of T40 is lesser as compared to those observed for the sorption of T20.

The values of entropy of activation for the non ionic surfactants (Table 4) are negative. A negative value of entropy of activation was also observed for the uptake of cationic surfactant CPC. The negative ΔS^* values indicate the lack of orientational effect upon the water environment of the nonionic species and their faster diffusion through the sorbent (36). It may also be inferred from negative values that the sorption of T20 and T40 does not cause any structural changes in the sorbent materials (16,17,20).

Hence, kinetic studies for the sorption of non ionic and cationic surfactants of lignin studied reveal that it can act as a good scavenger. The efficiency of it is better for cationic surfactants in comparison to nonionic.

Table-3

Effective diffusion coefficient (D_i) values for nonionic surfactants.

Temperature °C	$D_i \times 10^{10}$ ($cm^2.sec^{-1}$)	
	T20	T40
20	6.32	4.82
25	7.98	5.87
30	9.71	6.74
35	11.24	7.69

Table-4

D_o values and thermodynamic Parameters for nonionic surfactants.

Surfactants	$D_o \times 10^5$ ($cm^2.sec^{-1}$)	E_a ($Kcal.mole^{-1}$)	ΔS^* ($cal.deg^{-1}.mole^{-1}$)
T20	12.08	3.08	-11.48
T40	0.80	2.46	-16.89

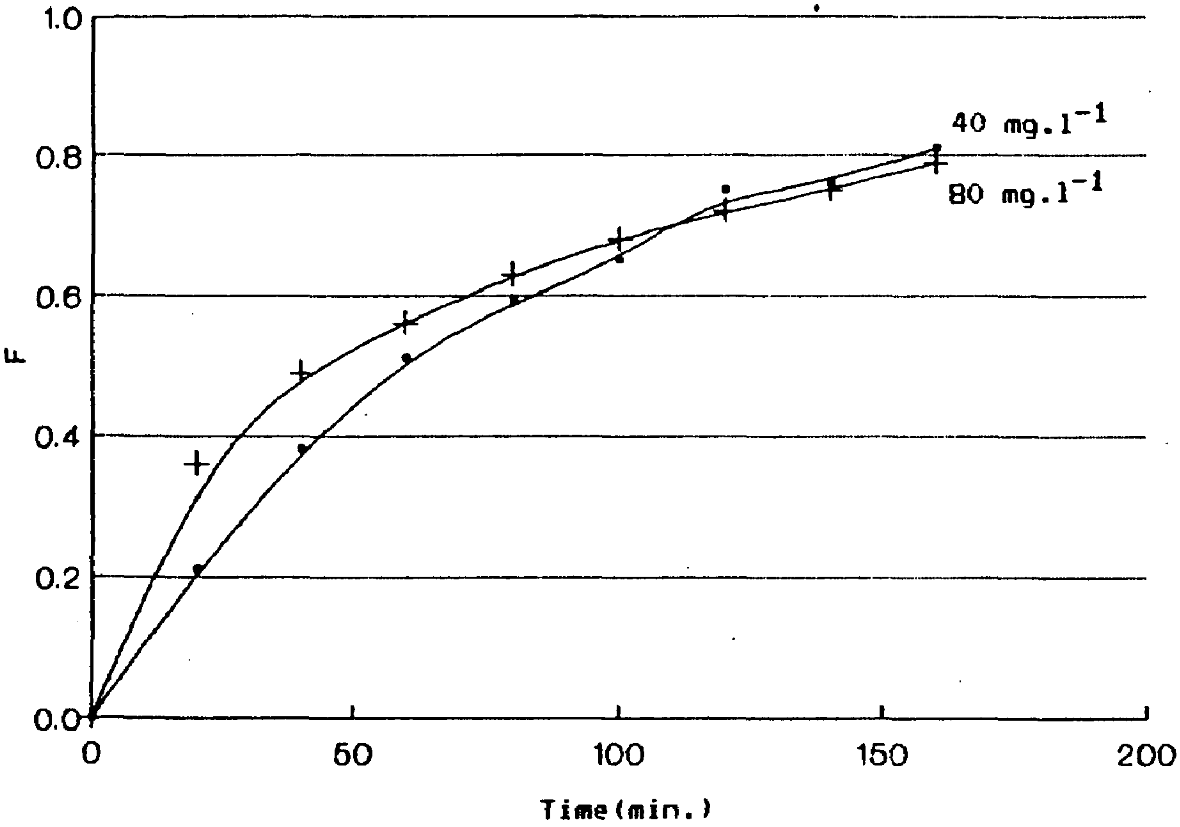


Fig. 12- Plots of F vs t for T20, using different solution concentrations.

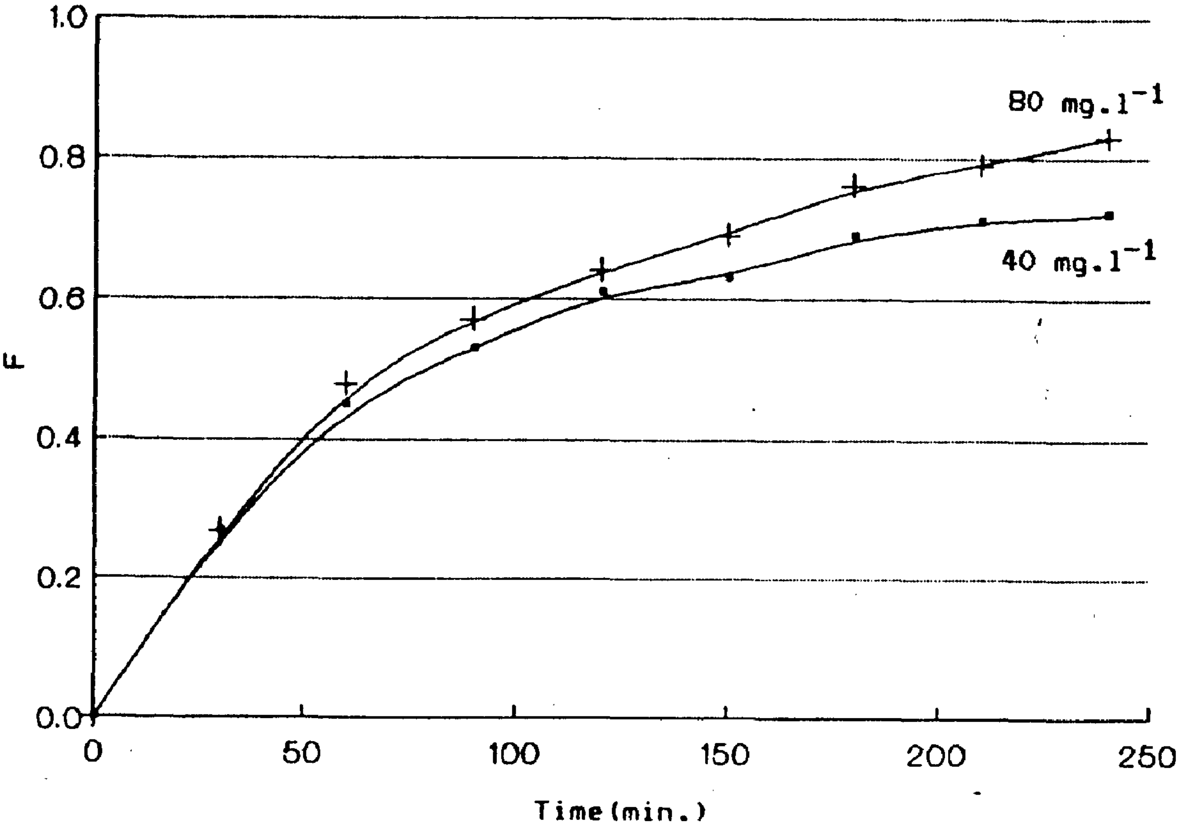


Fig. 13- Plots of F vs t for T40, using different solution concentrations.

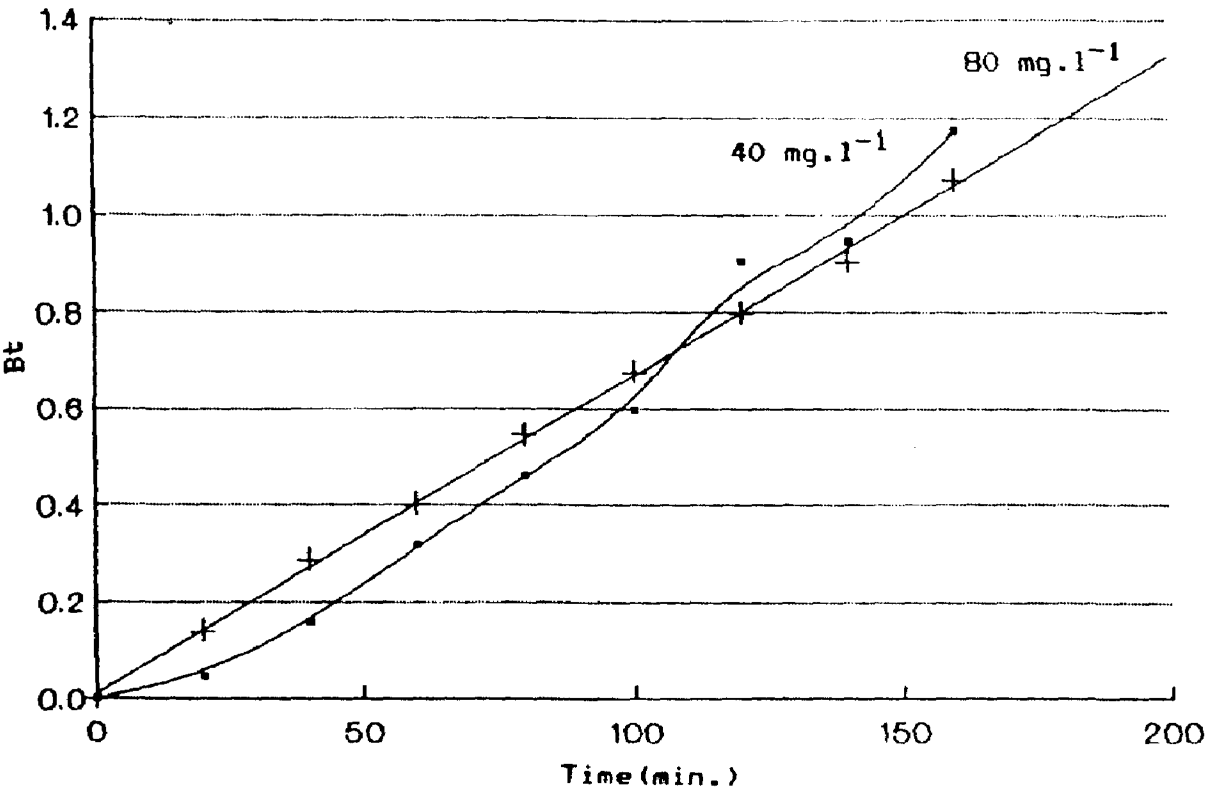


Fig. 14- Plots of Bt vs t for T20, using different solution concentrations.

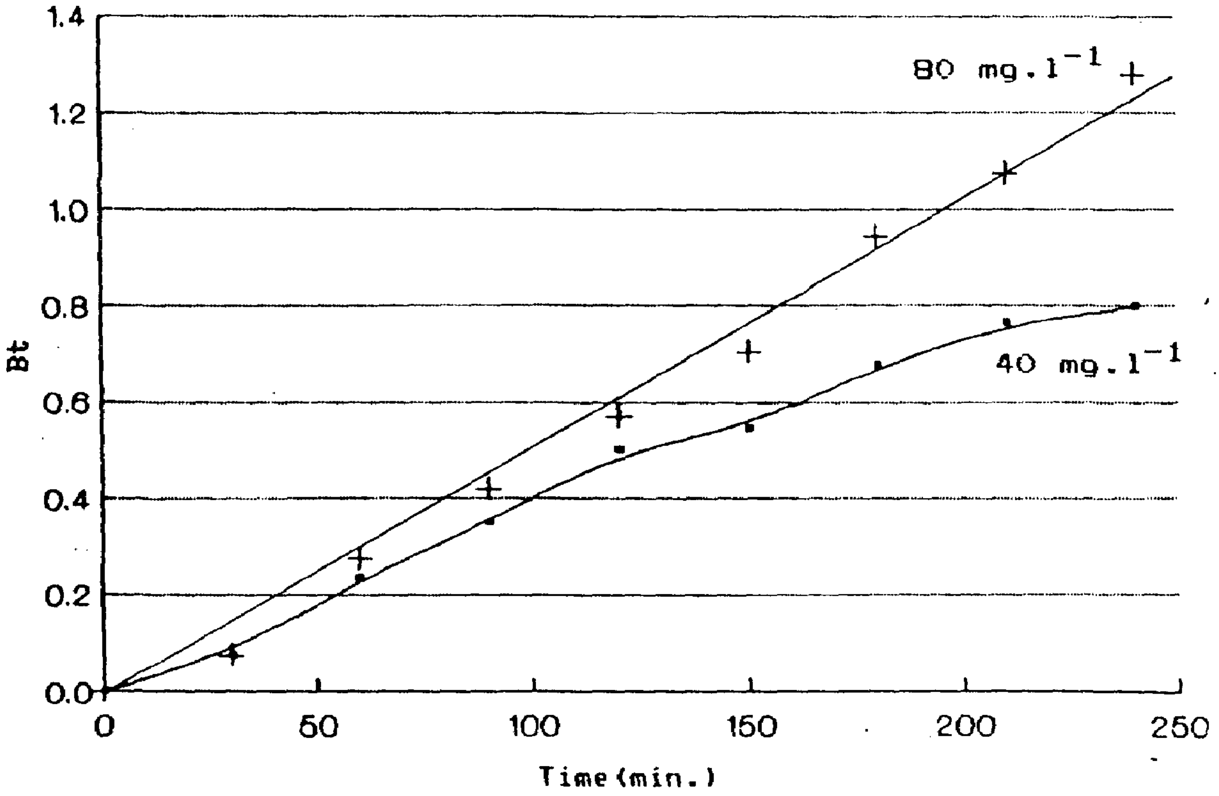


Fig. 15- Plots of Bt vs t for T40, using different solution concentrations.

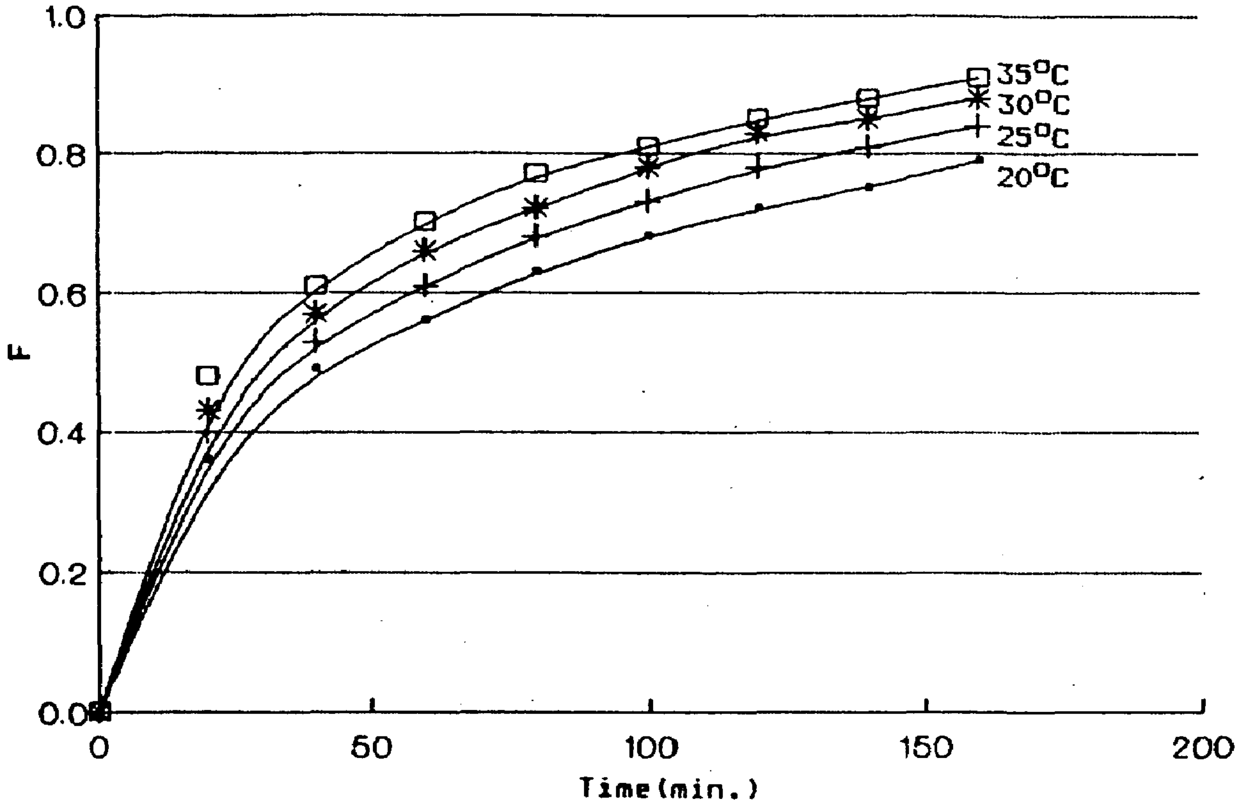


Fig. 16- Plots of F vs t for T20, at different temperatures and solution concentrations 80 mg.l^{-1}.

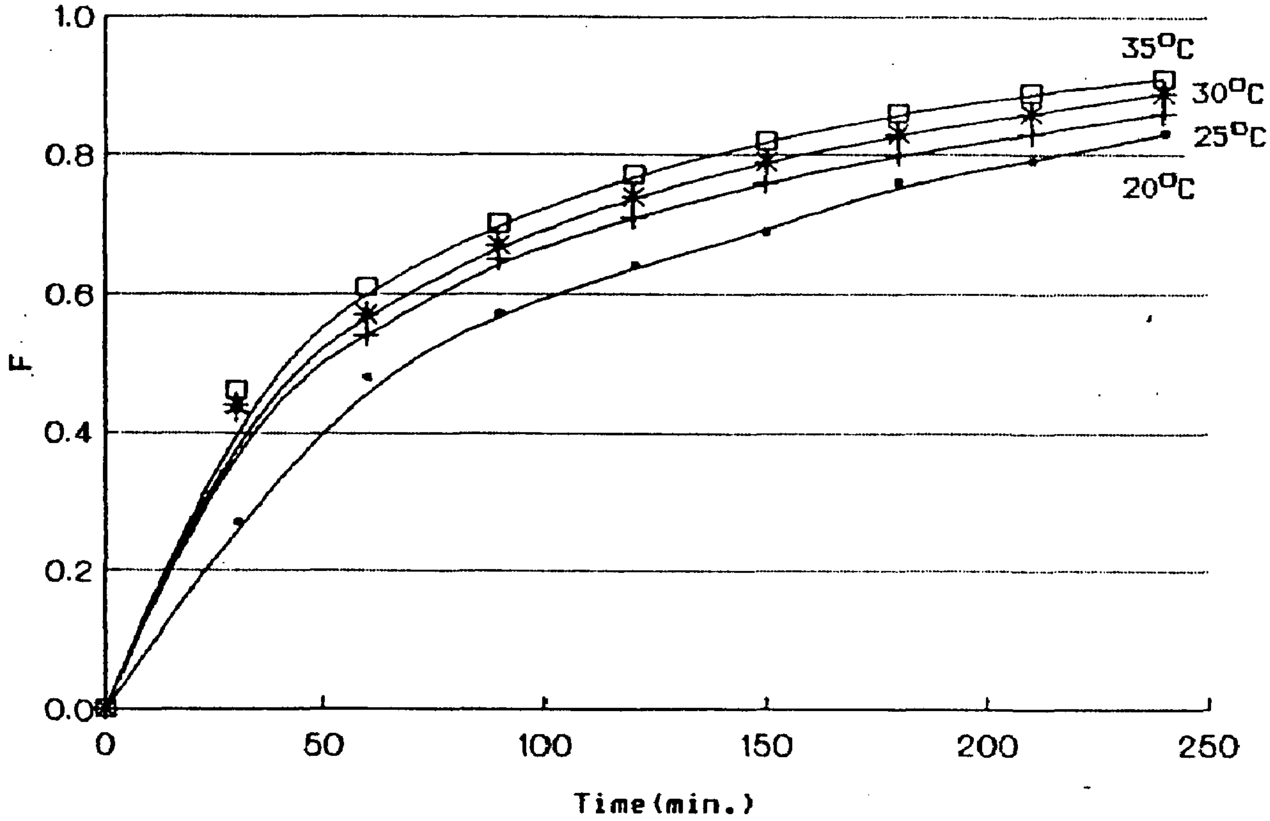


Fig. 17- Plots of F vs t for T40, at different temperatures and solution concentrations 80 mg.l^{-1}.

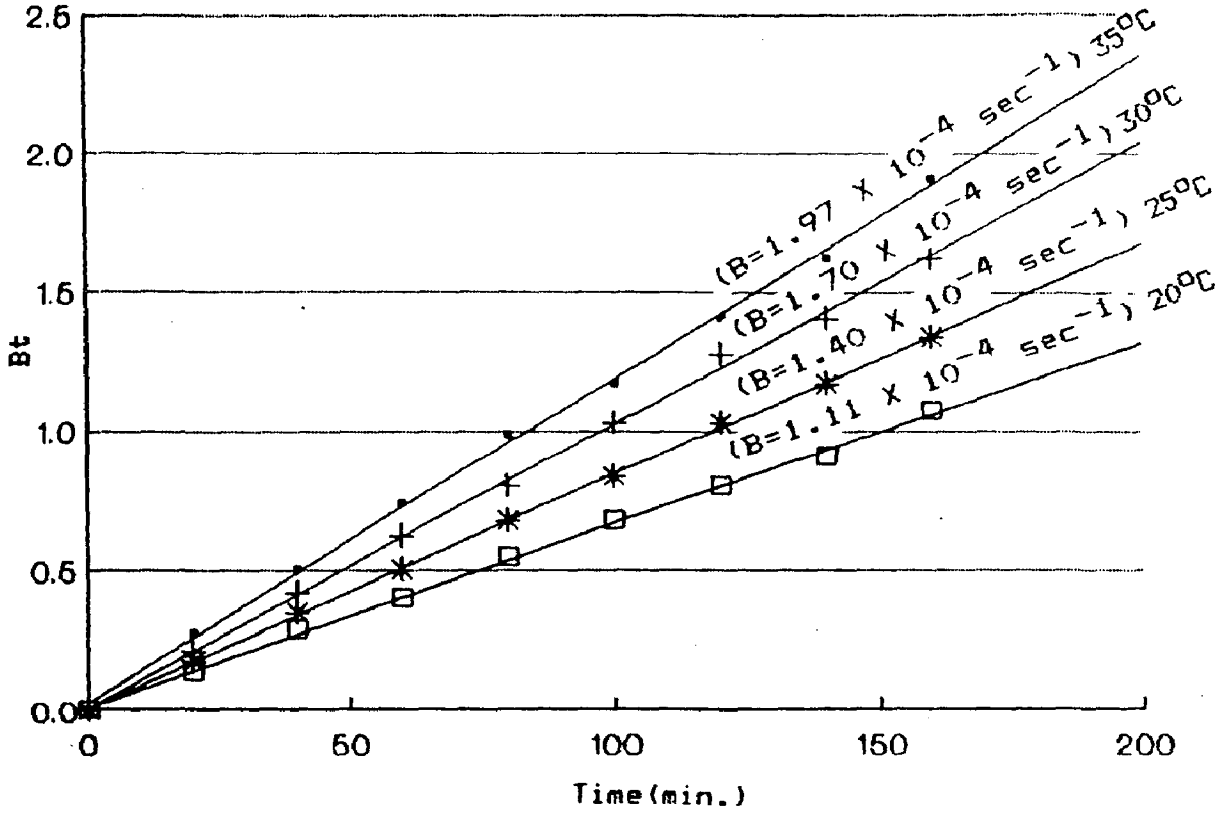


Fig. 18- Plots of Bt vs t for T20, at different temperatures and solution concentrations 80 mg.l^{-1}.

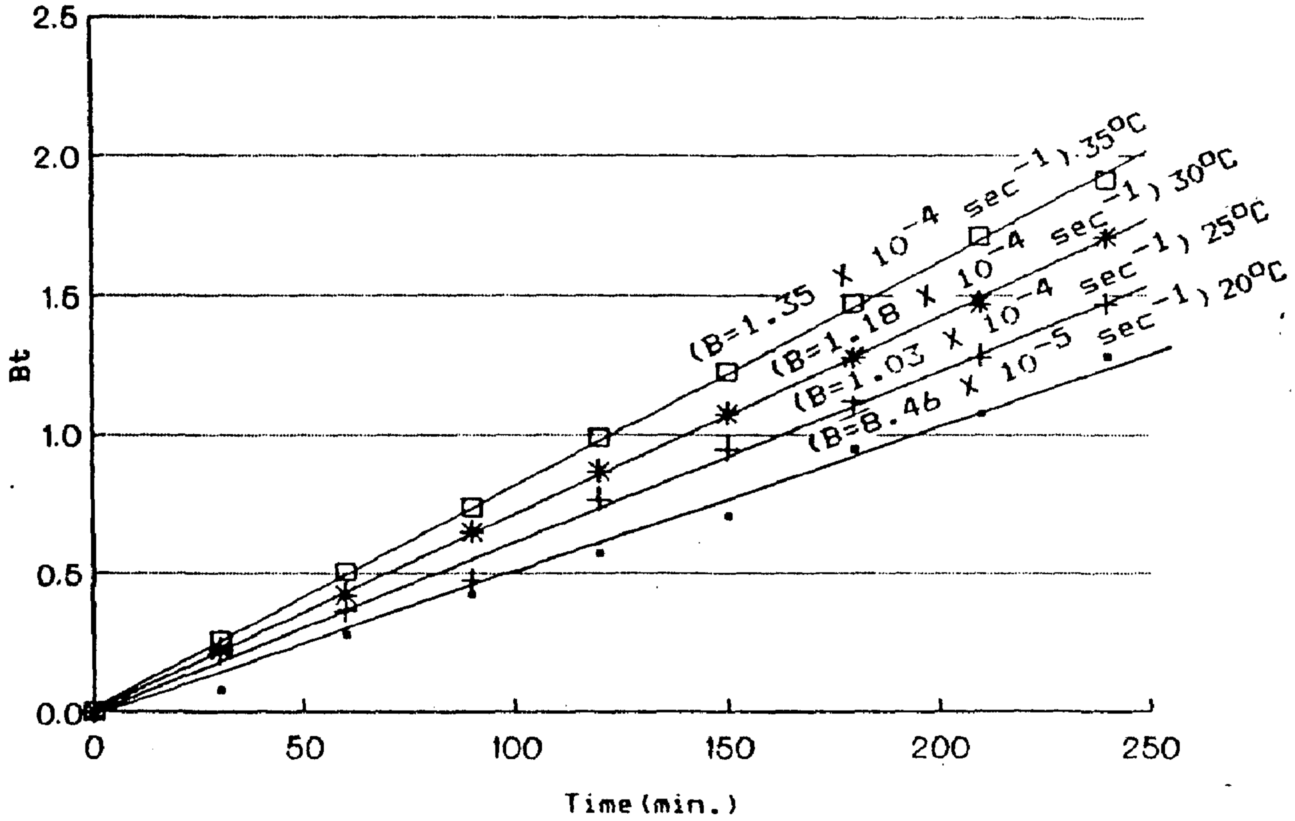


Fig. 19- Plots of Bt vs t for T40, at different temperatures and solution concentrations 80 mg.l^{-1}.

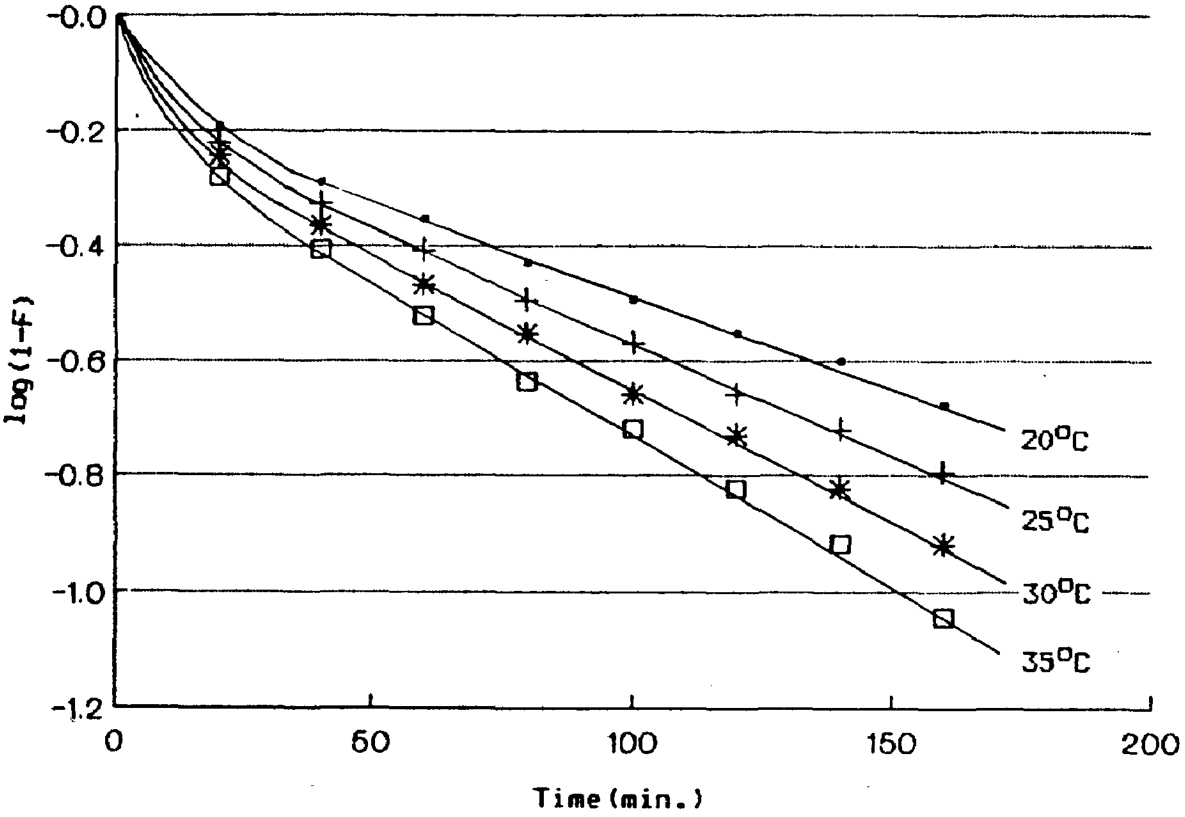


Fig. 20- McKay plots for the sorption of T20.

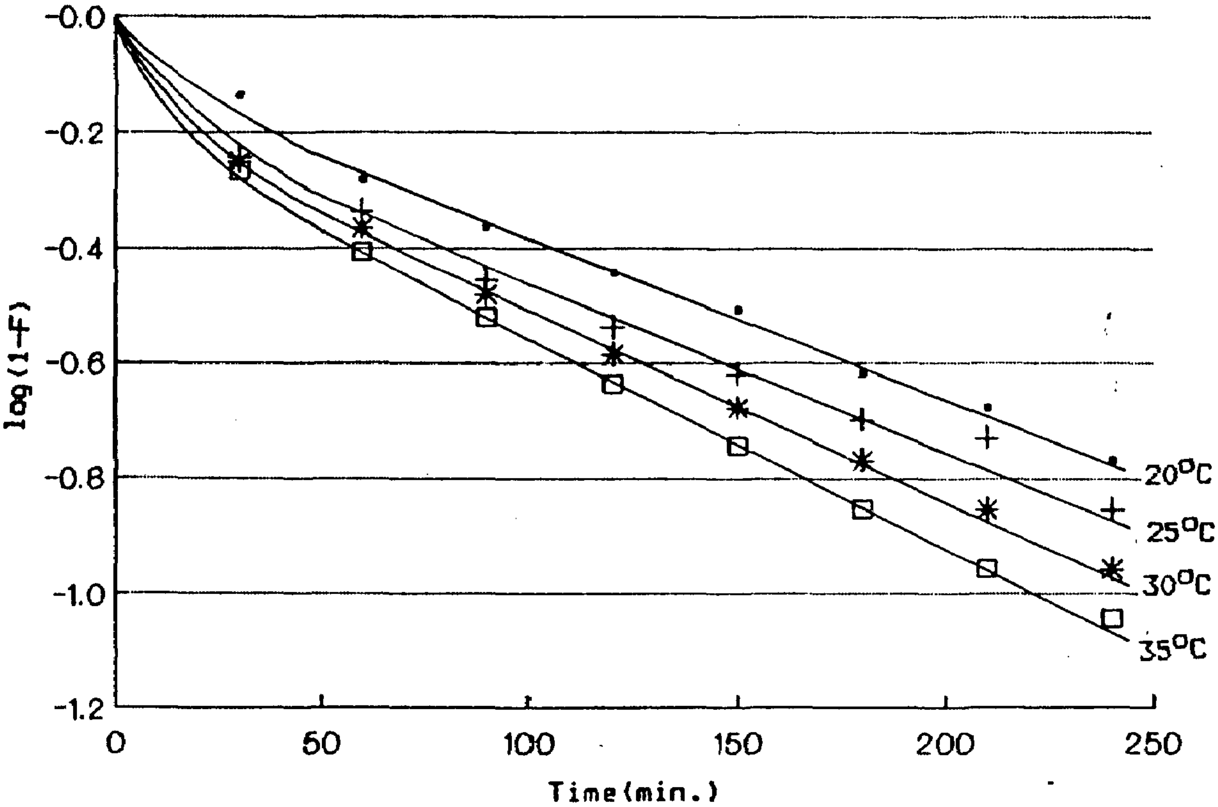


Fig. 21- McKay plots for the sorption of T40.

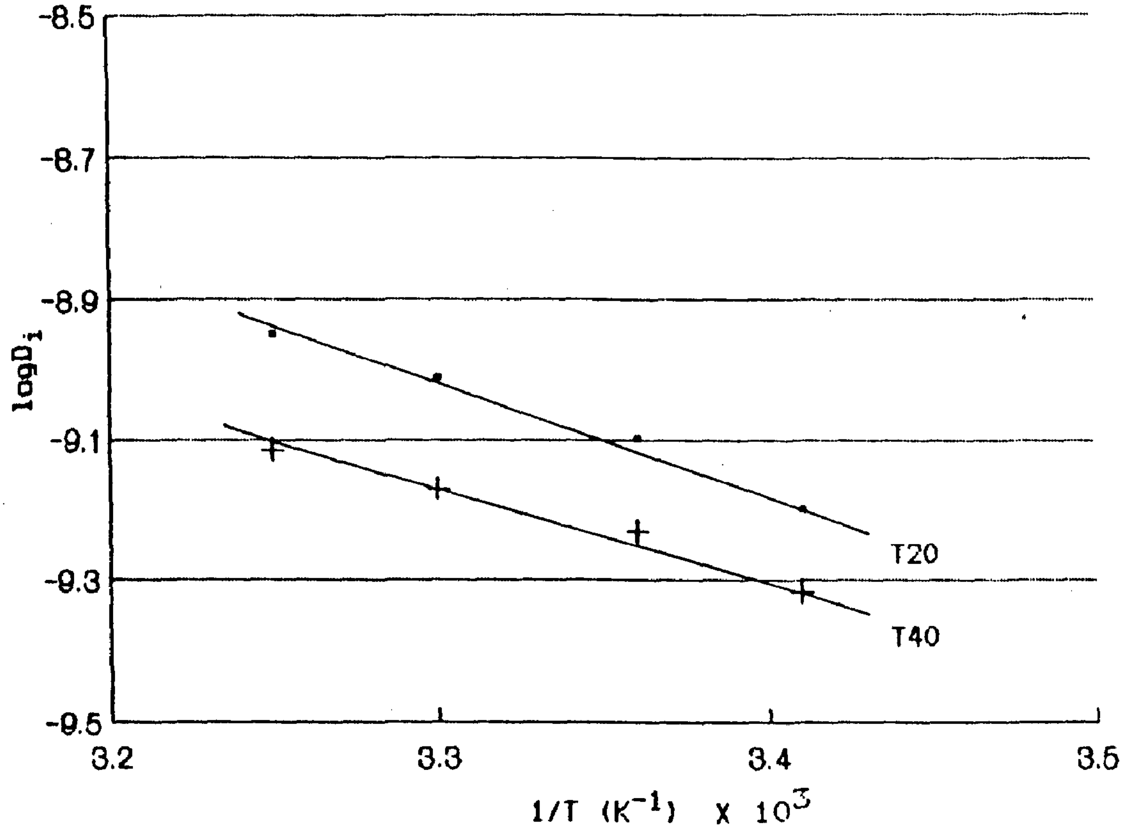


Fig. 22- Plots of log D_i vs 1/T for nonionic surfactants.

REFERENCES

1. J.R. Patton and J.B. Ferguson, Can. J. Rasearch, B15, 103 (1937).

2. F.C. Nachod and W. Wood, J. Am. Chem. Soc., 66, 1380 (1944).

3. F.C. Nachod and W. Wood, J. Am. Chem. Soc., 67, 629 (1945).

4. G.Schultze,Z. Physik. Chem.,89, 168 (1915).

5. F. Helfferich, "Ion Exchange",Mc'Graw-Hill, New York (1962).

6. W.J. Weber, Jr. and J.C. Morris, J. Sanitary Engg. Div., 89, 31 (1963).

7. J.S. Zogorski, S.D. Faust, and J.H. Haus, Jr., J. Coll. Int. Sci., 55, 329 (1976).

8. G. E. Boyd, A.W. Adamson, and L.S. Myers, Jr., J. Am. Chem. Soc., 69, 2836 (1947).

9. M. Nativ, S. Goldstein, and G. Schmuckler, J. Inorg. Nucl. Chem., 37, 1951 (1949).

10. J.C. Morris and W.J. Weber, Jr., U.S. Public Health Service Publication No. 999-WP-11 and No. 999-WP-9 (1964).

11. T.R.E. Kressman and J.R. Kitchener, Discuss. Faraday Soc., 7, 90 (1949).

12. S. Smith, B. Hiltgen, and A. Juhola, J. Chem. Engg. Progr. Symp. Ser., 55 (24), 25 (1959).

13. D. Reichenberg, J. Am. Chem. Soc., 75, 589 (1953).

14. J.P. Rawat and P.S. Thind, J. Phys. Chem., 80, 1384 (1976).

15. J.P. Rawat and D.K. Singh, J. Inorg. Nucl. Chem., 40, 897 (1978).

16. J. Mathew and S.N. Tandon, Can.J. Chem., 55, 3857 (1977).

17. J. Mathew, N.J. Singh, C.B. Gupta and S.N. Tandon, India J. Chem., 16A, 524 (1978).

18. I.P. Saraswat, S.K. Srivastava, and A.K. Sharma, Can. J. Chem., 57, 1214 (1979).

19. A.K. Sharma, Ph.d. Thesis, University of Roorkee, Roorkee, India (1979).

20. I.P. Saraswat, S.K. Srivastava, and A.K. Sharma, J. Inorg. Nucl. Chem., 43, 1653 (1981).

21. A.Dyer and J.M. Fawcett, J. Inorg. Nucl. Chem., 28, 615 (1966).

22. H. McKay, Nature (London), 142, 997 (1938).

23. C. Heitner - Wirguin and G. Markovits, J. Phys. Chem., 67, 2263 (1963).

24. G.H. Nancollas and R. Paterson, J. Inorg. Nucl. Chem., 22, 259 (1961).

25. C.B. Amphlett, L.A. McDonald, and M.J. Redman, J. Inorg. Nucl. Chem., 6, 220 (1958).

26. C.B. Amphlett, L.A. McDonald, and M.J. Redman, J. Inorg. Nucl. Chem., 6, 236 (1958).

27. G. Friedlander and J.W. Kennedy, 'Nuclear and Radiochemistry', John Wiley and Sons, Inc., New York, pp. 128-129 (1956).

28. R. Schlogl and F. Helfferich, J. Chem. Phys., 26, 5 (1957).

29. F. Helfferich and M.S. Plesset, J. Chem. Phys., 28, 418 (1958).

30. M.S. Plesset, F. Helfferich, and J. N. Franklin, J. Chem. Phys., 29, 1064 (1958).

31. F. Helfferich, J. Phys. Chem., 66, 39 (1962).

32. R.M. Barrer and J.D. Falconer, Proc. Roy. Soc. (London), A236, 227 (1956).

33. R.M. Barrer and L.V.C. Rees, Trans. Faraday Soc., 56, 709 (1960).

34. D.C. Freeman, Jr., and D.N. Stamires, J. Chem. Phys. 35, 799 (1961).

35. M. Kaisheva et al., Elektro Khimiya, 21(6) 832-6 (Russ) (1985).

36. V. Pekarek and V. Vesely, Talanta Review, 19, p. 1266 (1972).