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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
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SOME PHYSICO-CHEMICAL ASPECTS OF THE USE OF WETTING AGENTS IN FIREFIGHTING

1. THE LOSS OF WETTING AGENT BY ADSORPTION ON SOLIDS

by

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SUMMARY

A study has been made of the adsorption of wetting
agents on solids in relation to the use of these agents
in firefighting.   Wetting agents are adsorbed to an
extent that differs widely for different solids and agents.
The adsorption depends in a complex way on the concen-
tration of agent in solution, and in a way that may differ
somewhat for different agents;   adsorption appears to be
partly specific.

The adsorption isotherms have been used to calculate
the relative loss of agent in solutions of different agents
penetrating a porous solid.   With supplementary data on
wetting power, this calculation might be used to select the
most economical agent for a given application.   But the
selection of a wetting agent in this way would be a lengthy
procedure that would be justified only if no other method
were available.

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It is a matter of common experience that when water is applied to a solid it either forms a continuous film on the surface and penetrates any interstices or it rests on the surface in the form of drops. For practical purposes it may be said that in the former case water wets the solid, and in the latter case it does not do so. Occasionally a solid which is not wetted on the first application of water may become wetted after prolonged contact with water.

Wetting agents are substances which, when added to water, have the property of promoting the rapid wetting of solids which are either not wetted (in the sense described above) by water alone or are wetted only after prolonged contact. They belong to the general class of surface-active agents, each member of which may possess wetting, detergent, and emulsifying properties in varying degrees.

On the basis of their known properties, wetting agents have been used in firefighting - notably in the United States. There have been comparatively few controlled tests of fire extinction with water to which wetting agents have been added (known as "wet water"). The tests that have been carried out will be reviewed in detail elsewhere; here it may be said that the available results suggest that there are indeed situations in firefighting where wetting agents may be used with advantage, but such situations are less common than was originally supposed. Examples of possible worthwhile uses of wet water are the extinction of deep-seated fires in bales of fibrous materials such as cotton, or in granular materials such as sawdust, and for preventing the spread of fire in undergrowth. In all these examples the essential requirement is the efficient wetting of solid material with a high specific surface.

Further fire extinction tests are required before the value of wetting agents for firefighting can be more definitely assessed. Preparatory to carrying out these tests a laboratory study has been made of physico-chemical factors relating to the choice of a suitable type and concentration of agent for use.

The characteristic property of wetting agents depends on the fact that they are strongly adsorbed from solution both at the surface of the solution and at the wetted surface. Hence, one of the factors that will determine the initial concentration of agent used will be the provision of an adequate reserve in solution to make good the loss by adsorption as the water penetrates a mass of solid material; this requirement will be especially important where the solid has a high specific surface. At the same time there is not necessarily any direct relationship between the extent of adsorption of a wetting agent and its efficiency as such.

Measurements have been made of the adsorption of a series of wetting agents on a number of solid materials and are described in this report. The second report of this series will deal with the measurement of the relative wetting efficiency of wetting agents.

MEASUREMENT OF THE ADSORPTION OF WETTING AGENTS FROM SOLUTION

INTRODUCTION

Published studies of the adsorption of surface-active agents from solution have been concerned largely with adsorption on textile fibres in relation to detergency and dyeing. Neville and Jhanson[1] pointed out that the rate of depletion of wetting agent solutions was an important factor in the economics of the use of these agents. The loss in wetting power of a wetting agent solution, that accompanies such depletion is made evident in a quantitative manner by a corresponding increase in sinking time of the cotton skein in the Draves test.[2,3]

Harris [4] has reduced earlier adsorption measurements to a common basis from which it appears that some cationic agents and anionic agents (including soaps) may be adsorbed on cotton and certain other cellulosic fibres in amounts which vary between 0.3 and 2.0% of the dry weight of the fibre. In neutral solution of an anionic agent, sodium secondary alkyl sulphate, wool can adsorb roughly three times as much of the agent as cotton under similar conditions [5].

Recent determinations by Weatherburn and Bayley [6] of the adsorption of surface-active agents on a number of natural and artificial fibres showed that, of the agents tested in neutral solution, cationic agents were adsorbed to the greatest extent and non-ionic agents were adsorbed the least; anionic agents occupied an intermediate position. Wide variations occurred in the amount of adsorption on different fibres, and the arrangement of fibres in order of increasing adsorption varied with the type of agent and, occasionally, also between agents of a given type.

The adsorption of surface-active agents on fibres has been shown to depend on the hydrogen ion concentration of the solution [5-9]. As the reaction of the solution is changed from acid to alkaline the adsorption of anionic agents decreases and that of cationic agents increases. The adsorption of non-ionic agents has been found by Weatherburn and Bayley [6] to change with pH in the same direction as for anionic agents on both wool and cellulosic fibres, although Le Compte and Creeley [7] had previously found the adsorption of these agents on wool to be almost independent of pH.

Aickin [5] found that adsorption of a secondary alkyl sulphate on wool required forty-eight hours to reach a stationary value, in contrast to the time of less than thirty minutes required for the adsorption of this agent on cotton fibre; a large proportion of the agent adsorbed on the wool appeared to be held irreversibly. For the adsorption of an alkyl benzene sulphonate on cotton cloth Meader and Fries[10] found that equilibrium was reached in four hours and that the rates of desorption were comparable with the rates of adsorption, although 2 per cent of the adsorbed agent remained at the end of forty-eight hours.

The adsorption isotherms that have been published [5,6,10,11] show that the adsorption of surface active agents is by no means a simple function of the concentration of agent in solution, and it undergoes changes which appear to be associated with the formation of micelles in solutions above certain concentrations. There is so far no general agreement on the detailed explanation of the adsorption behaviour.

Comparison of the adsorption of different agents on a given adsorbent can best be made at equilibrium concentrations. In view of the complex variation of adsorption with concentration it is preferable that the agents should be compared, initially at least, over the whole range of concentrations at which they are likely to be used. In the following work the adsorption has been determined as a function of concentration for a series of different wetting agents on a pure substance, cellulose. A more limited comparison has then been made of the adsorption on a number of materials likely to be involved in fires for the extinction of which wetting agents might be used with advantage.

EXPERIMENTAL

(i) General

The wetting agents used were commercial preparations and are listed in Table I according to the manufacturers' general description of the principal surface-active constituent, and the adsorbents used are listed in Table II.

TABLE I

Wetting agents

Letter	Ionic type	Chemical type	State
A	Anionic	Sodium higher alkyl sulphates	Aqueous solution
B	"	Sodium salt of highly sulphated oil	Aqueous solution
C	"	Sodium salt of alkyl naphthalene sulphonic acid	Solid
D	Cationic	Cetyl trimethylammonium bromide	Aqueous solution
E	Non-ionic	Alkyl-phenyl substituted polyethylene glycol	Aqueous solution

TABLE II

Adsorbents

Adsorbent	Particle size (sieve)	Moisture content %
Cellulose wadding B.P.C.		7.1
Powdered cork	Passing 25 B.S.	7.3
Elm sawdust	Passing 12 B.S.	10.9
Granulated peat (Scottish)	Passing 12 B.S.	16.0

Adsorption isotherms for cellulose were obtained by shaking known weights of cellulose with known volumes of wetting agent solutions of different initial concentrations. The amount of wetting agent adsorbed, and which was in equilibrium with the final concentration in solution, was calculated from the difference between the initial and final concentrations of the wetting agents in solution as determined by the analytical procedures given below. Preliminary tests showed that equilibrium was approached to within the limits of experimental error in one hour for agents A and B, two hours for agents C and D, and three quarters of an hour for agent E. The adsorbent was removed by filtration before determination of the final concentration of wetting agent in solution. All adsorption determinations were carried out at a temperature of $20^{\circ}C$.

Usually two, and sometimes four, determinations were made of the adsorption of agents A, B, and C on the cellulose. Individual values differed from the mean of a set by from one to ten per cent of the mean in most cases. An exceptionally large variability occurred in the determinations of the adsorption of agent C at a concentration of about 2 per cent; thus in the four determinations that were made the extremes differed from the mean by as much as 50 per cent. Only one determination of adsorption was made for agent E at each concentration.

Two samples of cellulose were used. A comparison showed that the adsorption of agent B on sample 2 was 11 per cent greater than the adsorption of this agent on sample 1 at equal equilibrium concentrations. This observation was interpreted as a corresponding difference in specific surface of the two samples. Adsorption measurements of agents A and C on sample 2 were accordingly multiplied by the factor 0.91 for comparison with the adsorption of agents B and E as determined on sample 1.

The adsorption of the wetting agents on powdered cork, elm sawdust, and granulated peat was compared by determining, in duplicate, the adsorption from solutions of given initial concentration. The times allowed for adsorption were the same as for each agent on cellulose. This practice was shown to be adequate for agent B to reach equilibrium on cork but was subsequently found to be inadequate for the establishment of equilibrium of agent C on cork and on elm sawdust; an increase in the adsorption time from two to three hours resulted in a 50 per cent increase in the amount of agent C adsorbed on cork and a 20 per cent increase on elm.

In order to provide a basis of comparison between our results and the results obtained by others on the adsorption of wetting agents the surface-tension/concentration relationship was determined for solutions of each wetting agent in distilled water. Surface tensions were measured by the ring method, using a du Nouy tensiometer, at a temperature of approximately 20°C.

(ii) Analytical procedures

Anionic agents. The concentration of the anionic wetting agent was determined by the method of Barr, Oliver, and Stubbings [12] in which the anionic agent is titrated against a cationic agent in the presence of bromophenol blue over a layer of chloroform. The cationic agent used was cetyl trimethylammonium bromide at the recommended concentration of approximately M/1000; the anionic agents were diluted by a known amount to approximately 0.1 per cent for titration.

It had been found previously that an aqueous extract of cork caused an increase of about 2 per cent in the titre of agent B against the cationic agent cetyl pyridinium bromide. Therefore, all initial titrations in the determination of adsorption by cork, elm sawdust, and peat were carried out in the presence of aqueous extracts of these materials at the same nominal concentration as in the final titrations. It was, however, evident from the darker colour of the extract obtained in the presence of wetting agent that there was always, in practice, some difference in either the amount or nature of the extract present in the initial and final titrations.

Solutions of agents A and B showed an ageing effect when freshly prepared. This effect is described in an appendix to this Report. For practical purposes it is the stable aged solutions that are of interest. Adsorption measurements were always carried out with solutions which had been fully aged (usually overnight), and calculations of adsorption were based on the nominal initial concentration of the agents without regard to the ageing.

Cationic Agents. Unknown concentrations of the cationic agent, cetyl trimethylammonium bromide, were determined by back-titration against a standard solution of the agent after adding a known excess of a solution of the anionic agent C previously standardised against the cationic agent.

Non-ionic agent. The concentration of the non-ionic agent E was determined by a gravimetric method, due to Oliver and Preston [13], which depends on the formation of an insoluble compound with phosphomolybdic acid in the presence of barium chloride and hydrochloric acid.

RESULTS AND DISCUSSION

(i) Adsorption on cellulose

The weight of wetting agent adsorbed per unit weight of cellulose is shown in Fig. 1 as a function of the equilibrium concentration in solution for the agents A, B, C and E. The adsorption is expressed as milligrams of the technical preparation of an agent adsorbed per gram of dry cellulose (dried at 105°C), and the concentration in solution is expressed as percentage by weight of the preparation in solution.

The ranges of concentration in which the surface tension of solutions of the agents rapidly became independent of the concentration are shown in Fig. 1. It is generally accepted that these concentration ranges are those in which the formation of micelles, or aggregates of molecules of surface-active agents, becomes appreciable in the solution; for a pure substance this concentration range is usually narrow and it is possible to identify a "critical micelle concentration".

It will be seen (Fig. 1) that for the anionic agents A and C, and the non-ionic agent E, the adsorption increases to a maximum, as the concentration is increased from low values, and then decreases. In common with the adsorption behaviour of other agents for which isotherms have been published [5], [6], [10], [11], the increase of adsorption with concentration occurs mainly at concentrations below the range for micelle formation. More variable behaviour is in general apparent at higher concentrations. Thus, although adsorption maxima appear in the isotherms for agents A, C, and E in Fig. 1, Weatherburn and Bayley [6] found that the adsorption of a non-ionic agent on cotton, and an anionic agent on cotton and acetate rayon, increased to stationary values that were independent of the concentration in solution. Again, in the adsorption of an alkyl benzene sulphonate on cotton cloth studied by Meader and Fries [10], the amount adsorbed increases to a maximum then, as the concentration in solution is increased further, the adsorption falls to a minimum followed by a slow increase; a similar behaviour is evident in the adsorption of a secondary alkyl sulphate on wool [5].

The isotherm for the anionic agent B (Fig. 1) shows an almost linear increase of adsorption for a range of concentration in solution of approximately 0.1 - 5.0 per cent, while micelle formation for this agent begins in the concentration range 0.1 to 0.2 per cent; the behaviour of this agent is quite different from that of all others so far reported.

(ii) Adsorption on other solids

The results of measurements of the adsorption of agents A, B, C, and D on powdered cork, elm sawdust, and granulated peat, and of the adsorption of agent D on cellulose, are given in Table III for solutions of different initial concentrations. Except for the adsorption of agent B on cork the values given in the Table do not necessarily represent equilibrium conditions. Each value is the mean of two determinations.

TABLE III

Adsorption of wetting agents from solution by solids. (Milligrams of agent per gram of dry solid)

Agent	Initial concentration %	Time hours	Cellulose (Sample 2)	Powdered cork	Elm sawdust	Granulated Peat
A	0.8 $^V/v$	1	–	50 (0.62)*	30 (0.70)	70 (0.58)
	1.3 "	1	–	58 (1.10)	40 (1.16)	75 (1.06)
B	0.8 $^V/v$	1	–	26 (0.71)	32 (0.69)	48 (0.65)
	1.3 "	1	–	51 (1.12)	55 (1.11)	72 (1.07)
C	0.8 $^W/w$	2	–	28 (0.70)	35 (0.68)	55 (0.62)
	1.3 "	2	–	39 (1.15)	54 (1.11)	59 (1.10)
D	0.8 $^V/v$	2	44 (0.60)	–	130 (0.32)	–
	1.3 "	2	45 (1.12)	98 (0.94)	–	–
	1.5 "	2	–	103 (1.12)	127 (1.04)	183 (0.89)
	1.8 "	2	–	–	–	202 (1.15)

* Figures in brackets are the final concentrations of the solutions

It will be seen from Table III that after one hour, with a solution of given initial concentration, the adsorption of agent A on the elm sawdust is less than that of B; but, under the same conditions, the adsorption of A on both the cork and peat is greater than that of B. Also, for different agents, the adsorbing solids are arranged in different order of increasing amounts adsorbed in a fixed time: this order is elm, cork, peat for the adsorption of agent A, and cork, elm, peat, for the adsorption of agents B and C. These results indicate that the amount of adsorption for a given agent/solid pair is governed, at least partly, by an effect that is specific for each pair. The same observation has been made by Weatherburn and Bayley [6] for certain textile fibres.

(iii) Application of results

It has been pointed out in the General Introduction that, as a solution of a wetting agent penetrates a porous solid the concentration of the agent in the advancing front of the solution will be progressively decreased by adsorption of the agent on the solid. The isotherms in Fig. 1 can be used to estimate the relative decrease in concentration as solutions of the agents A, B, C and E penetrate a mass of cellulose wadding.

For this purpose it is convenient to consider a solution of wetting
gent penetrating a plane bed of cellulose, packed at a uniform density,
in a direction normal to the surface and at a uniform rate.   It is
assumed that the rate of penetration is sufficiently slow for adsorption
equilibrium to exist, to a close degree of approximation, throughout the
bed where solid and solution are in contact.   The progress of the
adsorption can then be calculated approximately by a stepwise method.
The weight of cellulose required to reduce the equilibrium concentration,
by a given small amount, in a thin layer of the advancing front of the
solution, of unit volume, is calculated for each of a chosen series of
successive small reductions of concentration.   Then the total weight of
cellulose, M, required to reduce the concentration of agent from a given
initial value, C_0, to a value C_r at the rth step is obtained from the
expression

$$ M = A \sum_{1}^{r} \frac{C_{n-1} - C_n}{X_n} \qquad n = 1, 2 \ldots\ldots\ldots r $$

where C_n = final concentration at nth step

X_n = weight of agent adsorbed per unit weight of cellulose in
equilibrium with solution of concentration C_n

A = constant.

The appropriate values for X_n are obtained from the isotherms in Fig. 1.

The packing density has been assumed to be uniform.   Hence the
weight of cellulose required to reduce the concentration by each of the
chosen steps, in the given element of the advancing front, will be
encountered in penetrating a distance proportional to the weight required
for each step.   Then the concentration will be reduced from C_0 to C_r in
a distance proportional to M.   The error arising in this method of
calculation depends directly on the size of the concentration "steps" used.

In the above way the concentration of agent has been calculated as a
function of the distance penetrated for each agent, and it is shown
graphically in Fig. 2.   The initial concentration for each has been taken
as 1.0 per cent by weight and the concentration reduction has been made
in equal steps of 0.1 per cent.   The distance penetrated is given in
arbitrary units which depend on the constant A and on the packing density
of the cellulose, neither of which need be specified here since relative
penetrations only are required.

Comparing the distances penetrated by the different agents, in which
the concentration in the advancing front is reduced to, say, 0.5 per cent
it will be seen that this reduction occurs for agent B in about one
quarter of the distance in which it occurs for agents C and E.
Agents C and E are thus apparently more economical than B for wetting a
mass of cellulose.   The true extent of this economy, however, cannot be
determined without a knowledge of the way in which the wetting power of
the agents, as measured by some appropriate test, is related to the
concentration.   When this relationship is known the agents can be
compared in terms of the initial concentration of each for which the
wetting power will be reduced to a given common value in a given depth
of penetration.   These initial concentrations can be determined from the
curves in Fig. 2 provided the standard depth is chosen so that the initial
concentrations do not exceed 1 per cent; otherwise a further set of curves
will be required.   The cost of equally effective solutions of the agents
can then be worked out from current prices.

Adsorption equilibrium may not, in practice, be approached closely
in the advancing front of a solution penetrating a porous solid.   If
this is so, and if the rate of adsorption of wetting agents differ
widely, the method suggested above for the comparison of wetting agents
may be unreliable.

Cellulose wadding is easily wetted by water and the use of wetting agents on it would be superfluous. The above discussion, however, is intended to show how adsorption data might be used for comparative purposes in cases where wetting agents are required.

From the experimental study it appears that the isotherms for the adsorption of wetting agents on solids do not show sufficient similarity to permit any simplification in either their determination or their use in calculation of adsorption losses, and, moreover, adsorption appears to be partly specific. Therefore, the selection of wetting agents on the basis of adsorption data with supplementary wetting data, as outlined above, would be a lengthy procedure; it would only be justified if no other method were available. It is, in fact, possible in many cases to make a satisfactory selection of agents by other and more simple methods of an empirical nature. One such method will be described in a later report.

CONCLUSIONS

1. Wetting agents are adsorbed on solids in amounts that vary widely with the agent and its concentration.

2. The adsorption isotherms for wetting agents are not sufficiently similar to permit any simplifying generalisation, and the adsorption of wetting agents on solids likely to be encountered in firefighting appears to be partly specific.

3. The adsorption isotherms can be used to estimate the relative loss of agent as solutions of different agents penetrate a porous solid.

4. Adsorption data, if supplemented by appropriate wetting data, might be applied to the selection of an economical agent for a given application; but the selection of agents by such a method would be a lengthy procedure that would be justified only if no other method were available.

ACKNOWLEDGEMENTS

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APPENDIX

AGEING OF SOLUTIONS OF CERTAIN ANIONIC AGENTS

Solutions of agents A and B, and another of the same type as A but
which was not used in the adsorption measurements, underwent a change on
standing. Their titres against the standard solution of cationic agent
decreased with increasing age of the solution until, in times which varied
between a quarter of an hour and four hours depending on the agent and its
initial concentration, values were reached which were stable apparently
indefinitely. The actual decrease, or ageing, observed depended on the
speed with which the initial titre could be determined after preparation
of the solution; the largest decrease was 25 per cent, which was observed
for 0.2 per cent solutions of the two agents of type A.

The ageing was consistent with the hypothesis that the agents of the
above types were each mixtures of anionic species, one or more components
of which decomposed rapidly in dilute solution while the remaining components
were stable. Thus the decrease of titre observed on ageing, became greater
as the initial concentration of the solution was increased from 0.05 per cent
to 0.2 per cent due, on the above hypothesis, to the increasing amount of
undecomposed components, present at the time of titration. The ageing
observed for a 2 per cent solution was small, about 5 per cent only; this
was because solutions of concentration greater than 0.2 per cent were
always diluted to 0.1 per cent before submitting to the titration procedure,
and the ageing observed with 0.1 per cent solution was only about 3 per cent,
i.e. decomposition was almost complete in the first few minutes before
titration. Further investigation would be required to confirm the details
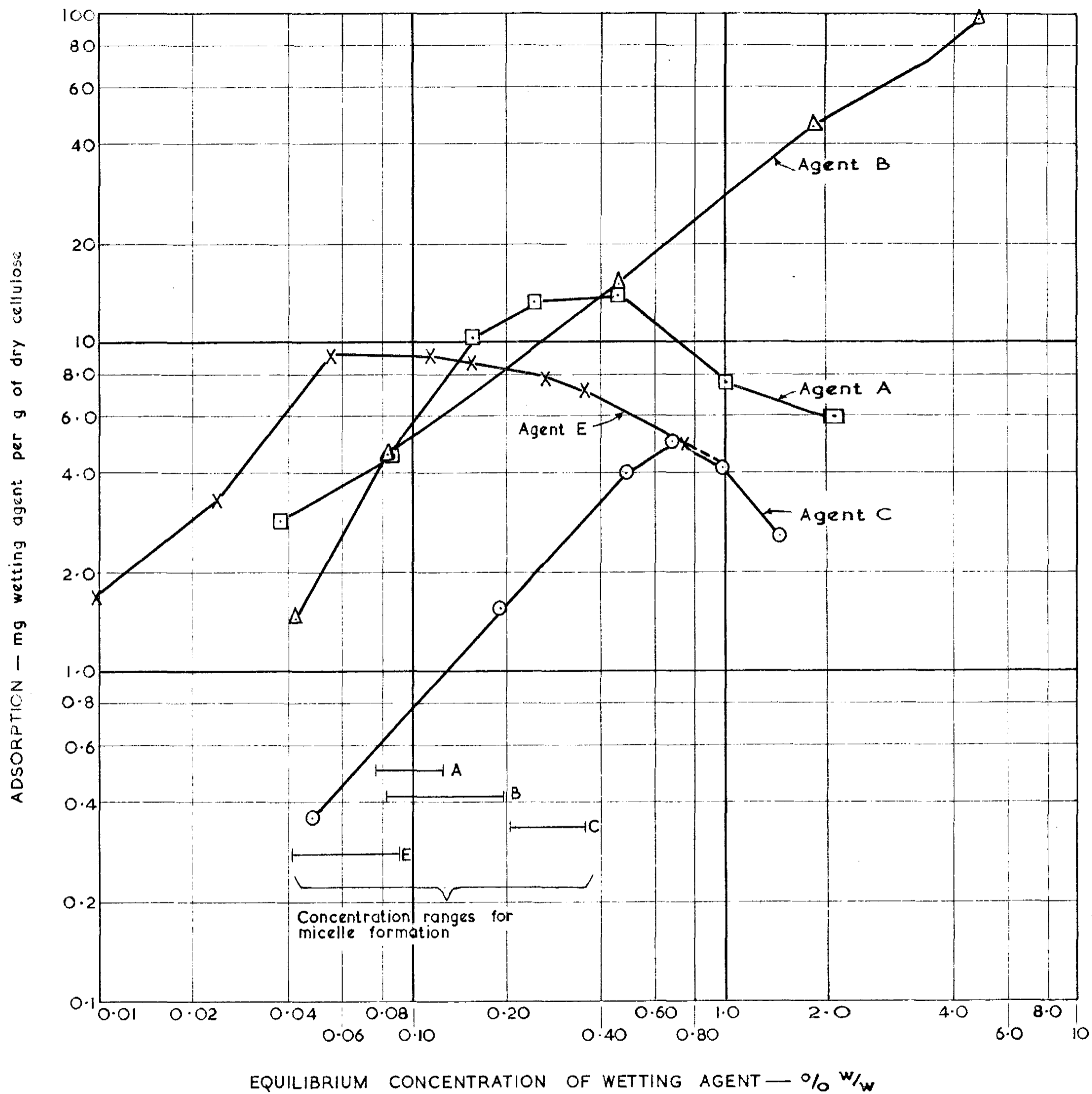of the effect and the correctness of the suggested explanation.

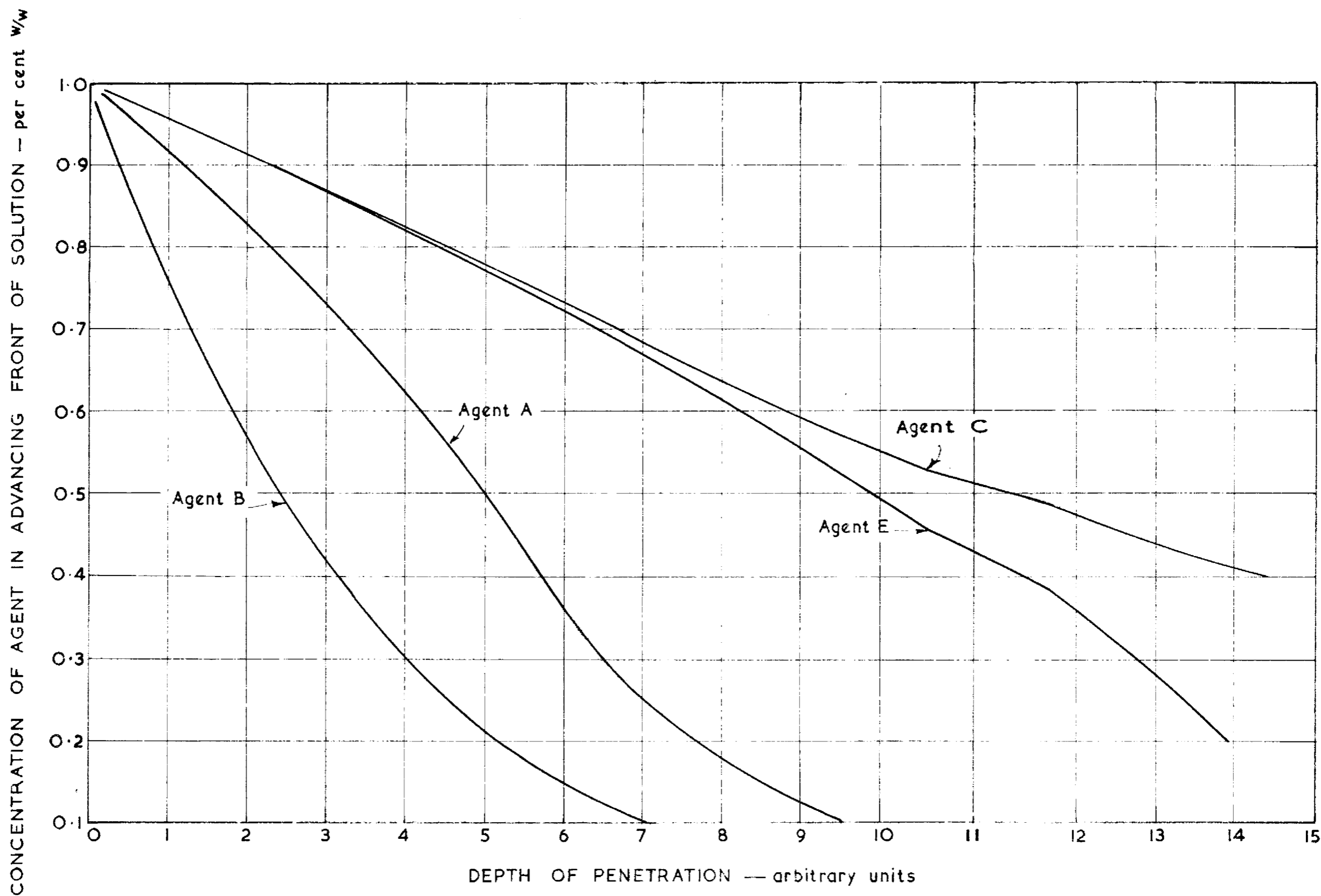FIG.1. THE ADSORPTION OF WETTING AGENTS FROM SOLUTION BY CELLULOSE WADDING

FIG.2. DEPLETION OF WETTING AGENT SOLUTIONS PENETRATING A BED OF CELLULOSE WADDING