

## THE BEHAVIOR OF IODINE SOLUTIONS AT LIQUID-SOLID INTERFACES.

### I. THE WETTING POWER OF IODINE FROM VARIOUS ANTISEPTIC SOLUTIONS.

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Antiseptics as a class are regarded as contact medicinals, and hence their behavior at surfaces is a factor that has an important influence on their effectiveness. With the exception of surface tension studies of antiseptics, which have been the subject of extensive discussion, little attention has been given to other physical properties of poly-component-uniphase systems under the conditions of use. As solvents are important in their influence on the surface behavior of solutions, we may well consider their influence upon the behavior of active medicinal ingredients dissolved in them.

Because the field of activity of a contact medicinal is usually at or begins at the medicinal-organism interface, we have chosen to consider its adsorption behavior at surfaces as a fundamental property. Adsorption concentration at equilibrium rather than the actual concentration in solution would be the governing factor determining the dose of active agent upon bacteria or tissue. Adsorption behavior should also affect penetration of the effective agent, because penetration rate is governed by the concentration gradient between the treated surface and the penetrated interior as well as the actual amount of solution passing through the membrane.

In order to obtain some idea of the surface conduct of iodine antiseptic solutions, this investigation has been made of the adsorption of iodine upon silk fibre from a series of iodine solutions, including those in aqueous potassium iodide, potassium iodide-alcohol-water and potassium iodide-water-glycerine.

#### EXPERIMENTAL PART.

Commercially scoured silk yarn was selected as a receiving medium, because it is a material that approaches skin in chemical nature and has a comparatively large surface per unit of weight. All the samples for the entire investigation were taken from a single cone of yarn. Weighed samples (approximately 0.4 Gm. when dry) were placed in 250 cc. of the solution under investigation, which was kept at 25° C. up to the time of immersion. These samples were allowed to remain until equilibrium was established between the free iodine deposited upon them and that in the solution. The samples were then removed and centrifuged for four minutes at 2200 r. p. m., shaken out to disturb capillary spaces, centrifuged again for a like period, and placed in an excess of standard thiosulphate solution until the free iodine had reacted; the residual thiosulfate was then titrated with acidified potassium iodate. The free iodine concentration in the solution at equilibrium was determined by analysis. The time of immersion of the samples was five minutes, which was taken as a standard time after it had been found adequate for the establishment of a practical equilibrium.

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Since the variation in the amount of free iodine adsorbed from different solutions disturbed their free iodine concentration, the data were adjusted to a common free-iodine standard before the curves were plotted. Following the procedure described above, adsorption values could be reproduced with less than 2 per cent variation, except in solutions high in free iodine.

#### DISCUSSION OF RESULTS.

The data from the investigation of these solutions are presented in the curves in Figs. 1, 2 and 3. Figure 1 shows the amount of iodine in mg. adsorbed per Gm. of silk, plotted against the potassium iodide present in the solution in excess of that contained in a saturated iodine solution of the prescribed concentration in aqueous potassium iodide. The horizontal scale indicating the amount of potassium iodide present in the solution in excess of that necessary for dissolving

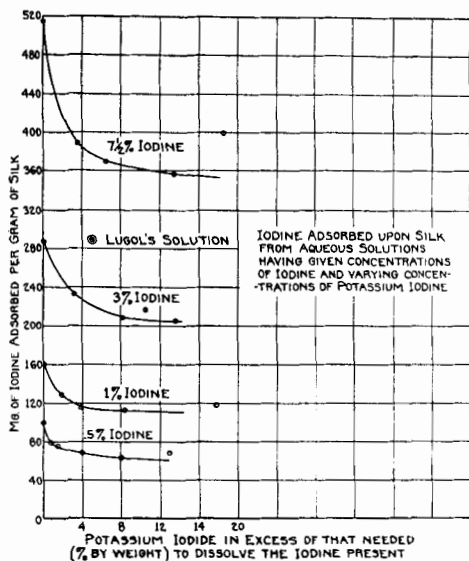


Fig. 1.

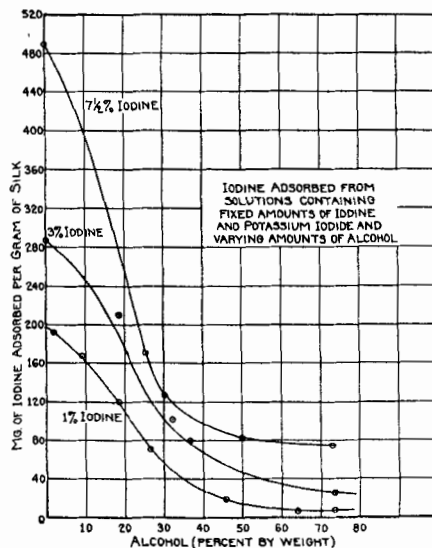


Fig. 2.

the iodine may be considered as an approximate comparative measure of its unused iodine solvent power. The curves for alcohol and glycerin are shown in Figs. 2 and 3, the horizontal axis representing the composition of the alcohol-water or glycerin-water constituent in which the iodine and potassium iodide are dissolved, the zero position representing, as in the aqueous potassium iodide curves, a saturated iodine solution of the indicated strength in potassium iodide. A similarity in the curves is evident in that there is a qualitative inverse proportionality between the unused solvent power, as indicated by increasing organic constituent, and the amount of iodine adsorbed per unit weight of silk. It has been found upon examination of the curves for potassium iodide solutions that the relationship referred to is approximately logarithmic. The decrease in the amount of iodine adsorbed from solutions of increasing alcohol and glycerin strength, however, is much more sharp and complete than would be indicated by this relationship to solubility to which the aqueous iodide solutions approximately conform. The extent of this

difference is evident from Fig. 4, in which the iodine adsorbed from 1 per cent solutions is plotted against the unused solvent power for iodine of the three types of solution investigated.

The practical consideration of greatest interest shown in these data is that surfaces are much more readily wet with iodine from aqueous iodide solutions than they are from alcohol or glycerin solutions of like iodine strength.

Though we are interested primarily in the adsorption values of our active agent from solutions in various solvents, as described above, it may be well, in the interest of further generalizations that may be made from the data, to consider the properties of the solution that govern the adsorption of a single constituent, which we may roughly term partial wetting power. Such a consideration is further advisable to determine whether some other and simpler approach may be made to the ques-

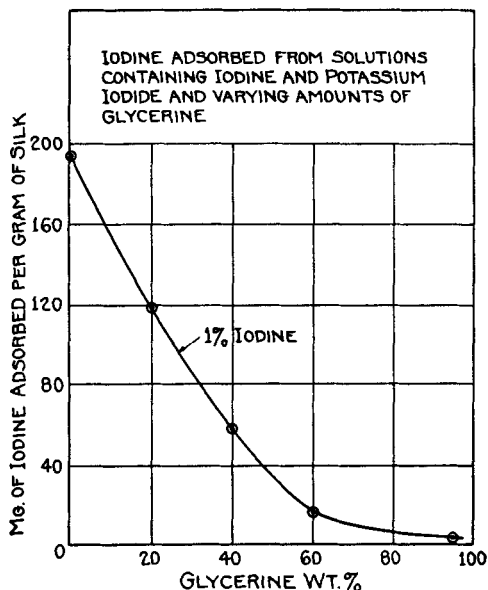


Fig. 3.

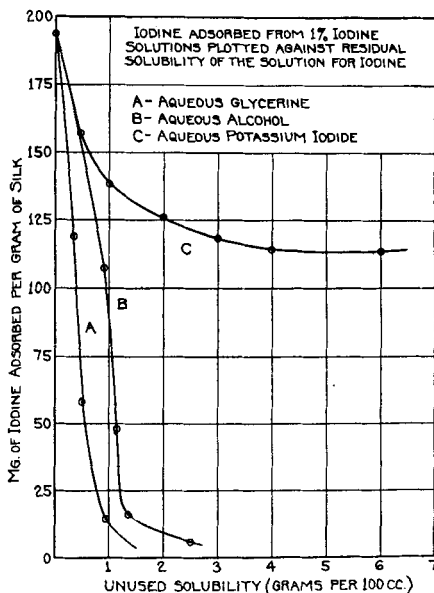


Fig. 4.

tion. Surface behavior is closely related to surface tension effects and for that reason we must first consider the data presented in the light of that important property.

The absolute surface tension of the solution bears but indirectly upon the adsorption of a single constituent upon a surface. That this is true is evident from the fact that aqueous potassium iodide solutions of iodine which differ only *slightly* from aqueous glycerin solutions of iodine, differ *greatly* from them in the degree to which iodine is adsorbed. Also, aqueous alcoholic solutions which *differ* considerably from glycerin solutions in their surface tensions are quite *similar* to them in this respect.

The adsorption coefficient considered from a physical standpoint is a function of two factors: one, the rate of change of surface tension with change of concentration of the adsorbed constituent; and the other, the rate of change of escaping

tendency with the concentration of the same constituent. These quantities are related by the formula  $u = \frac{ds/dn}{dF/dn}$ , where  $u$  is the adsorption coefficient, and  $ds/dn$  and  $dF/dn$  represent the change of surface tension and of escaping tendency with change of composition, respectively. The change of escaping tendency is not usually considered in studying adsorption effects, but it cannot be entirely ignored unless we are dealing with a perfect or with an infinitely dilute solution. In the absence of experimental data on the escaping tendency of the solutions involving several concentration variables, it suffices for our present consideration to say that, in general, the change of escaping tendency with increasing iodine concentration will have a positive value. It follows, then, that, if the surface tension of the solution is lowered as the iodine concentration is increased, the iodine adsorption coefficient will be increased accordingly. That this is true in aqueous potassium iodide solutions at the liquid-air interface is shown by the fact that 4.5 per cent iodine does effect a lowering of the surface tension of a 5 per cent potassium iodide solution by about three dynes per centimeter. That a similar condition obtains at the liquid-solid interface where the interfacial tension cannot be measured is evident from the adsorption data. The change of surface tension of alcohol and glycerin solutions is affected by dissolved iodine to a less extent, so much less, in fact, that in the latter case accurate measurement is difficult. This finding indicates that the adsorption at the liquid-air interface should be correspondingly less than in the aqueous iodide solutions of iodine. Support to this conclusion is observed in the behavior at the liquid-solid interface, as indicated by the adsorption measurements.

In this limited number of cases it is evident that, even when the quantitative consideration of escaping tendency is ignored, the change of surface tension with increasing iodine concentration permits qualitative prediction of adsorption at a liquid-solid interface where the surface tension cannot be measured. The smallness of the surface tension differences involved and the possibility of differences between the change of surface and interfacial tensions make it plain that direct adsorption measurements are of more significance when a wide variety of solvents are being considered.

#### SUMMARY.

The wetting power of iodine from aqueous iodide solutions is notably superior to that from alcohol and glycerin solutions.

The wetting power of iodine from aqueous iodide solutions is an approximate logarithmic function of the unused solvent power of the solution for iodine.

Absolute surface tension of the solution has only indirect bearing on the wetting power of a single constituent.

Though the wetting power of a single constituent, depending on the change of surface tension of the solution, and on the change of escaping tendency of the adsorbed constituent with change of composition of the same constituent, may be qualitatively predicted even for complicated concentrated systems, it can in some cases be determined directly with more ease and with accuracy suitable for practical consideration.