

*Selective Permeability: The Absorption of Phenol and other
Solutions by the Seeds of Hordeum vulgare.*

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Previous researches on the absorption of various aqueous solutions by the seeds of *Hordeum* (barley) have been directed mainly to a study of the phenomena attending the diffusion of the solvent through the semipermeable covering of the seeds.* The latter, however, is permeable not only to the water but also to certain classes of solutes in solution, such as the phenols and fatty acids; in fact, the membrane behaves in their presence as a selectively permeable one rather than a semipermeable one. In the present communication we deal more particularly with the extent to which certain of these permeable solutes enter the seeds together with the water, in the hope that the results may throw some light on the physical causes governing the phenomenon of selective permeability.

A preliminary investigation having given the somewhat striking result that phenol and aniline solutions enter the seeds in higher concentration than the solutions in which they are immersed, we decided to make a series of quantitative experiments with solutions of aniline, phenol and acetic acid of various concentrations.

1. *Extent to which Aniline, Phenol and Acetic Acid enter the Seeds from
Solutions of Various Strengths.*

(a) *Aniline Solutions.*—The seeds were steeped in approximately N/4, N/8, N/12, and N/16 solutions respectively for two days.

The amount of aniline which had entered was found by hydrolysing the seeds with dilute sulphuric acid. This operation, which was performed under reflux at about 80° C., was complete in from two to three days' time. After filtering, the solution was made up to a known volume, and the aniline precipitated and weighed as tribromaniline.† The accuracy of the method was tested by determinations of aniline solutions of known strengths, both alone and in presence of barley seeds which had been hydrolysed to sugar. The presence of the latter was found to have no influence on the results, which were found to be accurate to 3 or 4 per cent.

The results are given in Table I.

* A. J. Brown, 'Roy. Soc. Proc.,' B, vol. 81, p. 82 (1909); *ibid.*, with F. P. Worley, B, vol. 85, p. 546 (1912); *ibid.*, with F. Tinker, B, vol. 89, p. 119 (1915).

† Cf. section on Aniline in Allen's 'Commercial Organic Analysis.'

Table I.—Seeds in Aniline Solutions of Various Strengths.
Temperature 15° C.

Strength of aniline solution outside seeds.	Gain in weight of 5 grm. seeds after 2 days.	Weight of aniline found inside seeds.	Weight of water inside seeds.	Strength of solution inside seeds.	Ratio of strength solution inside to strength solution outside.
N/4 (2.30 grm. per 100 grm. water)	grm. 2.724	grm. 0.184	grm. 2.540	7.25 grm. per 100 grm. water	3.15
N/8 (1.16 grm. per 100 grm. water)	2.564	0.087	2.447	3.52 grm. per 100 grm. water	3.04
N/12 (0.87 grm. per 100 grm. water)	2.909	0.067	2.842	2.35 grm. per 100 grm. water	2.70
N/16 (0.575 grm. per 100 grm. water)	2.851	0.042	2.849	1.47 grm. per 100 grm. water	2.55

In each instance the aniline solution is stronger within the seed than in the outside solution. Moreover, the aniline solution inside the seeds becomes stronger as the outside solution becomes stronger, and is in each of the experiments about three times as strong as the latter. Further, it will be noticed that the solution diffusing into the seeds from N/4 aniline solution contains more aniline than does a saturated solution, *i.e.*, the adsorbed solution is highly supersaturated.*

(b) *Phenol Solutions*.—The procedure was exactly the same as in the case of aniline, the phenol being estimated as tribromphenol.† The results are given in Table II.

Manifestly concentration of phenol within the seeds takes place as in the case of aniline. The high degree of supersaturation of the solution adsorbed from the N/2 phenol is also very marked.

(c) *Acetic Acid Solutions*.—Acetic acid, unlike aniline and phenol, is miscible with water in all proportions, so that solutions of any chosen concentrations from 0 to 100 per cent. acetic acid can be employed.

To determine the concentration of the adsorbed solution within the seeds, the latter were hydrolysed with a known volume of standard sulphuric acid, the solution filtered, made up to a known volume (250 c.c.), and titrated with standard NaOH, correction being made for the sulphuric acid employed

* This fact possibly indicates that the solubility of the aniline is increased in the adsorbed film in contact with colloidal surfaces.

† A small correction had to be made for the solubility of the tribromphenol in water. When this was done the accuracy of the results was about the same as for aniline (3 or 4 per cent.).

Table II.—Seeds in Phenol Solutions of Various Strengths.

Strength of phenol outside seeds.	Gain in weight of 5 gm. seeds after 2 days.	Weight of phenol inside seeds.	Weight of water inside seeds.	Strength of solution inside seeds.	Ratio of strength solution inside to strength solution outside.
N/2 (5.00 gm. per 100 gm. water)	3.321	0.485	2.836	17.2 gm. per 100 gm. water	3.4
N/4 (2.50 gm. per 100 gm. water)	3.081	0.243	2.838	8.6 gm. per 100 gm. water	3.4
N/8 (1.24 gm. per 100 gm. water)	3.024	0.129	2.895	4.45 gm. per 100 gm. water	3.5
N/16 (0.64 gm. per 100 gm. water)	3.205	0.057	3.148	1.81 gm. per 100 gm. water	2.9

for the hydrolysis. The accuracy of the method was tested in the same way as in the case of aniline and phenol, and the error found to be within 5 per cent.

Table III.—Seeds in Acetic Acid Solutions of Various Concentrations.

Strength of outside solution x per cent. acetic acid to $(100-x)$ per cent. water.	Gain in weight of 5 gm. seeds after 2 days.	Strength of solution inside seeds.	Ratio of strength solution inside to strength solution outside.
	gm.	per cent.	
0	2.640	—	—
10	2.643	8.1	0.81
20	2.816	27.0	1.35
30	3.028	38.3	1.27
40	3.037	53.4	1.33
50	2.974	80.1	1.60
60	3.052	80.0	1.33
70	2.862	81.8	1.17
80	2.590	82.5	1.03
90	2.164	80.0	0.89
100	0.040	—	—

The graphical relation between the strength of the solution inside the seeds and that outside is shown in Diagram I. It will be seen that for all outside solutions stronger than 50 per cent., the strength of the adsorbed solution inside the seeds is constant at 80 per cent. Apparently the colloidal contents of the seeds cannot take up acetic acid unless at least 20 per cent. of water diffuses with the acid also. A striking confirmation of this is found in the absorption curve for water-acetic acid mixtures. Table IV

shows some typical absorption results, whilst Diagram II shows them graphically. The falling off of the absorption rate and also of the weight

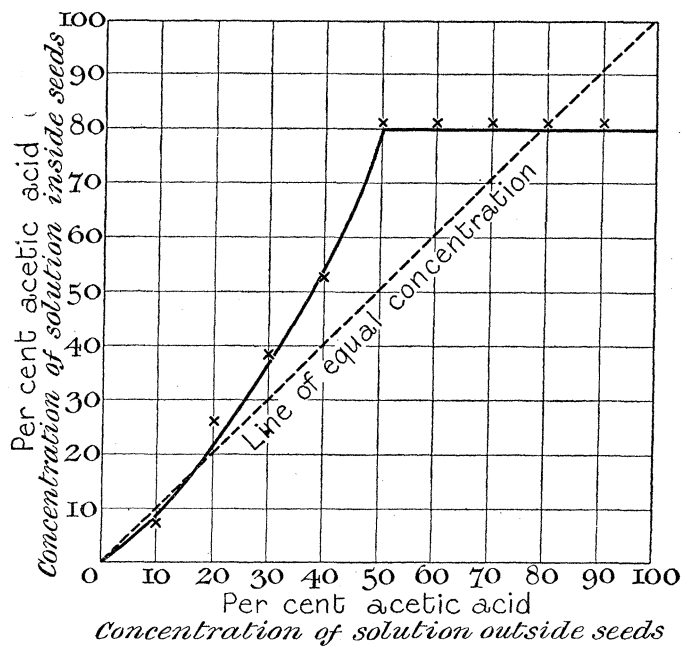


DIAGRAM I.—Acetic acid solutions.

of solution absorbed is very noticeable above the 80 per cent. mark. Pure acetic acid is not absorbed by dry seeds at all.*

Table IV.—Absorption Curves for Water-Acetic Acid Mixtures.

Strength of acetic acid solution.	Percentage gain in weight of seeds, due to absorption of solution after				
	2 days.	3 days.	6 days.	9 days.	13 days.
per cent.					
0	36.4	48.6	55.8	64.5	68.3
20	37.0	49.6	59.8	66.7	69.4
38.5	33.1	45.2	52.3	63.0	68.9
55.5	31.7	44.6	52.4	63.8	70.6
71.4	32.9	45.3	53.7	66.5	74.3
83.3	27.8	43.2	49.7	61.9	68.3
90.9	13.5	19.8	26.8	43.4	55.0
100	5.5	9.2	8.9	10.9	13.5

* *Loc. cit.*, A. J. Brown, 'Roy. Soc. Proc.,' B, vol. 81, p. 82 (1909).

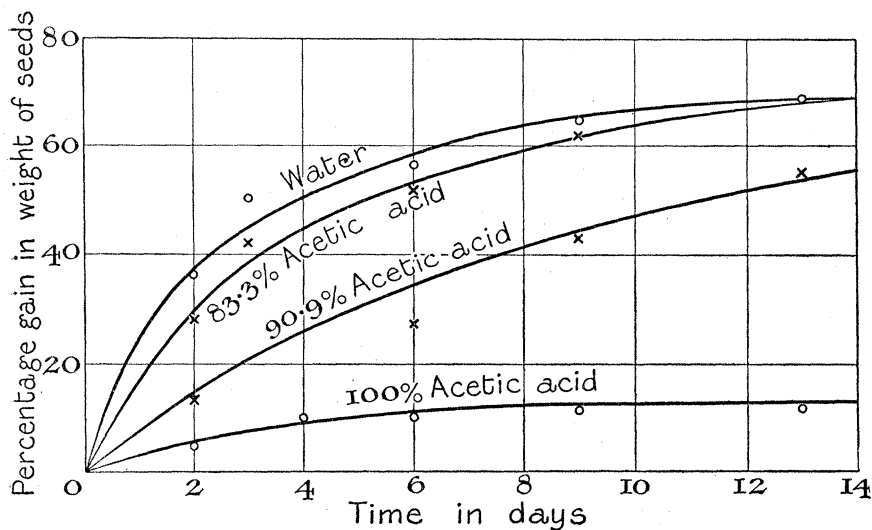


DIAGRAM II.—Absorption curves for water-acetic acid mixture.

2. *Relation between the Concentration of the Various Inside Solutions and the Amount Absorbed at Equilibrium.*

A comparison of these two quantities for acetic acid (Tables III and IV) shows that when the solution inside is stronger than that outside, the amount absorbed at equilibrium is greater than the amount of pure water absorbed when the seeds are in water only. Furthermore, as the relative concentration of the inside solution increases, the equilibrium point rises also, and is at a maximum when the relative concentration of the inside solution is at a maximum (with outside solutions of from 50 to 70 per cent. strength). In the same way, the equilibrium point is the same as that for pure water when the outside and inside solutions have the same concentration (80 per cent.). When the solution inside is weaker than that outside (at from 80 to 100 per cent. outside concentration), the equilibrium point is lower than it is for pure water.

Similar considerations hold for the solutions of aniline and phenol. They enter the seeds in a concentration greater than that of the outside solution, and the equilibrium point is higher than for pure water in their case also.*

Evidently the amount of solution taken up by the seeds at equilibrium is determined by the difference between the inside and outside concentrations. The equilibrium point is lower, equal to, or higher than it is for pure water according as the inside solution is weaker, the same strength as, or stronger than the outside solution.

* A. J. Brown and F. Tinker, 'Roy. Soc. Proc.,' B, vol. 89, p. 119 (1915).

Conversely, the position of the equilibrium point gives an indication of the extent to which the solute enters the seeds. Table V shows a series of organic solutes arranged approximately in the order of the equilibrium points they give,* and therefore in the order of the extent to which the solute enters. The surface tensions of the solutions are given in certain cases also.†

Table V.—Showing Order of Extent to which Various Organic Solute Enter the Barley Seeds.

Solute (molar).	Percentage increase in weight when seeds are immersed in molar solution.	Surface tension of molar solution (Traube).
		dynes/cm.
Cane sugar	39·3	76·5
Dextrose	40·8	75·7
Glycerol	41·5	74·1
Glycine.....	41·8	75·3
Tartaric acid	42·2	—
Urea	45·2	74·8
Ethylene glycol	52·7	71·8
Lactic acid	61·4	—
Glycollic acid	63·4	—
Acetaldehyde	66·6	—
Acetone.....	68·7	56·2
Acetic acid	68·0	61·5
Ethyl alcohol	69·6	57·9
Ethyl acetate	71·8	43·2
N/2 phenol	85·0	43·3

The explanation of this relation between the relative concentrations of the inside and outside solutions is quite simple. When there is a difference between the two concentrations in question, an extra osmotic force is introduced into the system beyond the forces which are present when there is no concentration difference. If the seeds are immersed in pure water, for instance, diffusion merely takes place until the surfaces of the colloidal contents are saturated with moisture. But, if the seeds are immersed in a solution, and the membrane acts selectively towards the latter, there is an outward or inward osmotic force according as the solution inside is weaker or stronger than that outside. In the former case the colloidal contents of the seeds will be prevented from taking up as much liquid on to their surfaces as they would otherwise do, so that the equilibrium point will be lowered. In the latter case still more solution will be driven into the seeds, and the equilibrium point raised.

* This Table is compiled from a previous paper, 'Roy. Soc. Proc.,' B, vol. 81, p. 82 (1909). The order is only approximate.

† The surface tensions are taken from J. Traube's paper, 'Journ. Phys. Chem.,' vol. 14, p. 460 (1910), and other papers.

3. Relation between the Selective Adsorption of the Various Solutions and their Surface Tensions.

An inspection of Table V shows that the solutes which are most strongly adsorbed by the seeds of *Hordeum*, such as aniline, phenol, and the organic acids, are those which give solutions having very low surface tensions. On the other hand, those solutes which are not adsorbed, such as the sugars and the polyhydric alcohols, give solutions which have relatively high surface tensions. In fact, the order giving the extent to which the solutes are adsorbed is almost the same as that for the surface tensions. Evidently, Gibbs' well-known rule connecting adsorption and surface tension is applicable with a fair degree of accuracy to adsorption by the colloidal contents of barley seeds.*

Most important of all, the fact that the solutes giving high surface tensions do not, as a rule, penetrate the membrane, suggests that the selective action of the latter is due to selective adsorption. This hypothesis accounting for the selective properties of membranes of the copper ferrocyanide type has already been advanced by one of us on other grounds.† The barley membrane, like almost all other membranes, is colloidal in nature, *i.e.* it is composed of aggregations of colloidal particles enclosing minute capillaries. Hence any liquid which enters its capillaries is adsorbed liquid; and that selective adsorption of solvent or solute into the capillaries will take place is practically certain.‡ The results of the present investigation indicate that these selective adsorption effects are both varied and considerable in magnitude; and great enough to account for the selective action. The kind and degree of the selective condensation at the surface of the membrane may not be exactly the same as at the surface of the starch granules, and both may differ from the selective effects at a solution-air interface. But the general agreement of each with Gibbs' relationship shows that a great similarity exists between them.

* The investigators have found this rule to be more or less applicable to many other boundary surfaces. *Vide* W. C. McLewis "On the Adsorption of Various Solutes at a Hydrocarbon Oil-Water Interface," *Phil. Mag.* (6), vol. 15, p. 449 (1908); *ibid.* (6), vol. 17, p. 466 (1908).

† Tinker, *Roy. Soc. Proc., A*, vol. 92, p. 357 (1916).

‡ *Loc. cit.*, the paper just mentioned.
