

An Explanation of the so-called Intertraction Phenomenon between Solutions, and the Molecular Significance of Negative Surface Tension.

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(PLATES 14–16.)

Sir A. Wright* and Schoneboom† have observed that when certain solutions‡ are superposed on other solutions, mixing occurs not by simple diffusion but by the development of streamers or “pseudopodia,” which start from the interface and make their way upwards and downwards through the body of the two solutions. The phenomenon is attributed to a special force, “intertraction,” which aids the mixing; and Schoneboom suggests that this is a spontaneous extension of the interface between the solutions, under the influence of the peculiar capillary forces present in this region.

Such a force at the interface would be of the greatest importance for the theory of capillarity. But in studying this phenomenon we have observed facts which are wholly out of accord with such an explanation. It seems that surface tension has nothing to do with the phenomenon, and that the two essential factors are the difference in the rates of diffusion of the solutes in the two solutions, and the direction of gravity. Moreover two rather different phenomena are exhibited in different circumstances.

We think the correct explanations are as follows. Suppose two solutions of solutes A and B, in the same solvent, A diffusing faster than B, are placed one above another carefully.

Case 1.—Suppose first the density of solution B is the less, and that the difference in density is not great. At the instant of contact of the solutions, there is a plane surface of separation if the solutions have been sufficiently carefully

* ‘Roy. Soc. Proc.,’ B, vol. 92, p. 118 (1921).

† ‘Roy. Soc. Proc.,’ A, vol. 101, p. 531 (1922).

‡ Schoneboom states that intertraction is obtained “with *all* inorganic and organic compounds without any exception, provided . . . that the substances are sufficiently soluble in water, and that there is not too great a difference in specific gravity between the upper and lower solutions.” The sequel shows that this is not the case, a definite difference in diffusivity between the dissolved substances in the upper and lower solutions being necessary for the phenomenon; it is also essential that the slower diffusing solution should be on top.

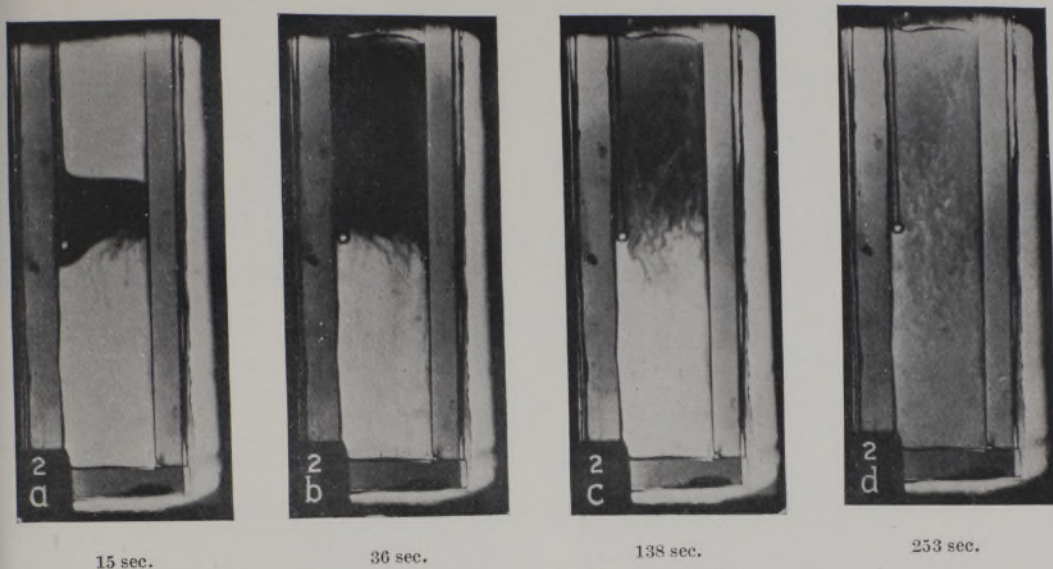


FIG. 2.—Salt, 1·0365; albumen, 1·034.

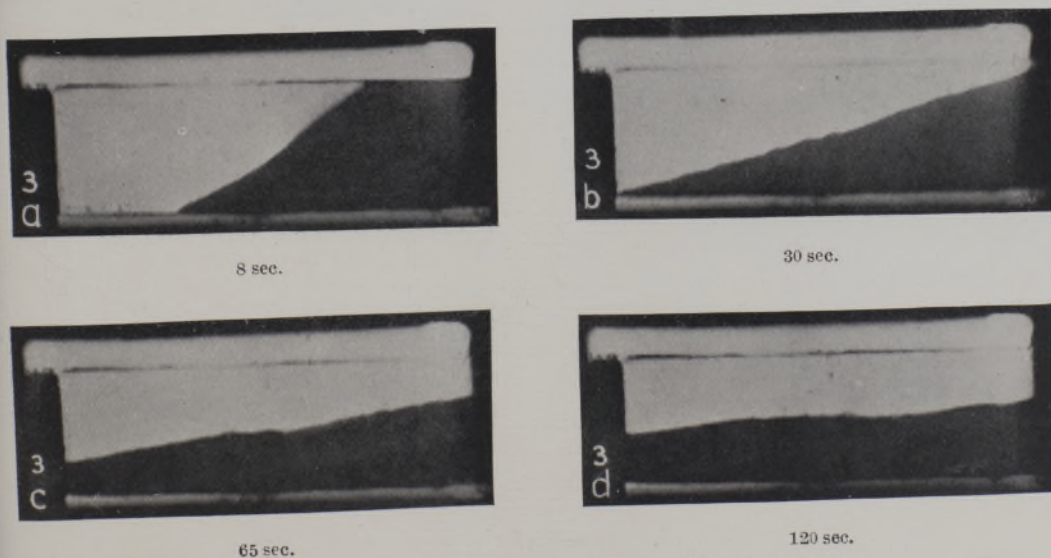
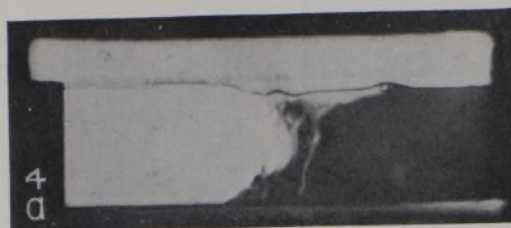
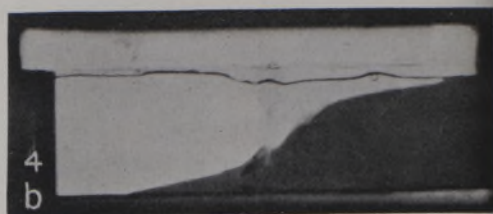


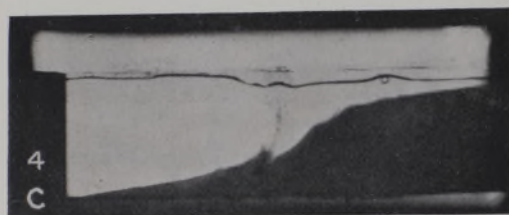
FIG. 3.—Salt, 1·032; albumen, 1·034.



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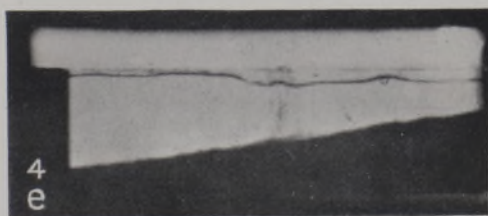
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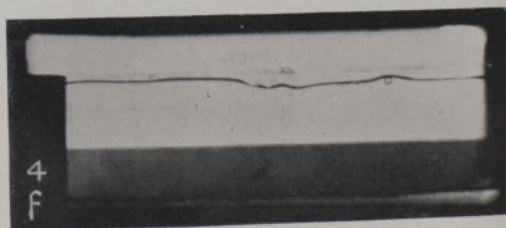
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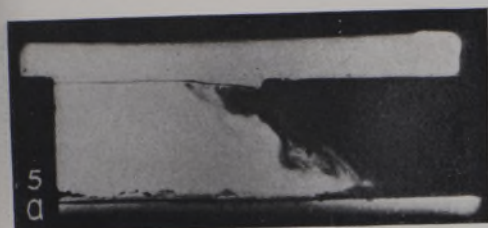


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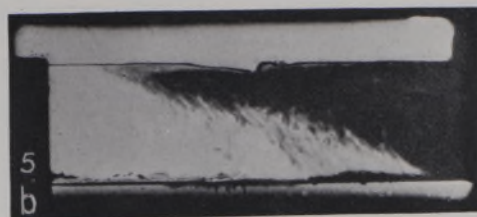


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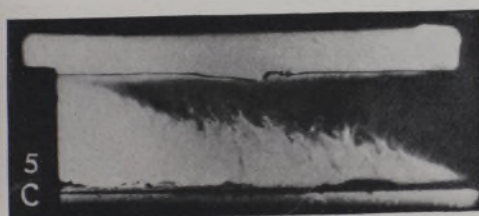
FIG. 4.—Salt, 1·034 ; albumen, 1·034.



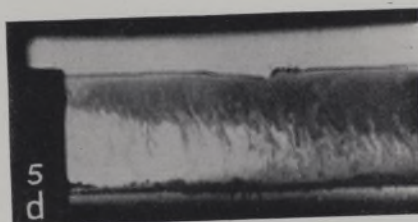
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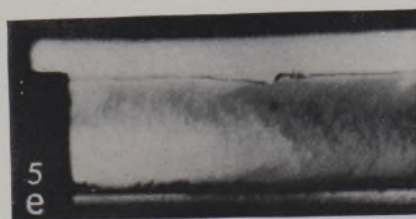
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FIG. 5.—Salt, 1·0365; albumen, 1·034.

placed in position. This is, of course, unattainable in practice, and there will always be irregularities in the surface of separation. From the moment of contact on, A diffuses upwards into B and B downwards into A. But since A diffuses faster than B, in a short time the layer of B just above the interface will have gained more solute than it has lost, and its density will be increased. If the difference in rate of diffusion is great enough, and the initial difference in density not too great, these layers of B will in time become denser than A. Thus the hydrostatic equilibrium of the liquids will be upset, and B will descend into A. The form of the motion in this case is determined as follows. At a point where there is initially a slight bulge of B down into A, conditions are specially favourable for rapid diffusion, as the interface is particularly large relatively to the volume of fluid B just behind. Therefore the increase of density of B will be more rapid in a bulge downwards than elsewhere, and the bulges will tend to be accentuated and to develop into streamers which will descend to the bottom of the vessel.

In a similar way, streamers of A will develop and move up into B, for at any point where there is a slight bulge of A upwards into B, the loss of salt from A to B, and the decrease of density of A, are more rapid than elsewhere. Since as a rule the initial bulges upwards and downwards will occur alternately, streamers will usually start upwards and downwards alternately from the interface.

Naturally much commotion is caused in the liquid by these streamers, and this aids mixing. The intertraction is, however, essentially an inversion of the layers of liquid, and the mixing is only secondary. If B is coloured and A uncoloured, usually after a few minutes the motion ceases, and the vessel is nearly uniformly coloured; but often, and especially when the streaming has been rapid, the lowest layers are deeper in colour than the remainder. In one case, using a hydrochloric acid solution coloured blue (A), and magnesium sulphate (B), A being 0.007 denser than B initially, very violent streaming occurred in a few seconds; after two minutes the motion had ceased, and the upper half of the vessel was deep blue, the lower half being only faintly coloured. In this case the difference in diffusion coefficients was about 2.0 sq. cm. per day, the largest difference used, and the difference in density was small.

If the difference in density is too great, the streamers do not develop. In aqueous solutions, when the difference in coefficients of diffusion was about 0.3 sq. cm. per day, well marked "intertraction" streamers were observed if the difference in density did not exceed 0.03, but if it exceeded 0.05 there was no intertraction. Most of our experiments were done in narrow glass

cells, 7 cm. long by 2 cm. deep by $1\frac{1}{2}$ mm. thick, open at the top edge. In these narrow cells we frequently noticed that the greater the difference of density between the solutions, the thinner were the streamers. The limits of difference of density within which the streamers develop have not been worked out, but probably a greater difference of density is permissible with greater differences of diffusion coefficient than with smaller.

Case 2.—A and B placed in contact, side by side, in a shallow pool on a glass plate. If the pool is only about $\frac{1}{2}$ mm. deep, there is no rapid movement of the liquids into one another, except for a disturbance at the moment of first contact, which may result in a curious stationary pattern being formed for a few minutes. No streamers develop from one liquid to the other. We have tried this with albumen (B) and sodium chloride (A), and with hydrochloric acid (A) and potassium nitrate (B), two pairs of substances which give very marked streaming under the conditions of Case 1. Except for the direction of gravity all forces between the liquids are the same as in Case 1. This proves that capillary forces are not concerned in the phenomenon.

Case 3.—B denser than A, liquids superposed. We have never observed streamers like those of Case 1, when the rapidly diffusing solution is above the other. If the difference of density was more than about 0.025, with aqueous solutions no motion of the boundary was observed. If the difference was less than this, local disturbances of the boundary often occurred, which were always few in number, and quite different from the streamers of Case 1. They began as a slight elevation of the lower liquid at the boundary, which assumed a sharp point and sent up a very thin wisp of the lower solution into the upper; there was a rapid circulatory motion of the liquid visible at these points. With aqueous solutions these vortices were usually small and often moved slowly along the boundary; but with alcoholic solutions they were more marked and more persistent. Occasionally, one vortex would disappear and another appear at another point. Fig. 1 is a sketch of the vortices obtained with alcoholic solutions of resorcin (B) 0.832 s.g., and iodobenzene (A) 0.826 s.g., the difference in diffusion coefficients being about 0.45.

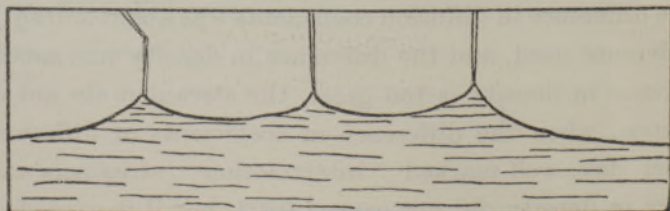


FIG. 1.—Vortices with rapidly diffusing solutions uppermost.

Probably the explanation is that the diffusion of the solutes across the boundaries causes the upper layers of B (the lower liquid) to become denser, and the lower layers of A to become lighter. There is, therefore, set up a circulation in each liquid, through the lower layers changing place with the upper. This produces eddies in certain places, and if the difference in specific gravity of A and B is not too great, the disturbance at the boundary may cause a small amount of A to be carried along with the eddy in B, and *vice versa*. The reason for the difference in this phenomenon, with aqueous and alcoholic solutions, has not been investigated.

Fig. 2 (Plate 14) shows photographs of the intertraction observed when a coloured egg albumen solution (s.g. 1.034) was superposed on a sodium chloride solution (s.g. 1.036). The vessel used was a narrow cell about $1\frac{1}{2}$ mm. thick; the albumen shows black. The times given are from the moment of commencing to run the albumen on the surface of the salt. The streamers resemble closely the currents of a liquid descending into, and partly mixing with, a less dense liquid. There is constant swirling motion; the streamers enlarge at the front end and move downward in a rather erratic manner, often changing their course, and sometimes dividing, or even disappearing, when they meet currents of displaced liquid streaming upward (*see* Plates 14–16).

Figs. 3, 4 and 5 (Plates 14–16) show what happens when salt and albumen solutions are mixed in a narrow cell, $1\frac{1}{2}$ mm. wide, 2 cm. deep, and 7 cm. long, the solutions being introduced separately into the two ends and kept apart till the moment of mixing by a narrow vertical barrier. In fig. 3 the albumen was slightly denser than the salt, and simply flowed underneath it. A few slight irregularities in the surface are due to the vortices of case 3 above. In fig. 4 initially the albumen was of nearly the same density as the salt, and in this case also it flows under the salt without intertraction; but the times show clearly that the flow is slower than when the albumen is initially the denser. Evidently the albumen becomes denser than the salt, through contact with it, but an appreciable time is necessary for the density difference to become great enough to move the liquids. The slight initial disturbance in the photograph is due mainly to a slight leakage through the barrier before the moment of mixing. In fig. 5, where the albumen is initially less dense than the salt, the albumen begins to run over the top of the salt, but cannot remain there, and streams down rapidly to the bottom. Mixing by the streamers was not quite complete; at the end of 30 minutes the lower 4 mm. of the cell was distinctly deeper in colour than the remainder.

Direct observation of the increase in density of an albumen solution through

contact with a salt solution was also made. In one experiment, albumen of s.g. 1.034 was pipetted carefully to the bottom of a beaker containing salt of s.g. 1.032, and removed after two minutes standing. Its density had been increased to 1.0365. In this experiment the albumen was in a layer about 8 mm. deep, and the increase in density represents the average increase through this layer. Evidently much greater increases in density may be possible quite close to the boundary. Calculation from Stokes' law shows that a sphere of r mm. radius will fall through a liquid of the viscosity of water (taken as 0.0114) at a rate of $0.383 r^2$ cm. per second, if its density exceeds that of water by 0.002. The front ends of the streamers were generally of diameter 1 to 2 mm., and the rate of descent of some of the fastest streamers was observed, with the albumen and salt, to be about 1.7 mm. per second. Evidently the increase in density necessary to cause the observed rate of descent is easily attainable on the present explanation.

In all, we have used fifteen different pairs of substances, in aqueous or alcoholic solution; these are given, with their diffusion coefficients, obtained from Landolt and Börnstein's tables or Jellinek's 'Lehrbuch.' The substances were selected to give a wide range of diffusion coefficients and to be as various as possible in chemical properties. The solutions varied much in concentration; of a pair one was made up arbitrarily, and the other made up in several dilutions so as to give various differences of density. In some cases a pair of solutes was compared at several concentrations. Densities were determined with a small pyknometer without a thermostat and are accurate only to 0.001. In every case, streaming or "intertraction" was observed only when the more slowly diffusing solution was uppermost, and when the difference of density was not greater than about 0.05. From 0.02 downwards it was very marked.

In four cases where the coefficients of diffusion were nearly the same, no streaming could be observed, even when the difference of density was only about 0.005.

It is possible that, by properly taking advantage of this phenomenon, the amount of mechanical stirring required to mix pairs of fluids might be considerably lessened.

Pairs of Solutions giving Streamers when the more slowly diffusing Solution is Uppermost, the Density Difference being 0.03 or less.

Aqueous Solutions.—

CuSO_4 (0.28) and CoCl_2 (0.5).
 MgSO_4 (0.3) and CoCl_2 (0.5).
 CuSO_4 (0.28) and urea (0.92).
 CuSO_4 (0.28) and KNO_3 (1.2).
 Albumen (0.06) and NaCl (0.97).
 KNO_3 (1.2) and HCl (2.3).
 MgSO_4 (0.3) and HCl (2.3).

Alcoholic Solutions.—

Resorcin (0.36) and iodobenzene (0.81).
 Glycerine (0.35) and iodobenzene (0.81).
 Resorcin (0.36) and pyridine (0.89).
 Glycerine (0.35) and pyridine (0.89).

Pairs of Solutions giving no Streamers, whichever Solution is Uppermost, the Density Difference being 0.004 to 0.009.

CuSO_4 and MgSO_4 .
 NaCl and urea.
 Resorcin and glycerine (in alcohol).
 Pyridine and iodobenzene (in alcohol).

The figures in brackets are the approximate diffusion coefficients, at room temperature.

Negative Surface Tension.

One of us has recently* discussed the mechanism of the ordinary capillary phenomena, in order to examine whether there is any evidence that the molecules in the surface of a liquid form themselves into any structure which can be regarded as a contractile skin, producing the surface tension. It was concluded that there is no evidence of such a structure, and that it is improbable, or impossible, without assuming properties of molecules which are unknown in other states of matter; whereas it is possible to give a rational explanation of capillary phenomena, assuming no other properties of the molecules than size, attractive force fields, and thermal agitation, if the idea of a contractile skin is not introduced. The mechanisms suggested do not conflict with the idea

* 'Nature,' vol. 115, p. 512 (1925).

of a special free energy resident in the liquid and proportional to its surface, and therefore are consistent with the classical theory of capillarity, except where this introduces a mechanical structure in the surface as the seat of the "surface tension."

The mechanism which tends to contract a liquid interface which possesses positive free energy or "surface tension" is that the molecules, being attracted inwards and perpendicularly to the surface by the underlying molecules, leave the surface for the interior, and since the molecules possess size, the surface must diminish. This inward force, at an interface between two liquids, acts to restrain diffusion of the molecules of one liquid into the other. "Negative surface tension" is properly the becoming negative of this inward attractive force on the surface molecules. If it could exist at the free surface of a liquid, it would be a force tending to drive the molecules away from the liquid into the vapour. At the interface between two liquids it would be a force driving the molecules of one liquid into the other, or an attraction of one fluid for the molecules of the other greater than the attraction of these molecules for the other fluid. It is therefore properly manifested as a diffusion of one liquid into the other.

The passage which Schoneboom quotes from Clerk-Maxwell's article* cannot be considered to be a prediction of the "intertraction" phenomenon, since this is not due to capillary forces, as we have shown. It does, however, show, in a striking way, the difficulties into which one is led, if the surface of a liquid is regarded as being a kind of membrane in tension. After discussing the mathematical expression for the free energy at the interface between two liquids, Maxwell considers what will happen if the expression becomes negative, and concludes that "the displacement of the liquids which tends to enlarge the surface of contact would be aided by the molecular forces, so that the liquids . . . would at length become thoroughly mixed. No instance . . . has been discovered, for those liquids which mix of themselves do so by the process of diffusion, which is a molecular motion, and not by the spontaneous puckering and replication of the bounding surface, as would be the case if T (the surface tension) were negative." There would be no probability of the "puckering and replication" process, if there were no surface bounding membrane. And if there is no bounding membrane in a liquid, diffusion becomes, as we have seen, the normal manner of mixing, as the interfacial tension becomes zero or negative.

* 'Works,' vol. 2, p. 553; 'Ency. Brit.,' Art. on "Capillary Action."

Summary.

The so-called "intertraction" phenomenon between two solutions only occurs (1) if the solutions are placed one above another and not side by side; (2) if there is a difference in the rates of diffusion between the solutes in the two solutions. Quite different phenomena are observed if (a) the faster, (b) the slower, diffusing solution is uppermost.

Regular streaming as described by Sir A. Wright only occurs if the slower diffusing solution is uppermost; the movements when the faster diffusing constituent is above mainly occur in each layer independently, but eddies may result in a comparatively small amount of mixing of the two layers.

The movements are due to the hydrostatic equilibrium of the layers being upset by the diffusion of the solutes across the interface at different rates. They occur in alcoholic as well as aqueous solutions. Intertraction is not in any way due to capillary forces.

Negative surface tension means that those forces of cohesion perpendicular to the interface, which act when there is positive surface tension to restrain the diffusion of molecules away from the interface, become negative. It is properly manifested in diffusion away from the body of the liquid.
