Physiology. — *"On the spontaneous transformation to a colloic state of solutions of odorous substances by exposure to ult violet light."* By Prof. H. ZWAARDEMAKER and Dr. F. HOGEWI

(Communicated in the meeting of April 26, 1918).

The literature contains a number of records concerning the spon neous transformation to a colloidal state of substances wh molecules contain a noticeably large number of atoms (BLIT colouring matters) or which are of a considerable molecular weig (J. TRAUBE[2]) alkaloids). As one of us had noted the spontaneo transformation of eugenol in glycerin, when these substances a rapidly mixed up, and had been able to establish at the sa time several details, we resolved to investigate more systematica the transformation of solutions of odorous substances in wat glycerin, and paraffin. After being rapidly mixed up, the solutic were allowed to stand for weeks and subsequently examined up Tyndall's effect and observed ultramicroscopically[3]).

It appeared that the following solutions yield a strong Tynd effect.

In water	*In glycerin*	*In paraffin*
Eugenol	Eugenol	Anilin
Cressol	Safrol	Eugenol
Guaiacol	Creosote	Cumidin
Carvacrol	Nitrobenzol	
Citral		
Cumidin	Cressol	
Thymol	Apiol	
Hypnon		

In this table the odorous substances have been arranged accordi to their degree of transformation. In a number of cases the oblique

[1]) BLITZ, Album J. v. BEMMELEN, 1910, p. 110 (boundary value between and 55 atoms)

[2]) J. TRAUBE, Int. Ztsch. f. Physik. Chem. Biol. Bd. I, p. 35, 1914 (bound value between 208 – 275 molecular weight).

[3]) The examination upon Tyndall's effect was performed in the light-cone o small electric arc-lamp, while watching the complete extinction of the obliqu

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diffused light has been measured after the method of KAMERLINGH ONNES and KEESOM[1]). The values of the quantitative determinations in the series of the aqueous solutions are in the ratio of 43 : 39 : : 37 : 20 : 15 : 15 : 10; in the paraffinous solutions 23 : 18 : slight.

Besides the above solutions also the aqueous solutions of apiol, creosol, paraxylenol, anysaldehyd appeared to yield a markedly distinct effect. The Tyndal phenomenon is fairly distinct in old aqueous solutions of xylidin, orthotoluidin, chinolin, durol. A moderate effect we discovered of old aqueous solutions of methylcinnamylate, paratoluidin, salicylaldehyd, naphtalin, cumarin, toluol, anthranil-acid methylester, benzylbenzoate. A very slight effect was evinced by aqueous solutions of safrol, vanillin, anthracene, nitrobenzol. Tyndall's effect did not appear in old aqueous solutions of iron, heliotropin, moschus, isomuscon[2]).

The solutions were fully saturated. This is, however, not necessary for odorous substances with a strong tendency for transformation such as eugenol, cressol, guaiacol, carvacrol etc.

In glycerin solutions the phenomenon is of less frequent occurrence. We demonstrated the absence of Tyndall's effect in a number of old solutions in glycerin of odorous substances, which, when dissolved in water, became colloidal within a few days. Also in a solution in paraffin transformation occurs rarely.

When there is hardly any solubility, Tyndall's effect cannot be expected in the long run with odorous substances, but also, even when e.g. fluorescence shows us that molecules are thrown into solution, transformation to the colloidal state is sometimes lacking altogether, even when the solution has been standing for a long time. Such is the case with heliotropin. Eugenol is the substance that, both in water and in glycerin, attains a more intense colloidal condition than all other odorous substances examined. Also in paraffin eugenol becomes colloidal; anilin, in this solvent, still more so.

Generally speaking, odorous substances becoming intensely colloidal

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diffused light by means of a Nicol prism in the large apparatus of ZSIGMONDI. The solutions in glycerin, however, could not be taken up in an ordinary cuvette, the stuff with which the quartz windows are fixed, being soluble in glycerin. In this case we therefore used Zeiss' paraboloid condensor, or a Leitz' darkground-condensor-cuvette.

[1]) KAMERLINGH ONNES and KEESOM, Acad. Amst. 29 Feb. 1908.

[2]) The list of odorous substances that are transformed spontaneously has since been lengthened considerably. Also the alkaloids that become at length colloidal in aqueous solutions, are very numerous. It is interesting to contrast with them the crystalloid condition of nearly all solutions of antipyretica (non-alkaloids).

have a greater molecular weight than those that are not transformed or hardly so; again, the former generally bring about a more considerable lowering of the surface-tension of water. For the solutions examined upon their Tyndall effect the number of droplets decreased in an orderly manner. Calling the number of droplets for pure water 49, that of eugenol is 90, crissol 80, carvacrol 80, citral 72, thymol 72, guaiacol 70, cumidin 65, hypnone 54. This series corresponds approximately with the one holding for Tyndall's effect. On the whole there is an orderly decrease in the power to produce a lowering of the surface tension between air and water, similar to that of the power to bring about a colloidal condition of the saturated or half-saturated solution.

When examining our solutions ultramicroscopically while standing for days and weeks, at various intervals, the number of submicrons appears to augment [1]) to the detriment of the amicrons, which formed the base of the cone. In strong colloid solutions there ultimately appears a precipitate, as in the case of eugenol. By the addition of $^1/_2$ n. sodium-carbonate solutions the markedly opalescent fluid at once becomes rather more translucent, in which process amicrons re-appear, this time to the detriment of the spontaneous submicrons previously formed.

Prior to and subsequent to transformation the surface-tension of the solution is approximately equal (with a eugenol solution 1 : 1500 fresh 67 and old 67 droplets for the stalagmometer volume). Also the smell-intensity is the same before and after transformation. Upon this basis we feel justified in terming the transformed odorous solutions "suspensoids". Exposed in the usual way in an U-tube to the action of a constant electric current, the particles in these suspensoids were all moved towards the anode. It follows then that the particles themselves must be negatively charged. The arm with the + pole was getting more opalescent, the one with the — pole cleared up.

After reversal of the current the previous state was restored. Likwise the previous intensity of Tyndall's effect is restored by mixing the contents of the two arms. The following table gives the quantitative relations of the light-intensities of the Tyndall effect of the solutions,

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[1]) The fluids, the colloidal as well as the fresh-prepared control fluids, were instantly filtered in the cuvette through a paper filter. Consequently with pure water only half a dozen submicrons at the most were discernible in a microscopic field. With water a base of amicrons was altogether lacking, similarly with the fresh control-fluids; but in the saturated or partly saturated solutions that through standing had been changed into suspensions, we discerned besides a base of amicrons a very large number of submicrons in active Brownian movement.

tabulated above, after allowing a current to pass through for one hour:

INTENSITY OF THE OBLIQUELY DIFFUSED LIGHT.

	Initially	At the — pole	At the + pole
Eugenol..........	37	33	41
Guaiacol.........	37	29	35
Cressol..........	24	19	23
Carvacrol........	20	16	24
Citral	20	16	22
Cumidin	15	12	18
Thymol..........	15	10	16
Hypnone.........	10	slight	16

After displacement of the micellae in the suspensoids through the influence of the current, the surface tension in the arm of the positive pole appears to become somewhat less than in the arm containing the negative pole.

NUMBER OF DROPLETS (CALLING THAT OF WATER 49).

	Previously	At the — pole	At the + pole
Eugenol.........	90	87	89
Carvacrol........	84	79	80
Cressol..........	80	78	79
Citral	73	71	74
Thymol....	72	70	71
Guaiacol.........	70	70	71
Hypnone	55	54	56

When heating an aqueous eugenol solution 1 : 1200 beyond 40°, the opalescence decreases, whereas it returns on cooling and after a few days becomes more intense than before. Below 30° no change occurs, even when the solution is maintained at 30° for 24 hours.

Similarly a colloidal solution of eugenol in glycerin appeared to be much less opalescent on hot summerdays than on cooler days preceding or following.

The gradual transformation of solutions of odorous substances beginning with the formation of amicrons, that develop into submicrons, appears to be largely influenced by light. When kept in the dark, the process is slow in aqueous solutions. There are even several substances, e.g. chinolin, in which it does not appear at all, but in which it comes forth distinctly in daylight. It should also be observed that the effect of ultra-violet light is much stronger than that of daylight [1]).

When exposing a eugenol-solution in a quartz test-tube at $^1/_2$ m. distance from the light of a mercury quartz lamp, opalescence is attained within half an hour, which otherwise is not arrived at in a fortnight. An electric arc-lamp has the same effect in a smaller degree. This quickening of transformation does not occur when the quartz-tube is enclosed in stanniol-paper. The same was observed with all other solutions. Even a heliotropin solution, ultramicroscopically empty, shows, after half an hour's radiation, numerous micellae.

Besides by the ordinary light-waves and the ultra violet rays, odorous substances can also be rendered colloidal by radiation with radium kept in vitro. In order to ascertain this we took two perfectly equal glass cuvettes with parallel walls, each filled with saturated odorous solution. In one of the cuvettes a closed glass tube was inserted, in which 200 mgrs of a mixture of radium- and barium-bromide containing 0,18 $^0/_0$ $RaBr^2$. If the experiment was performed with a saturated heliotropin solution, the control fluid remained ultramicroscopically empty, whereas the solution, in contact with the radium tube, showed in 24 hours a base of amicrons and 10 submicrons per microscopic field. Something similar occurred in a short time also with the other odorous solutions of the table, though with every following substance of the series more time was required to obtain a difference in dispersity between the radium-cuvette and the control-cuvette.

Not only the admitted electro-magnetic waves of the visible light, the ultraviolet light and the γ-rays of the radium, but also the mechanical energy is competent to give to a fresh-prepared, saturated multitomic odorous solution the energy needed for an amount of surface-energy sufficient for the formation of numberless amicrons and submicrons, to be observed in the gradually developed suspensoid. By shaking the fluid forcibly, transformation is largely promoted. In

[1]) Besides opalescence also fluorescence is generated. We are unable to decide whether there is any relation between light electricity and the observed highly accelerated transformation to a colloidal state. Cf. HELLWACHS on Light-electricity in Marx's Hab. d. Radiol. Vol. III p. 438.

a heliotropin solution e.g. that remained free from submicrons, even after standing for months, they appear in a rather large number directly after the old solution was shaken for some time in the closed cuvette. The same occurs with glycerinous solutions. Eugenol poured on glycerin without shaking renders the latter non-opalescent in five days. When it is vigorously shaken, however, the fluid is rendered slightly opalescent, and colloidal in the real sense of the word. It also retains its suspensoidal character in the subsequent phase of the process.

It is not likely that chemical energy should also come into play, since the process also takes place in chemically all but indifferent fluids, such as paraffin, though it must also be added that entire deoxidation of paraffin inhibits transformation also in ultraviolet light. However, there must be still another unknown source of energy, apart from the radiation of light and the mechanical energy, which supplies the newly generated micellae with surface-energy, with or without the aid of oxygen, since eugenol solution enclosed in a leaden casket, kept in utter darkness, becomes undoubtedly

TRANSFORMATION TO A COLLOIDAL STATE OF AQUEOUS SOLUTIONS IN THE ANILIN-SERIES.

	Molec. weight	Number of Atoms	Tyndall's effect
Anilin..........	93	14	hardly distinguishable
Toluidin........	107	17	rather distinct
Xylidin.........	121	20	" "
Cumidin........	135	23	distinct

ID. IN THE BENZOLSERIES.

	Molec. WEIGHT	NUMBER OF ATOMS	Tyndall's effect
Benzol..........	78	12	hardly distinguishable
Toluol..........	92	15	little distinct
Xylol...........	106	18	
Pseudocumol...	120	21	little distinct
Durol...........	134	24	rather distinct

suspensoidal within a few days. However, to obtain this, large dissolved molecules are required. This is clearly shown when comparing the terms of an homologous series inter se.

Odorous substances never have very large molecules. [1]) Therefore, there will never be an extremely strong tendency to form amicrons, subsequently submicrons, as soon as the supply of energy that may pass into surface-energy, is established. This accounts for the process being hitherto unobserved. But when working with much larger molecules, we may readily presume that the process of transformation is highly facilitated, and will show itself very distinctly, whenever electromagnetic waves, mechanical energy, or the unknown source of energy, suggested above, are present, from which the particles to be formed, derive their surface-energy.

[1]) The odorous substances examined by us, had a molecular weight between 78 and 199; the number of their atoms amounted to from 14 to 27, on the understanding that no multiple of the chemical formula should be taken.