

# SCIENTIFIC PROCEEDINGS.

## ABSTRACTS OF COMMUNICATIONS.

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#### I (818)

**On reversible emulsions and the role played by electrolytes in determining the equilibrium of aqueous oil systems.**

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The "oil-water" emulsion obtained by shaking equal volumes of olive oil and water with a sufficient amount of  $n/10$  NaOH to render the external aqueous phase alkaline to phenol phthalein, may be readily converted into a "water-oil" emulsion by shaking with a solution containing an amount of  $\text{CaCl}_2$  slightly in excess of the chemical equivalent of the NaOH employed in the preparation of the "oil-water" emulsion. The resulting "water-oil" emulsion may be re-converted into an "oil-water" emulsion by shaking with further additions of NaOH until the total amount of that substance in the system slightly exceeds the chemical equivalent of the  $\text{CaCl}_2$  previously employed.

When chemically equivalent proportions of  $\text{Ca}^{++}$  and OH are employed in a system containing equal volumes of oil and the aqueous phase, neither type of emulsion appears to predominate. At this critical point the system is in a state of extremely unstable equilibrium. Shaking with a trace of NaOH solution converts it almost instantaneously into an "oil-water" emulsion, while a trace of  $\text{CaCl}_2$  exerts the reverse effect, a "water-oil" emulsion being formed.

Magnesium functions in a manner similar to calcium, one ion being equivalent to two of OH; iron and aluminium exert a greater effect, one ion being equivalent to three of OH, at the critical point, provided equal volumes of oil and water have been employed. NaCl exerts no effect on a system of this type. If certain oil-water systems are slowly transformed through the critical point to water-oil systems or vice versa, figures resembling those in karyokinesis may be observed microscopically.

Bancroft<sup>1</sup> concludes that the production of a stable emulsion depends on the formation of a concentration film or membrane at all points of contact between the dispersed and continuous phases, and that the relative solubility of this film in the aqueous and oil phases and the consequent surface tension relations on its two sides determine the nature of the emulsion formed. From the above experiments it appears probable that positive ions adsorbed by a stabilizing fatty acid film render the later relatively more soluble in the oil or less soluble in the water phase thus lowering the surface tension on the oil as compared with the water side. The tension on its two faces being unequal, the membrane tends to develop a spherical curvature, the concave side being presented to the water and the convex side to the oil phase. This causes the production of a "water-oil" emulsion, the number and size of the water globules formed depending on the relative proportion of positive ions adsorbed by the film and the consequent differences in surface tension on its two sides. The adsorption of negative ions on the other hand renders the membrane more soluble in the aqueous phase, and consequently lowers the surface tension on that side causing the membrane to curve in such a manner as to present its concave face to the oil phase, an "oil-water" emulsion being formed. At the critical point the proportion of positive and negative ions adsorbed by the membrane must be such that the surface tension remains practically the same on both sides of the film which consequently fails to develop a curvature in either direction. Further support is lent to this point of view by the fact that the fatty acid salts of calcium, magnesium, iron, aluminium, etc., are relatively freely soluble in oil and relatively insoluble in water. In order to deter-

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<sup>1</sup> *Journal of Physical Chemistry*, 1913, 17, p. 501.

mine more accurately the relative capacity possessed by different positive ions to inhibit the solvent effect of negative ions on the stabilizing fatty acid film formed by contact between aqueous and oil phases, solutions containing varying proportions of positive and negative ions were run through oil from a Traube stalagmometer. By observing the relative number of drops formed by equal volumes of different solutions, or the concentration of solutions giving an equal number of drops, it was possible to determine the relative facility with which films of this nature were formed and maintained. It was found that equal volumes of  $m/1000$  NaOH,  $m/50$  Ca(OH)<sub>2</sub> and  $m/10$  Fe(OH)<sub>3</sub> gave an equal number of drops. Furthermore the concentrations of NaCl, CaCl<sub>2</sub> and FeCl<sub>3</sub> required to precipitate a sodium oleate solution were found to be .4 *M*, .02 *M*, and .004 *M*, respectively. Since these ratios of 100 : 5 : 1 are the inverse of those observed above, and since they represent approximately the logarithmic ratio observed by Hardy for the precipitation of negatively charged colloids by mono-, di-, and trivalent kations, it may be concluded that the maintenance of equilibrium of an aqueous oil system of this type depends upon the relative proportion of kations and anions present in the system and adsorbed by the stabilizing film and the extent to which the adsorbed kations, by counteracting the solvent action of adsorbed anions promote the continuity of the stabilizing film. From the experiments of Loeb, and his pupils, it must be concluded that di- and trivalent kations exert a far greater effect than monovalent kations in maintaining the equilibrium of biological systems. Since these ratios are frequently approximately logarithmic, the question suggests itself whether the positive ions concerned do not function by counteracting the destructive effect of negative ions on protoplasmic films or membranes in a manner similar to that indicated above for purely physical systems.