

DISCUSSION

Prof. H. R. Procter : I do not wish to criticise anything that has been said, but merely to add a small fact which has come to my knowledge, and which may be of interest to some people who have been engaged in the subject. We have been making experiments in my laboratory upon the surface tension lowering of solutions of sulphonated oils. That is a practical question in the leather trade, and also has general bearings. We have been making these experiments by the ordinary method of dropping a mineral oil below the surface of a solution of sulphonated oil, and we find that the surface tension is largely dependent upon the exact hydron concentration. It rises steadily with increasing hydron concentration up to a certain point, at which it reaches a maximum and then begins to diminish, so that there is a point somewhere between the alkalinity and acidity, a point in the wide region between the colour change of methyl orange and the colour change of phenolphthalein, at which the surface tension in this particular case is at a maximum.

Mr. E. Hatschek : I think that Mr. Bhatnagar's parallel between the reversal of phases in emulsions and the precipitation of suspensoids by electrolytes may be questioned, and there may be an alternative explanation. What the thing really turns on is the relative solubility of the fatty acid salt formed in water and in oil. The fatty acid salts of the tri- and some bi-valent cations are soluble in oil, while those of the univalent ones are soluble in water. If a film of oil-soluble soap is substituted for the film of water-soluble soap, it seems to me that reversal of the phases would naturally follow, provided both are present in sufficient amount. In this point, too, the parallel with suspensoids fails, as none exist in which the phase ratio even remotely approaches 1 : 1.

Prof. J. W. McBain : The results obtained by Mr. Bhatnagar show no parallelism between protective action and solubility of the soaps in aqueous phase. I have no knowledge of the relative solubilities in oil of the soaps examined; perhaps someone else has that information.

Prof. W. C. McLewis : I was particularly interested in one point Prof. Donnan raised, namely, that one could get a stable emulsion with two absolutely pure phases. I would like to ask Prof. Donnan for a little more information on that point, because I have got an idea that ultimately the stability will depend upon the presence of at least one further substance. Of course, in the case which Prof. Donnan cited, oil and water, under conditions in which the oil and water were extremely pure, you cannot avoid having the ions of water there, and I would like to know if his idea is that, even in that case, the ions would be the stabilisers. Another point with regard to emulsions in general: emulsions can be de-emulsified by the ions of electrolytes, and the de-emulsifying action depends upon the valency. Hitherto, of course, comparisons have been drawn in terms of concentration, *i.e.*, we have compared the de-emulsifying powers of various electrolytes of the same concentration, but the

idea which suggests itself to me is that we should compare electrolytes not at the same concentration, but at the same thermo-dynamic activity. I will not go into the question of thermo-dynamic activity, but, as you know, it has thrown a great deal of light on many other problems, and it seems to me that it is quite probable that work in other fields dealing with the measurement of thermo-dynamic activity of various ions might, if brought into the field of emulsions and of colloidal solutions, tend towards a revision of our knowledge as regards both coagulative and protective effects. There is one other point, and it is one raised by Mr. Clayton and one he would have dealt with had he been here. Nearly all emulsions and colloidal solutions are electrically charged and, as a rule, the ions with the opposite charge have a coagulating power. Mr. Clayton, however, considers that he has found a case in which a suspension can be coagulated by a colloid of the same electrical sign. If this is really the case, the observation becomes one of the greatest importance as it certainly would diminish greatly the value of the so-called electrical view of stability of dispersed systems. It has always been a moot point as to how far we should consider such phenomena as electrical or as capillary. Probably, ultimately we shall have to bring in both effects though, of course, that helps us very little at the present time, in view of the fact that the theory of electro-capillarity is so very little developed. In connection with Mr. Clayton's observation, I would draw your attention to the behaviour of a benzene emulsion. You can make an emulsion of benzene in water containing a very little gelatine and obtain a highly concentrated emulsion. The benzene is

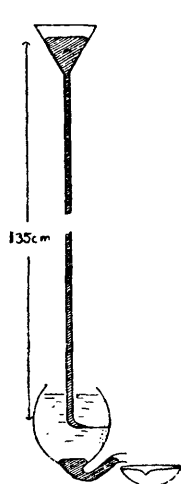


FIG. 1.

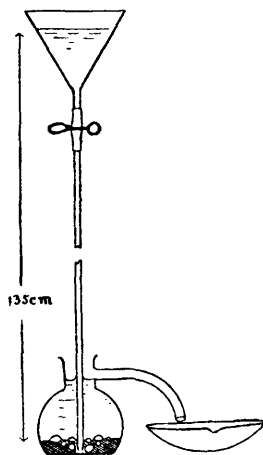


FIG. 2.

the disperse phase. Further, it can be shown that the benzene particles are negatively charged. This emulsion can be de-emulsified by hydrogen ion, and also by hydroxy ion. The effect of the hydrogen ion is to be expected; that of the hydroxyl ion is quite unexpected. In this case, however, the paradox is easily explained. What happens probably is that the caustic soda attacks the protecting gelatine, and the emulsion becomes de-emulsified by removal of the stabiliser and not by a direct action of the hydroxyl ion. How far other anomalies might be brought into line is an open question.

Dr. T. Svedberg : I should like to call attention to a special case in the emulsifying of mercury. The rather striking experience was made by a friend of mine, Dr. I. Nordlund, at Upsala. This experiment is of interest because it shows that there are two different methods of preparing emulsions of substances that have a very high surface tension. If mercury is pressed through a glass tube into water in form of a fine jet striking against a glass wall (Fig. 1), you get a mercury-water emulsion with rather coarse particles. On the contrary, if you press water through the mercury (Fig. 2), there are formed, as the water bubbles rise to the surface, thin membranes of mercury, and these lamellæ when bursting produce very fine particles. Thus a real, though very diluted, mercury hydrosol, pale yellowish-brown in colour, is obtained. In order to prevent coagulation and maintain the primary structure, a trace of potassium citrate should be added to the water (suitable concentration : 0.0025 normal).¹ I have repeated the experiment with oil and water, but in this case no difference was found between the products obtained by the two procedures.

Prof. Procter : With regard to Mr. Bhatnagar's paper, there is an extraordinary similarity between the structure he describes and the structure of connective tissue. The connective tissue consists of fibres, made up of small fibrils of about $1\ \mu$ in diameter, parallel to each other, and apparently these are not living cells. They have no nuclei, but seem to be produced by the cells which exist among them, and which possibly move along the fibres.