THE OXIDATION OF EMULSIFIED AND SOLUBILISED BENZALDEHYDE

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Carless and Nixon (1960) observed that when methyl linoleate was emulsified by cetomacrogol or potassium laurate, it oxidised at a rate greater than when it was solubilised. The rate of oxidation appeared to depend on the relative amounts of emulsified and solubilised oil present.

Subsequent work on the oxidation of aliphatic aldehydes in cetomacrogol solutions (Carless and Mitchell, 1962) supported this view. It was found that the oxidation rate depended on the saturation of the dispersion and not on the concentration of aldehyde and cetomacrogol, except in so far as these controlled the saturation. The degree of saturation of the dispersion was expressed as a Saturation Ratio (R) equal to X/Y, where X is the concentration of aldehyde present, and Y the concentration of aldehyde required to cause a saturated solution. Hence in a saturated solution R = 1, in an emulsion R > 1, whilst for a solution R < 1.

In an attempt to obtain further evidence we prepared an homologous series of pure ampholytic betaines of general formula

$$R-\overset{+}{N}\overset{\displaystyle Me}{\underset{\displaystyle Me}{\diagup}}CH_2COO^-$$
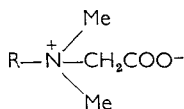
where R is a normal alkyl chain containing 8, 10, 12, 14, 16 and 18 carbon atoms. The rate of oxidation of benzaldehyde when solubilised and emulsified in aqueous solutions of these betaines, was investigated.

It must be emphasised that the term emulsion is used to cover all forms of dispersion in which oil is present in excess of its apparent solubility in aqueous soap solutions. Thus the term is used to cover not only the conventional definition of a dispersion containing two isotropic liquids, one being the continuous phase and the other the disperse phase, but also other dispersions of a more complicated nature containing an isotropic liquid or liquids with a liquid crystal phase.

Results and Discussion

Solubility curves of benzaldehyde in aqueous betaine solutions at 25° were determined by visual observation of the first turbidity. It was found that the apparent solubility of benzaldehyde decreased as the chain length of the soap increased. Examination of the dispersion under polarized light showed that the onset of turbidity marked the phase boundary between isotropic liquid and isotropic liquid plus a liquid crystal

phase.   Winsor (1954) has emphasised that phase changes, similar to those noted above, occur at decreasing amphiphile concentration when the molecular weight of the soap is increased.   Hyde, Langbridge and Lawrence (1954) have also stressed the importance of identifying the phases present.   Failure to do this has led to confusion in interpreting solubility data.
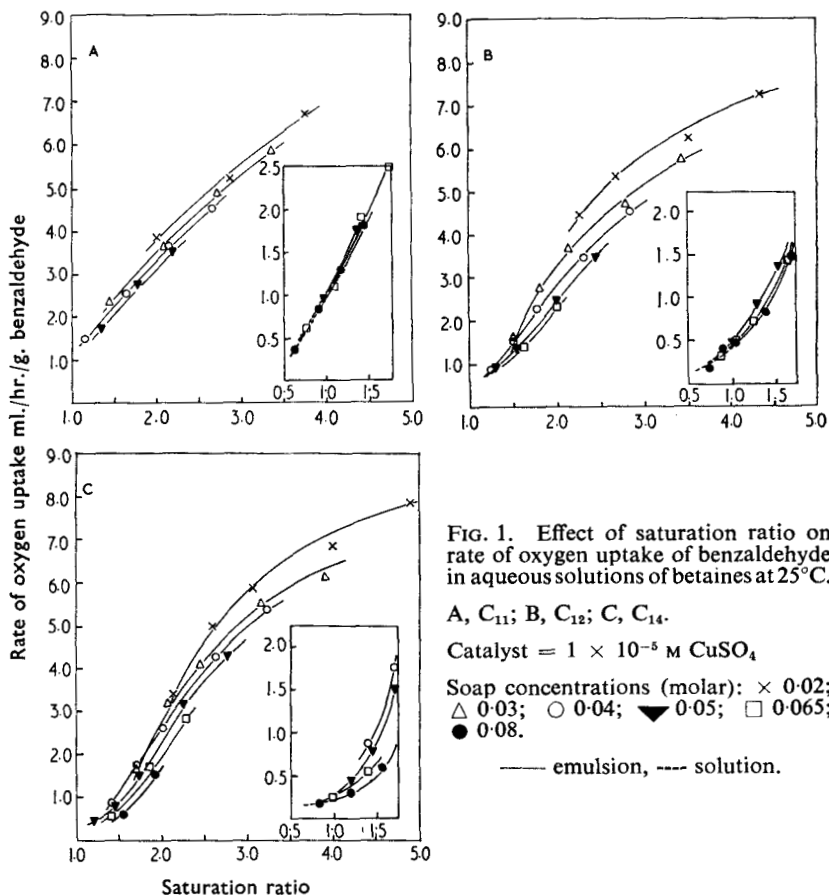

FIG. 1.   Effect of saturation ratio on rate of oxygen uptake of benzaldehyde in aqueous solutions of betaines at 25°C.

A, C_{11}; B, C_{12}; C, C_{14}.

Catalyst $= 1 \times 10^{-5}$ M $CuSO_4$

Soap concentrations (molar): $\times$ 0·02; $\triangle$ 0·03; $\bigcirc$ 0·04; $\blacktriangledown$ 0·05; $\square$ 0·065; $\bullet$ 0·08.

——— emulsion, ---- solution.

The rates of oxygen uptake of benzaldehyde in water/betaine mixtures at 25°, were determined manometrically as described previously by Carless and Nixon (1957).

The relation between oxidation rate and saturation ratio (R) is shown in Fig. 1, A, B and C for betaines C_{11}, C_{12} and C_{14} respectively.

In all three instances, increase in soap concentration for any one particular value of R results in a slight, but consistent, lowering of the oxidation rate.

These results, together with others obtained for aldehydes dispersed in potassium laurate and cetrimide (Mitchell, 1960), show that R is not

applicable to these dispersions. Thus, even though the concept of a saturation ratio applies in the case of aldehydes dispersed in cetomacrogol, we believe that R is not of a fundamental nature.

Work in this department (Mulley, 1961) and elsewhere (Hyde, Langbridge and Lawrence, 1954; Dervichian, 1957) indicates that a variety of phases are likely to occur in soap-water-amphiphile systems, together with associated changes in the physical properties of the components.

A complete ternary phase diagram, such as that of potassium caprate-octanol–water (Dervichian, 1957), shows that it is possible, by varying the relative proportions of the three components, to:

(a) change the phase or phases in existence,

(b) alter the composition of the phases, although the type and number of these remain the same,

(c) alter the relative proportions of the phases present, even though the composition, type and number remain constant.

Thus, although various mixtures of components of a ternary system, giving rise to two or more phases, may possess the same saturation ratio, they will not contain, in the same proportions, similar phases of identical composition.

We feel, therefore, that only from a consideration of the ternary phase diagrams for these systems will it be possible to relate oxidation rates to the concentration and nature of the oil present.

Work is now in hand to obtain the ternary phase diagrams for the betaine–water–benzaldehyde systems, in those regions where oxidation rates are being studied.

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