

PHASE EQUILIBRIA IN SOME BETAININE-BENZALDEHYDE-WATER SYSTEMS

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Received January 31, 1963

The phase equilibrium diagrams for six betaine-benzaldehyde-water systems have been determined at 25°, with particular reference to those phases in which future oxidation studies are to be carried out. A progressive increase in the amount of benzaldehyde solubilised in aqueous betaine solutions was found on increasing the betaine chain length from 8 to 11 carbon atoms. Further increase in the betaine chain length from 12 to 16 carbon atoms brought about a progressive decrease in benzaldehyde solubility. These results are discussed in the light of the phases separating at these solubility limits.

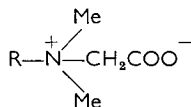
WORK by Carless and Mitchell (1962) showed that the oxidation of aliphatic aldehydes dispersed in cetomacrogol solutions depended on the saturation of the dispersion and not on the concentration of the aldehyde and cetomacrogol, except in so far as these controlled the saturation. Recent work by the present authors (Carless and Swarbrick, 1962) on the oxidation of benzaldehyde emulsified and solubilised in aqueous solutions of betaines showed that the rate of oxidation did not, in the systems examined, depend upon the saturation ratio *R*, as defined by Carless and Mitchell. Since therefore the conception of *R* did not appear to be of a fundamental nature we expressed the feeling that, due to the likely complex nature of the dispersions, it was only from a consideration of the ternary phase diagrams for these systems that it might be possible to relate oxidation rates to the concentration and nature of the oil present.

In the furtherance of this hypothesis we have determined the relevant parts of the ternary phase diagrams for six different betaine-benzaldehyde-water systems, in which the alkyl chain length of the betaine molecule contained 8, 10, 11, 12, 14 and 16 carbon atoms.

EXPERIMENTAL

Materials Used

Benzaldehyde. Analar benzaldehyde was distilled under reduced pressure and stored in ampoules, under nitrogen, in the dark until required for use. *N-Alkyl NN-dimethylglycines (Betaines).* These ampholytic surface active agents, of general formula



were prepared by the method of Beckett and Woodward (1963). Those homologues in which *R*, a normal alkyl chain, contained 8, 10, 11, 12,

14 and 16 carbon atoms were used. Distilled water was used in the preparation of all dispersions.

Determination of the Phase Boundaries

Dispersions containing two of the three components were prepared such that the percentage w/w of each was accurately known. All such two component dispersions lie on one of the three lines which form the boundary of the triangular diagram. A weighed amount of the third component was then added, dispersed by shaking and the whole system

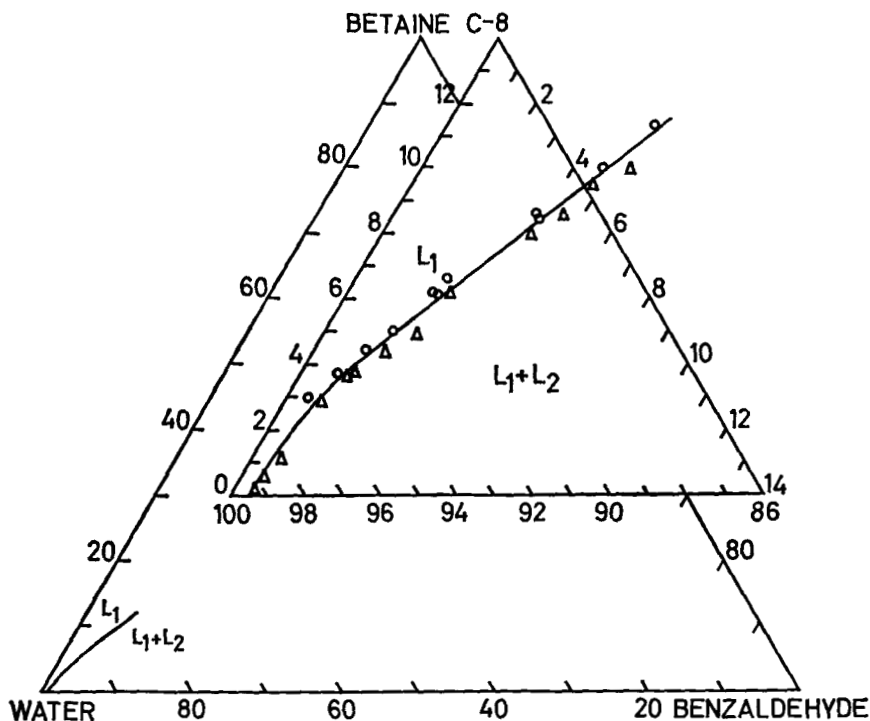


FIG. 1. System containing C_8 betaine.

- Dispersions found to contain phase L_1 .
- △ Dispersions found to contain phases L_1 and L_2 .

allowed to reach equilibrium at 25° . If necessary the system was centrifuged for 3 to 5 min. and re-equilibrated at 25° . The phases present were noted, the system redispersed, and centrifuged again. Only when the separated phases remained unchanged after being returned to the water-bath at 25° following centrifuging, was the system taken to be in equilibrium. The period of centrifuging was kept to a minimum since prolonged centrifuging causes an appreciable rise in temperature, thus altering the equilibrium of the system.

All dispersions were examined under polarised light, where a birefringent appearance denoted the presence of a liquid crystalline phase.

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The addition of known amounts of the third component was continued until a change in the number of phases occurred. Calculation of the weight percentage of each component present enabled this phase change to be defined on the ternary phase diagram. Further known increments of the third component were then added and subsequent phase changes, if any, plotted on the triangular diagram.

The above procedure was repeated with different mixtures of betaine and water, water and benzaldehyde and benzaldehyde and betaine. Benzaldehyde, betaine and water were used respectively as the diluents.

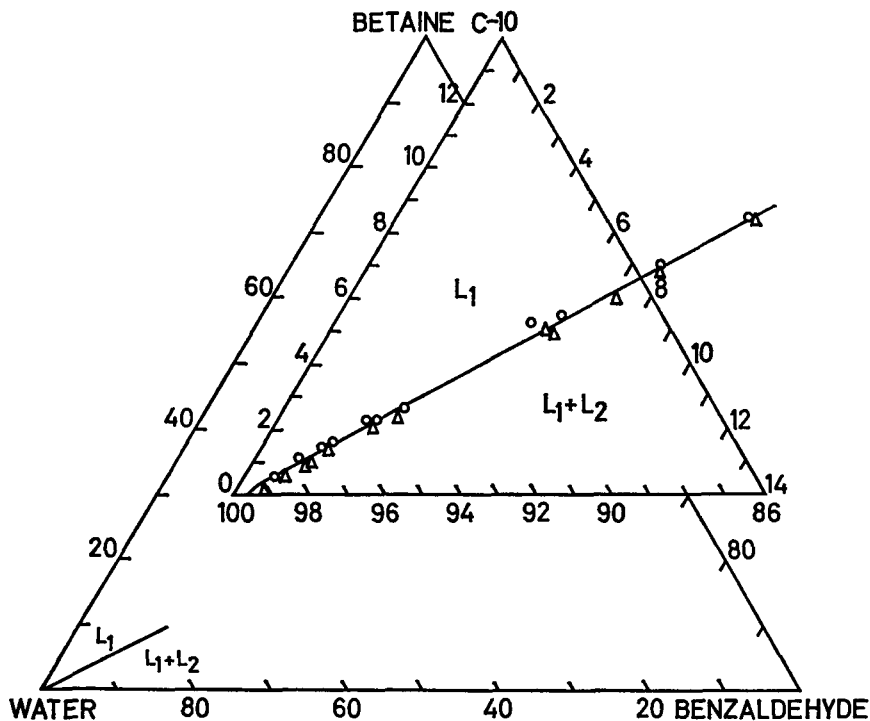


FIG. 2. System containing C_{10} betaine. Symbols as for Fig. 1.

The following terms are used in all subsequent discussions to depict the various phases found to exist in these systems. The region designated L_1 consists of isotropic liquid, the phase boundary being equivalent to the solubility curve for benzaldehyde in aqueous solutions of a particular betaine. L_2 describes a second isotropic liquid phase, the boundary in this case marking the limit of solutibility of water in benzaldehyde-betaine dispersions. The region $L_1 + L_2$ contains two isotropic liquid phases and is the only region where the conventionally defined emulsion is capable of existence. LC denotes an anisotropic liquid crystalline phase, or mesophase, which is intermediate in structure between the liquid and crystalline states. The molecules of the liquid crystalline

phase possess an ordered, laminar arrangement. The phase has a birefringent appearance under polarised light. The region $L_1 + LC$ contains both an isotropic liquid phase L_1 and a liquid crystalline phase LC . The triangular, ternary phase region contains all three phases and is therefore designated $L_1 + L_2 + LC$. Winsor (1954) has used the terms S_1 , S_2 and G to describe the phases denoted here by L_1 , L_2 and LC .

All systems are referred to by the length of the alkyl chain of the betaine homologue they contain. Thus the system betaine C_8 -benzaldehyde-water is denoted by the term C_8 .

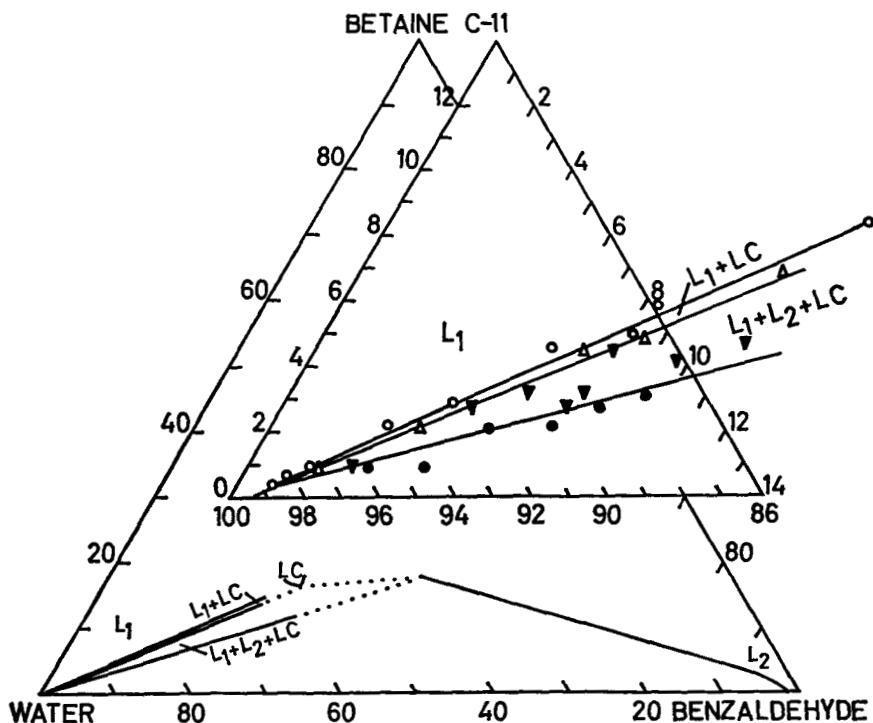


FIG. 3. System containing C_{11} betaine.

- Dispersions found to contain phase L_1 .
- △ Dispersions found to contain phases L_1 and LC .
- ▼ Dispersions found to contain phases, L_1 , L_2 and LC .
- Dispersions found to contain phases L_1 and L_2 .

RESULTS

Since no quantitative determinations of the composition of the phases present were attempted in the present work there was no need to achieve complete separation of the phases. However a certain degree of separation was necessary in order to determine both the number and type of phase present. Normally, dispersions separate into their constituent phases if allowed to stand at the equilibrium temperature for a period of hours or perhaps days. Unfortunately, this technique was not

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permissible with the dispersions examined here since the benzaldehyde is prone to oxidative attack. Prolonged standing would therefore have led to appreciable decomposition in some samples with a consequent reduction in the weight of benzaldehyde present. This, coupled with the appearance of by-products of the oxidation, would be likely to cause a shift in the position of the phase boundary. This effect has in fact been noted when old samples of benzaldehyde have been used. The addition of an antioxidant was not favoured since this would set up a four component system which would probably affect the phase equilibrium of the system.

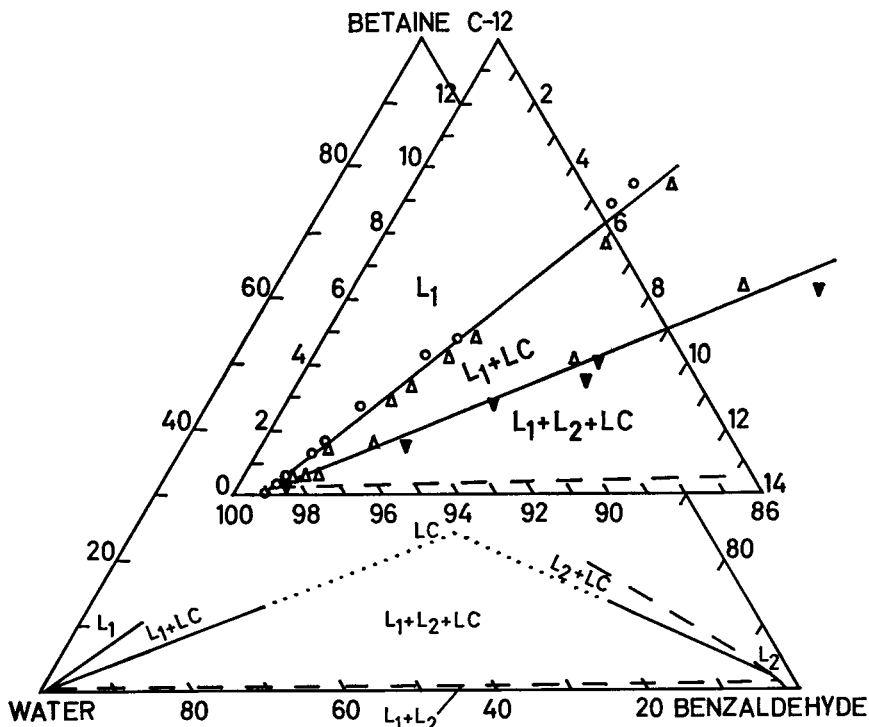


FIG. 4. System containing C_{12} betaine. Symbols as for Fig. 3.

The dispersions were therefore centrifuged and re-equilibrated as previously described in order to achieve separation as quickly as possible. Even so, in those dispersions containing appreciable amounts of the rapidly oxidising organic phase L_2 , some loss of benzaldehyde must have taken place. This means that some phase boundaries could not be defined as accurately as others. For example, the extent of the L_1 and the $L_1 + LC$ phases were determined accurately and were reproducible, whereas the $L_1 + L_2$ boundaries were not so well defined.

Therefore, in the accompanying figures a continuous line has been used to denote an accurately determined phase change. Those cases

determined with less certainty are shown by broken lines. The region containing L_1 , L_2 and LC is triangular, the compositions of the three phases being given by the three corners of the triangle. If the slopes of the lines constituting this region are known, the corner points of the triangle can be calculated by extrapolation. All assumed phase boundaries of this type are shown by dotted lines.

In Figs. 1 to 6 the triangular insert is an enlargement of the lower left hand corner of the main diagram. The experimentally determined

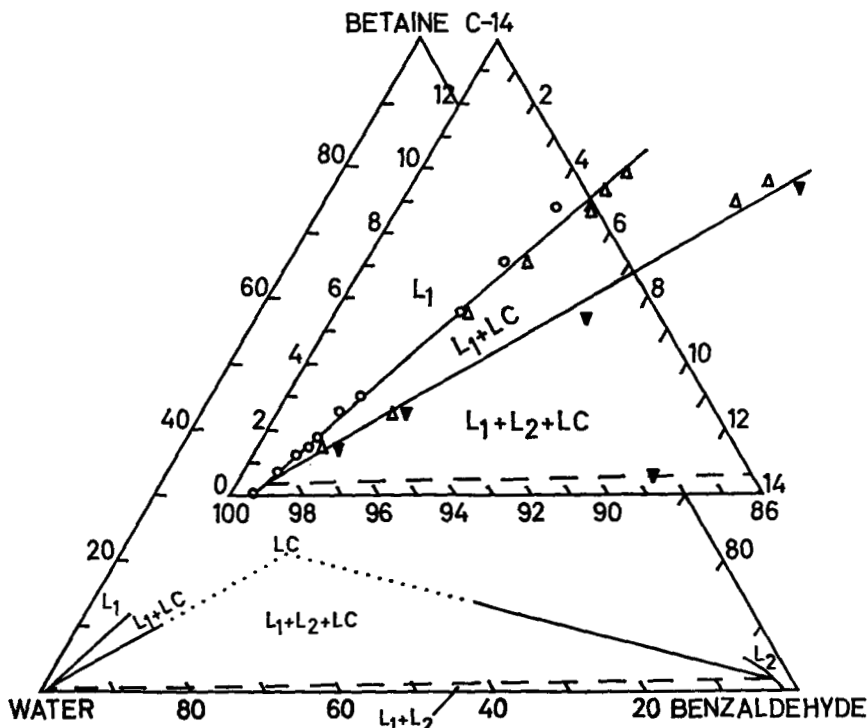


FIG. 5. System containing C_{14} betaine. Symbols as for Fig. 3.

points which have been used to define the phase boundaries are shown therein.

In the systems C_8 and C_{10} (Figs. 1 and 2) no liquid crystalline phase was observed. Thus all dispersions prepared in which the benzaldehyde was in excess of its solubility, when present in an aqueous solution of betaine, contained the two liquid phases, L_1 and L_2 . It was found that the solubility of benzaldehyde increased when the alkyl chain, R, of the betaine was increased from 8 to 10 carbon atoms.

In the C_{11} system (Fig. 3) still more benzaldehyde was solubilised for the same weight percentage of betaine than in the above two systems. Further addition of benzaldehyde above the limit of the L_1 phase led to the

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formation of a narrow $L_1 + LC$ region, as distinct from the two liquid phases formed in systems C_8 and C_{10} . In addition a small triangular three phase region, $L_1 + L_2 + LC$, was found.

Some uncertainty exists as to the exact nature of the phases occupying the large area below the $L_1 + L_2 + LC$ triangle. On occasions three liquids have been observed, although the third liquid may be a non-birefringent liquid crystalline phase. No attempt was made to investigate this region.

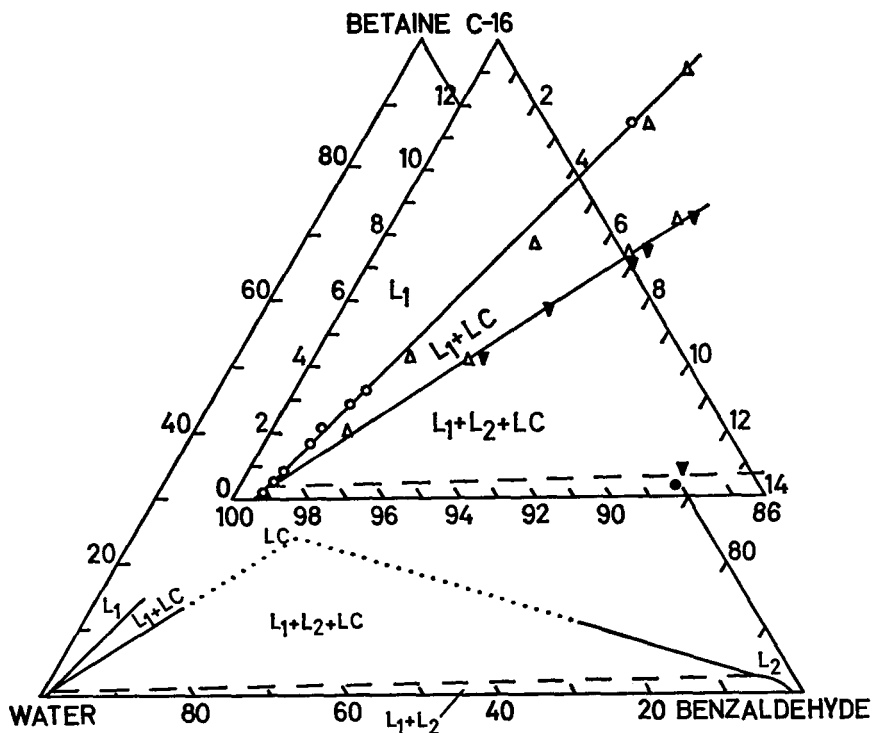


FIG. 6. System containing C_{16} betaine. Symbols as for Fig. 3.

Fig. 4 denotes the phase equilibrium boundaries which exist within the C_{12} system. When compared to system C_{11} (Fig. 3) it is seen that although the three phase region has been enlarged, the position of the $L_1 + LC/L_1 + L_2 + LC$ boundary has undergone but little change. The $L_1 + LC$ region has increased; however, at the same time, the extent of the L_1 phase has been reduced. Such a reduction is in contrast to the previous increases in the amount of benzaldehyde solubilised which occurred when the alkyl chain of the betaine molecule was changed from 8 to 10 and then to 11 carbon atoms.

In the systems C_{14} and C_{16} (Figs. 5 and 6) the aqueous solubility of benzaldehyde is progressively reduced as the higher betaine homologues

are used. Similarly, the appearance of the three phase region occurs at lower concentrations of benzaldehyde.

These results are best illustrated by reference to Table I, which shows the weight per cent of benzaldehyde necessary to cause phase changes in 5 and 10 per cent w/w aqueous solutions of the respective betaines at 25°. The weight per cent of benzaldehyde solubilised in the latter solutions are plotted against the number of carbon atoms in the betaine alkyl chain in Fig. 7.

TABLE I
WEIGHT PER CENT OF BENZALDEHYDE NECESSARY TO CAUSE PHASE CHANGES IN AQUEOUS BETAINE SOLUTIONS AT 25°

Ternary system	5 per cent w/w betaine		10 per cent w/w betaine	
	Weight per cent benzaldehyde		Weight per cent benzaldehyde	
C ₈	1.9*	—	5.0*	—
C ₁₀	5.7*	—	11.2*	—
C ₁₁	7.8†	8.6‡	15.3†	16.3‡
C ₁₂	3.8†	9.0‡	6.7†	17.0‡
C ₁₄	3.0†	5.4‡	5.4†	10.3‡
C ₁₆	2.5†	4.8‡	4.4†	9.1‡

* denotes a L₁ → L₁ + L₂ phase change.
 † denotes a L₁ → L₁ + LC phase change.
 ‡ denotes a L₁ + LC → L₁ + L₂ + LC phase change.

Table II shows the concentrations at which phase changes were observed in the four binary betaine-water systems C₁₁, C₁₂, C₁₄ and C₁₆ examined. In each case the phase transition was from isotropic L₁ + LC, the concentration at which this occurred decreasing as the betaine chain length was increased.

TABLE II
PHASE CHANGES IN BINARY BETAINE-WATER SYSTEMS AT 25°

Binary system	Concentration betaine per cent w/w	Phase change
C ₁₁	47.7	L ₁ → L ₁ + LC
C ₁₂	43.1	L ₁ → L ₁ + LC
C ₁₄	34.4	L ₁ → L ₁ + LC
C ₁₆	24.2	L ₁ → L ₁ + LC

DISCUSSION

The term amphiphile is used to describe substances possessing, within the same molecule, distinct regions of hydrophilic and lipophilic character (Winsor, 1954). That these molecules have opposing solubility tendencies is due to the presence of both polar and non-polar groups. Such a description covers a wide range of substances from the short chain alcohols, amines and carboxylic acids to the longer chain ionic surface-active agents or soaps. Whilst Winsor refers to all such compounds as amphiphiles Lawrence (1961) prefers to exclude the surface-active agents and reserve the term for those substances which are insoluble or poorly soluble in water alone.

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It is necessary to distinguish between those amphiphiles which are either predominantly hydrophilic or lipophilic, and amphiphiles of intermediate molecular weight which show marked miscibility with both water and organic solvents. We define the former as O-amphiphiles and the latter as S-amphiphiles. O-amphiphiles are considered to be solutes which undergo "interaction solubilisation", a term suggested by Lawrence and Mills (1951), with the S-amphiphiles.

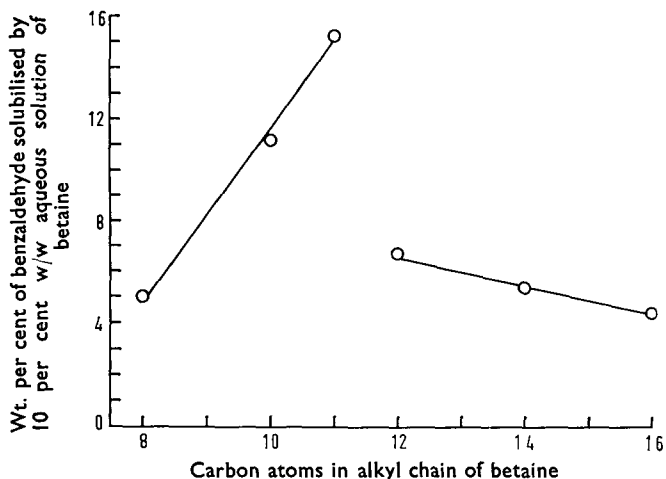


FIG. 7. Plot of weight per cent benzaldehyde solubilised in betaine solutions vs. the number of carbon atoms in the betaine alkyl chain.

Lawrence (1937) was the first to distinguish between the solubilisation of non-polar compounds and O-amphiphiles. With non-polar, water-insoluble materials such as hydrocarbons solubilisation takes place in the centre of the micelle. With O-amphiphiles, such as benzaldehyde, which is partially water-soluble, solubilisation occurs in the palisade layer of the micelle.

The continual addition of a non-polar liquid to an L_1 system containing micelles eventually causes the separation of another phase due to saturation of the interior of the micelles. The phase which separates contains excess non-polar liquid together with only negligible amounts of the other components of the system. When increasing amounts of an O-amphiphile are added the micelles themselves become sufficiently lipophilic, due to the inclusion of the additive in the palisade layer, to cause the separation of two phases (Klevens, 1950).

These effects are reflected in the behaviour of organic liquids when solubilised in aqueous solutions of S-amphiphiles of increasing molecular weight. In the case of non-polar organic liquids, Durand (1946) found increasing solubilisation of benzene by aqueous solutions of an homologous sodium n-alkanoate series, when the alkyl chain length was increased

over the range C_3 to C_{11} . Klevens (1950) has collected results for the solubilisation of ethylbenzene and n-heptane dispersed in solutions of potassium fatty acid soaps of increasing molecular weight which show a similar effect.

With O-amphiphiles a more complex variation in behaviour has been observed. Using different normal primary alcohols and amines, Harkins and Oppenheimer (1949) found, with most systems, an initial increase in the amount solubilised, which amount then tended to reach a constant value as the length of the fatty acid soap chain was increased further. With the C_{12} alcohol there was again an initial increase in solubility with increase in the length of the soap molecule, followed by a decrease with further increase in the number of carbon atoms in the fatty acid soap. These workers determined the solubility by a turbidimetric method, making the assumption that as the saturation point was exceeded the excess oil was emulsified; the solutions became therefore increasingly turbid. Unfortunately no attempt was made to identify the phases which separated. Both Hyde, Langbridge and Lawrence (1954) and Winsor (1954) have stressed the importance of identifying the nature of the phases separating in ternary systems since it is only when such phase changes are similar can valid comparisons as to solubility in different systems be made.

The complex variation in behaviour for liquid O-amphiphiles mentioned above is also shown by the betaine-benzaldehyde-water systems investigated in this paper. Fig. 7 shows that an essentially linear relationship exists between the weight of benzaldehyde solubilised and the alkyl chain length of the betaine up to, and including, the system C_{11} . Beyond this a decrease in solubility occurs but the relationship is still of a linear nature. This change in solubility coincides with the appearance of a relatively extensive $L_1 + LC$ region in the C_{12} system.

Lumb (1951) observed the formation of two isotropic liquid phases in equilibrium on the addition of octanol-1 to certain concentrations of potassium n-butyrate in water. Such a precipitation, according to Winsor (1954), resembles that in his Type I systems containing hydrocarbons. The apparent solubility of the alkanol in an alkanolate solution of given concentration would be expected to increase with the molecular weight of the alkanolate. The results obtained in this paper for benzaldehyde solubilised in systems C_8 and C_{10} are in agreement with this prediction.

In the systems C_{12} , C_{14} and C_{16} , the addition of benzaldehyde to aqueous betaine solutions leads to the precipitation of the two phases $L_1 + LC$, and a reduction in the solubility of the benzaldehyde. Winsor (1954) has noted that with certain polar organic liquids, where solubilisation is limited by the formation of such an $L_1 + LC$ system, an increase in the molecular weight of the surface-active agent produces a reduction in the apparent solubility of the solubilisate. The decrease in solubility found with the systems studied here is paralleled by the decreasing concentration at which the L_1 to $L_1 + LC$ phase transition takes place in the four binary systems C_{11} , C_{12} , C_{14} and C_{16} . It is presumably this transition

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in the binary system which reduces the solubility of benzaldehyde in the ternary system by progressively reducing the area of the L_1 phase.

In the system C_{11} the increase in the amount of benzaldehyde solubilised per CH_2 group has been maintained. However the nature of the phase change is such that, in the light of the previous discussion, a reduction in the apparent solubility of benzaldehyde would have been expected. The formation of the narrow $L_1 + LC$ region in this system has had, therefore, little or no effect on the amount solubilised.

As mentioned earlier a dispersion consisting of three liquid phases has been observed in this system, in an area where, with the higher betaine homologues, the ternary $L_1 + L_2 + LC$ triangle exists. A similar situation has been observed by Mulley and Metcalf (1961). It may be that the third liquid is in fact a non-birefringent liquid crystalline phase.

These facts suggest that system C_{11} is of a transitional nature and offer some explanation for the results obtained.

The relevant parts of the ternary phase diagrams discussed above were determined in an attempt to rationalise the study of the oxidation of benzaldehyde when dispersed in solutions of betaines. In previous oxidation studies it had been assumed that all material in excess of its solubility in aqueous solutions of surface-active agents formed dispersions containing two liquid phases. In the systems studied in this investigation such a situation was found to exist only when the C_8 and C_{10} betaine homologues were used. The presence of a liquid crystalline phase in the other systems studied obviously invalidates an assumption of this nature.

Investigations which are concerned with the effect of the different phases found in these systems on the oxidation rate of benzaldehyde will form the subject of future communications.

Acknowledgement. The authors wish to thank Dr. B. A. Mulley for many helpful discussions.

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