RESEARCH PAPERS

THE OXIDATION OF SOLUBILISED AND EMULSIFIED OILS

PART II. SOLUBILITY OF BENZALDEHYDE, CYCLOHEXENE AND METHYL LINOLEATE IN POTASSIUM LAURATE AND CETOMACROGOL SOLUTIONS

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The solubility of benzaldehyde, methyl linoleate and cyclohexene in solutions of potassium laurate and cetomacrogol is reported. A marked increase in the solubility of these water-insoluble materials was observed in solutions of potassium laurate above the critical micelle concentration (CMC). In cetomacrogol, the CMC could not be detected from inspection of the solubility curves, since the solubility was a function of cetomacrogol concentration over the entire concentration range studied. The solubility of methyl linoleate and cyclohexene was directly proportional to cetomacrogol concentration. The solubility curve of benzaldehyde showed a steep rise at low concentrations of cetomacrogol, and the possibility of this being due to a water soluble complex between benzaldehyde and cetomacrogol is discussed. The effect of temperature and the presence of sodium chloride on benzaldehyde solubility is reported.

IN a previous paper results of the oxidation of emulsified and solubilised benzaldehyde were presented[1]. These studies have been extended to cover the oxidation of methyl linoleate[2,3], and cyclohexene[3] in potassium laurate and cetomacrogol. As a preliminary to the study of their oxidation, the solubility of these "oils" in the two soaps was determined. The effect of temperature and addition of sodium chloride, on the solubility of benzaldehyde was also studied.

EXPERIMENTAL

Materials

Potassium laurate. Prepared from lauric acid and carbonate-free potassium hydroxide. Recrystallised from ethanol. *Cetomacrogol* (Texofor AIP, Glovers Chemicals Ltd.). Melting point 45° to 46°. Acetyl value 41·3. Other physical characters of this batch have been described[1]. *Polyethylene glycol "1300".* Prepared by melting together proportionate amounts of polyethylene glycols 600 and 1500 to give a product of average molecular weight 1300. *Benzaldehyde.* Analar benzaldehyde, redistilled under reduced pressure in an inert atmosphere was used, as in previous work[1]. *Methyl linoleate.* Prepared from cotton-seed oil by a bromination:debromination process, followed by esterification with methanol.[4] The ester was fractionated under reduced pressure and further purified by low temperature crystallisation from acetone. Wij's iodine number 263·6; iodometric peroxide value 30. The pure methyl linoleate used in oxidation experiments was found to have the same solubility

as this prepared material. *Cyclohexene.* Redistilled Analar material was used from which the peroxide had been previously removed with acidified ferrous sulphate.

Methods

General method. Known quantities of organic liquid were weighed into ampoules and the required quantity of surface active-agent solution
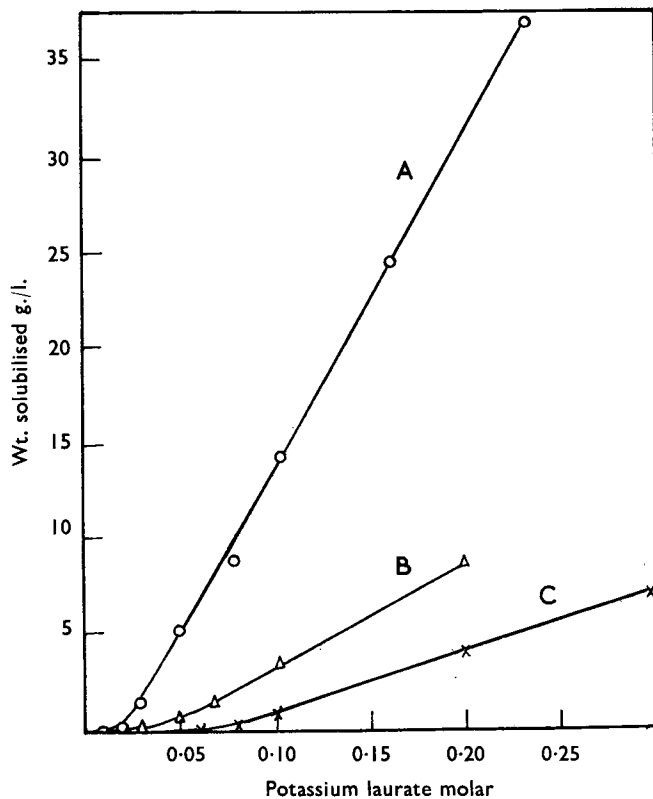

FIG. 1. Solubility* of benzaldehyde, cyclohexene and methyl linoleate in potassium laurate solutions at 20°. A, benzaldehyde; B, cyclohexene; C, methyl linoleate.

* Corrected for solubility in water.

and distilled water added from a burette. The ampoules were sealed by fusion of the glass and rotated for 5 hours at room temperature. They were then placed in a water bath at the desired temperature $\pm 0.05°$ for at least a further 2 hours before reading the end point, which was taken as the average between an under-saturated and an over-saturated solution. For low concentrations of soap, 100-ml. flasks closed with ungreased glass stoppers, were used instead of ampoules.

Determination of the solubility of methyl linoleate in potassium laurate. Methyl linoleate was rapidly soluble in concentrated solutions of potassium laurate. This allowed the preparation of stock solutions which

TABLE I

THE SOLUBILITY OF BENZALDEHYDE, METHYL LINOLEATE AND CYCLOHEXENE IN POTASSIUM LAURATE AND CETOMACROGOL SOLUTIONS AT 20°

Soap	Organic liquid	Concentration of soap M	Wt. solubilised g./l.*	Moles organic liquid/Moles soap
Potassium laurate	Benzaldehyde	0·01 0·02 0·03 0·05 0·07 0·10 0·225	0·04 0·16 1·56 5·32 8·98 14·44 36·76	0·04 0·07 0·49 1·00 1·21 1·36 1·54
	Methyl linoleate	0·03 0·06 0·08 0·10 0·20 0·30	0·02 0·11 0·28 1·15 4·29 6·95	0·002 0·006 0·012 0·040 0·073 0·079
	Cyclohexene	0·01 0·02 0·03 0·05 0·07 0·10 0·20	0·05 0·14 0·32 0·72 1·47 3·51 8·91	0·01 0·09 0·13 0·17 0·25 0·43 0·54
Cetomacrogol	Benzaldehyde	0·000051 0·000103 0·00103 0·00253 0·00507 0·0126 0·0439 0·1013	0·53 0·82 2·72 3·83 4·72 6·69 12·77 24·86	98 76 25 14 8·8 5·0 2·7 2·3
	Methyl linoleate	0·0028 0·0086 0·0207 0·0470 0·0998	0·16 0·43 0·94 2·43 5·23	0·19 0·17 0·15 0·17 0·18
	Cyclohexene	0·0005 0·001 0·005 0·01 0·05 0·10	0·04 0·16 0·59 1·06 5·27 10·47	1·1 2·0 1·4 1·3 1·3 1·3
Polyethylene glycol 1300	Benzaldehyde	0·005 0·01 0·03 0·06 0·10	0·25 0·51 1·65 3·25 6·05	0·47 0·48 0·51 0·51 0·56

* Corrected for the solubility in water.

could be diluted with further soap solution and distilled water to contain known varying amounts of methyl linoleate. These were then treated in the same manner as in the general method.

Determination of the solubility of methyl linoleate in cetomacrogol solutions. A constant weight of cetomacrogol was weighed into a number of 250-ml. glass stoppered flasks and varying quantities of methyl linoleate added. The stopper was inserted, the contents of the flask melted at 50° and gently shaken to disperse. The calculated weight of distilled

water was then added and the flask left in the constant temperature bath overnight. The end point was determined as previously.

RESULTS

The solubility of benzaldehyde in distilled water was found to be 3·45, 3·49 and 3·97 g./l. at 20°, 25° and 30° respectively. The solubility of cyclohexene was 0·13 g./l. at 20°. The water solubility of methyl linoleate was so low that it could not be detected.
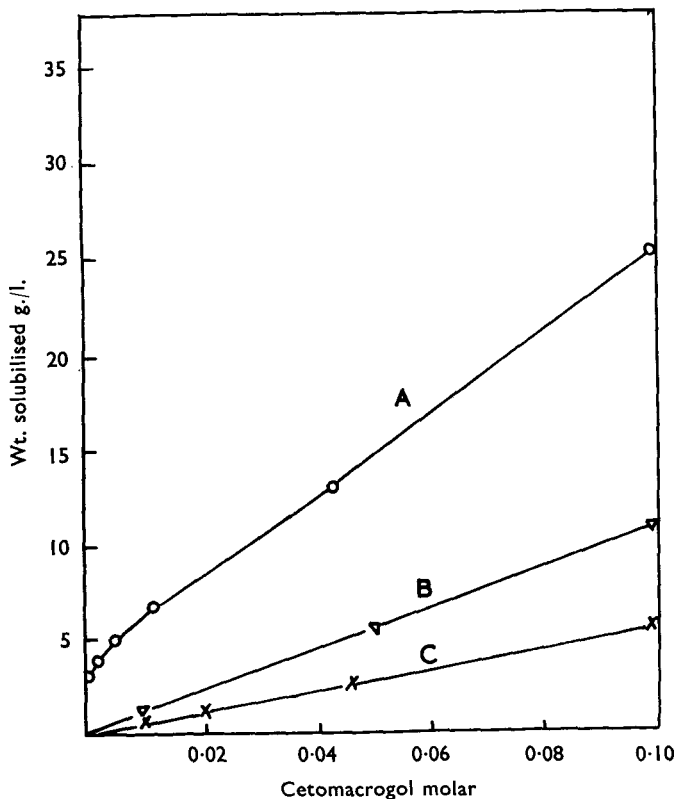

FIG. 2. Solubility* of benzaldehyde, cyclohexene and methyl linoleate in cetomacrogol solutions at 20°. A, benzaldehyde; B, cyclohexene; C, methyl linoleate.

* Corrected for solubility in water.

In solutions of potassium laurate the solubility of all three organic liquids began to increase at a soap concentration of approximately 0·03M and quickly became proportional to soap concentration throughout the range of concentrations studied (Fig. 1, Table I).

Within experimental error the solubility of methyl linoleate and cyclohexene was directly proportional to cetomacrogol concentration (Fig. 2). The increase in the solubility of benzaldehyde with increasing concentrations of cetomacrogol was greater at low concentrations but became

proportional to cetomacrogol concentration between 0·05 to 0·10M. In polyethylene glycol "1300" the solubility of benzaldehyde increased in direct proportion to the polyethylene glycol concentration.

The effect of temperature on the solubility of benzaldehyde is shown in Table II. In potassium laurate solutions the increase in the amount

TABLE II

THE INFLUENCE OF TEMPERATURE ON THE SOLUBILITY OF BENZALDEHYDE IN POTASSIUM LAURATE AND CETOMACROGOL SOLUTIONS

Soap	Concentration of soap M		0·01	0·03	0·07	0·10	0·225
Potassium laurate	Solubility* g./l.	20°	0·04	1·56	8·98	14·44	36·76
		25°	0·07	1·35	8·64	14·25	37·26
		35°	0·10	1·49	9·21	15·02	37·34
Cetomacrogol	Soap concentration Molar		0·002	0·005	0·013	0·044	0·101
	Solubility* g./l.	20°	3·83	4·72	6·69	12·77	24·86
		25°	4·12	5·17	7·62	15·03	30·62
		35°	0·01	0·08	2·73	9·88	29·74

* Solubility corrected for solubility in water at the appropriate temperature.

TABLE III

THE INFLUENCE OF SODIUM CHLORIDE ON THE SOLUBILITY OF BENZALDEHYDE IN POTASSIUM LAURATE AND CEOTMACROGOL SOLUTIONS

Soap	Concentration of soap M	Solubility* g./l. in		
		Water	0·1M NaCl	1·0M NaCl
Potassium laurate	0·05	5·3	9·3	10·0
	0·08	10·2	16·1	17·0
	0·10	14·4	19·8	21·5
	0·20	33·5	41·5	44·0
Cetomacrogol	0·005	4·8	4·9	5·0
	0·01	5·3	5·4	6·2
	0·02	7·8	8·0	9·3
	0·05	14·2	15·2	17·8

*Corrected for the solubility of benzaldehyde in the appropriate salt concentration.

dissolved is almost accounted for by the increase in the water solubility at the higher temperatures. In cetomacrogol the changes in solubility with temperature are slightly more complex. At 25° the amount of benzaldehyde solubilised increased at all concentrations of cetomacrogol but at 35° the initial rise in solubility was absent and the solubility did not rise above that in water until a concentration of approximately 0·004M cetomacrogol was reached. At higher concentrations of surface-active agent the increase in solubility was proportional to soap concentration and the slope of the curve was greater than that of the 25° solubility curve.

Sodium chloride was found to depress the water solubility of benzaldehyde. In 0·1M sodium chloride the solubility fell to 2·85 g./l. and in 1·0M sodium chloride it was 2·80 g./l. at 20°. However, the presence of salt caused an increase in the amount of benzaldehyde solubilised by a given soap concentration. This increase was much larger in potassium laurate than in cetomacrogol, Table III.

DISCUSSION

From the experimental results it will be seen that considerable amounts of benzaldehyde, cyclohexene and methyl linoleate are solubilised by the anionic and non-ionic soaps.

The solubility curves of the three materials in the anionic soap, potassium laurate, exhibit the form normally associated with solubilisation measurements. At low concentrations of soap the solubility is approximately the same as in water and it is only after passing the critical micelle concentration (CMC) that there is a rapid increase in solubility as is shown by the increase in the ratio moles solubilisate : mole soap. At soap concentrations of 0·07M and higher, this ratio approaches, but does not reach, a limiting value. This has been interpreted by Hartley[5] to indicate a continued increase in micellar size from the CMC to the point of almost constant molar ratio. At higher soap concentrations he envisaged an increase in the number of micelles with little further increase in size. The present results bear interpretation in this manner.

In solutions of cetomacrogol the solubility curves of methyl linoleate and cyclohexene are straight lines passing through the zero, but with benzaldehyde there was a rapid increase in solubility at low soap concentrations which decreased until it was proportional to cetomacrogol concentration. It will be seen, Table I, that the molar ratio benzaldehyde : cetomacrogol increases rapidly at low concentrations instead of falling as with anionic soaps. As pointed out by Stearns and others[6], molar ratio curves of this type are usually due to a failure to correct for the solubility of the organic liquid in water but in this work this correction has been applied.

Valko and Epstein[7] have reported an increase in the solubility of tripropyl phosphate below the CMC of sodium decyl sulphate. They suggested that this was due to the formation of mixed micelles, the increase in the solubility of tripropyl phosphate commencing at the CMC of the latter. There was no break in the solubility curve in the region of the CMC of sodium decyl sulphate. In the present studies the increased solubility occurred immediately soap was added but the break in the curve still occurred in the region of the CMC of the soap. Mixed micelles cannot therefore readily account for the present solubility results for benzaldehyde in cetomacrogol.

It has been suggested by Wurzschmitt[8] that non-ionic surface active agents exist either as a cationic form or as an equilibrium between a cationic and non-ionic form. He suggests that the cationic form could be written:

$$\left\{ \begin{matrix} H \\ \vdots \\ ROCH_2[CH_2OCH_2]_x[CH_2OCH_2]_yCH_2OH \end{matrix} \right\}^+ \quad [OH]_x^-$$

Wurzschmitt also found that cationic soaps form addition compounds with phenol and a number of instances have been recorded in the literature of complex formation between phenols and non-ionic soaps[9,10]. Mulley and Metcalf[10] consider that the acidic nature of the phenolic hydrogen accounts for the strong hydrogen bonding tendency of the phenolic

hydroxy group. The ultra-violet absorption method they used to show hydrogen bonding, is inapplicable in the present studies because the dilution required to produce a suitable benzaldehyde solution would render the aldehyde water-soluble, and changes due to hydrogen bonding with the soap would be masked. The hydrogen of the carbonyl group of benzaldehyde is much less acidic in nature and hydrogen bonds formed through it should be weaker than those with phenol.

A satisfactory interpretation of the results appears to be that in the non-ionic soaps, benzaldehyde forms a complex with the soap, this complex being more soluble than the benzaldehyde. Consequently there is a marked increase in solubility at low concentrations. When enough uncomplexed soap is present to form micelles the benzaldehyde is preferentially solubilised into the interior of these and a break in the curve results. The change-over does not take place suddenly but gradually as one mechanism of solubilisation takes over from the other. Further evidence for the formation of a complex is found in the increase in solubility of benzaldehyde in polyethylene glycol 1300 solution. This material does not form micelles and might be expected to show a normal solvent effect. Low concentrations have only a slight influence on the water solubility of benzaldehyde, but benzaldehyde solubility was found to increase proportionately to polyethylene glycol 1300 concentration as would be expected if a water soluble complex was being formed.

The effect of temperature on the solubilisation of benzaldehyde also indicates the possible formation of a weak hydrogen bonded complex. The slope of the solubility curve in cetomacrogol increases at higher temperatures, but at 35° the initial rise in solubility found at lower temperatures is absent and solubilisation begins at approximately 0·004M. The disappearance of the initial increase in solubility would be expected if it was due to a weak complex because an increase in temperature would split the complex so that no increase in the solubility of benzaldehyde would result until micelles are present. A concentration of 0·004M is higher than the CMC of cetomacrogol, 1×10^{-6}M, reported earlier[1]. Sjoblom[11] has found that the solubilisation of oestrone in the non-ionic Tweens does not begin until relatively high concentrations are reached, much higher than those needed to solubilise methylcholanthrene. Thus it appears that solubilisation in non-ionic soaps does not necessarily begin at the CMC, which is often indefinite, but at some higher soap concentration.

The presence of salts was found to increase the amount of material solubilised. Sodium chloride lowers the repulsive forces between the ionised soap molecules thus allowing formation of micelles at lower soap concentrations[12], and results in increased solubilisation. It is difficult to see how this argument can be applied to the increase in solubilisation in non-ionic systems unless the non-ionic soaps can exist in a cationic form.

Whilst observations of electrolyte effect on non-ionic soaps are rare, similar increases have been reported by McBain[13]. The increase in solubility with non-ionic soaps is smaller than with anionic soaps possibly

indicating an increase in size of micelle as was suggested by Hutchinson[12] and Kushner[14].

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