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Spectroscopic examination of the solubilisation of benzoic acid by a non-ionic surfactant

M. DONBROW* AND C. T. RHODES†

Ultraviolet and nuclear magnetic resonance spectroscopy have been used to examine the location of benzoic acid within the cetomacrogol micelle. Evidence has been obtained that the solubilised benzoic acid is probably located at the junction of the hydrocarbon nucleus and oxyethylene palisade layer, supporting the hypothesis advanced earlier on the basis of potentiometric observation.

SOLUBILISATION of organic acids by non-ionic surfactants has been examined in detail by the present authors using solubility and potentiometric methods (Donbrow & Rhodes, 1963a, b, 1964, 1965; Rhodes & Donbrow, 1965). The uptake of benzoic acid by the surfactant observes the Langmuir isotherm, which implies that the acid is located at a surface or pseudo-surface.

Since the micelles of non-ionic surfactants consist of a hydrocarbon nucleus surrounded by a palisade layer of hydrated polyethylene oxide chains, solubilised material could occur in three different regions: (1) within the hydrocarbon nucleus, (2) at the junction of the hydrocarbon nucleus and the palisade layer, (3) within the palisade layer.

Riegelman, Allawala, Hrenoff & Strait (1958) have suggested that ultraviolet absorption spectroscopy may be used to determine the location of solubilised material, as the ultraviolet spectra of many compounds are sensitive to changes in environment. Because micelles are characterised by possession of regions of different polarity, an estimate of the location of solubilised material within micelles can be made from ultraviolet spectra. The aqueous solubilities of the compounds examined by Riegelman and his colleagues were in most instances low. They were therefore able to assume that the ultraviolet spectra they measured in surfactant solutions were entirely due to micellar material. For more polar materials, such as benzoic acid, this assumption cannot be made. In the present paper, possible methods for overcoming this difficulty are proposed and the micellar ultraviolet spectrum of benzoic acid is presented.

The presence of solubilised material within the micelle would also be expected to modify the electronic environment of the protons associated with or influenced by the solubilisation process. Changes in the electron "screening" of protons may be observed by measuring the chemical shift of the protons by means of nuclear magnetic resonance spectroscopy (nmr).

Such changes in chemical shift should be most pronounced for the protons of the surfactant immediately adjacent to the solubilisate, and

From the School of Pharmacy, Chelsea College of Science and Technology, London, S.W.3 and the *School of Pharmacy, P.O.B. 517, Hebrew University, Jerusalem, Israel.

† Present address: Department of Pharmacy and Physiology, College of Technology, Portsmouth.

could be used to determine the location of solubilised material within the micelle; nmr data are presented and utilised here for this purpose.

Experimental

Materials. Benzoic acid* A.R.; cetomacrogol B.P.C.†, the mean molecular formula of which was shown by nmr to be $C_{16}H_{33}[C_2H_4O]_{24}OH$; spectroscopically pure cyclohexane and diethylether.

Ultraviolet spectroscopy. The ultraviolet spectrum of benzoic acid, between 250 and 300 mμ, was examined in the following solvents: 0·005N hydrochloric acid, cyclohexane, ether, 1, 5, 10 and 20% solutions of cetomacrogol and 10% solutions of polyethylene glycols 1500 and 3000. All spectra were obtained by use of a Unicam SP800 Recording Spectrophotometer (1 cm cell) and were rechecked using a Hilger Ultrascan (5 mm cell). In all instances the solutions contained about 0·0015M benzoic acid, which gave an absorbance of the order of 1·5 (1 cm cell). Aqueous solutions were acidified with hydrochloric acid. The reference cell contained the appropriate solvent or surfactant solution. Fig. 1 shows the spectra obtained. The spectral characteristics at the maxima are listed in Table 1.

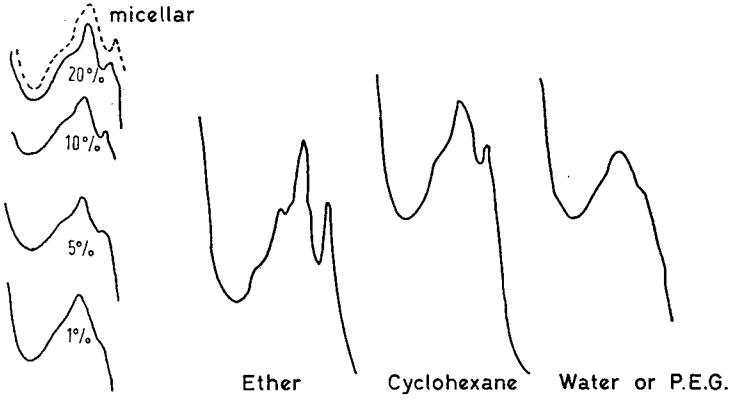

FIG. 1. Ultraviolet spectrum of benzoic acid (0·0015M) in 1, 5, 10 and 20% cetomacrogol solutions, and spectrum of benzoic acid in ether, cyclohexane and water or polyethylene glycol acidified with hydrochloric acid. Scales linear in absorbance (ordinate) and wavelength. (For λ_{max} and ϵ_{max} values see Table 1).

Nuclear magnetic resonance. The nmr spectrum of cetomacrogol, alone and in the presence of benzoic acid, was recorded in D_2O. Tetramethyl silane, in a capillary tube, was used as an external reference. A Varian Associates HR-60 high resolution spectrometer was employed. The changes in chemical shift of the signals of the alkyl protons and polyethylene oxide protons of the surfactant resulting from the presence of benzoic acid: Δ shift in cps, CH_2, 7; OCH_2, 3. Mean molecular

* Supplied by B.D.H. Ltd., Poole, England.
† Supplied by Evans Medical Co. Ltd., Bradford, England.

TABLE 1. ULTRAVIOLET ABSORPTION CHARACTERISTICS OF BENZOIC ACID (0·0015 M APPROX.) IN VARIOUS MEDIA (HILGER ULTRASCAN, 0·5 CM CELL)

Solvent	λ_{max} mμ	ε_{max}	λ_{max} mμ	ε_{max}	λ_{max} mμ	ε_{max}	λ_{min} mμ
Cyclohexane	275	1130	283	980	266–70s	—	258
Ether*	272	895	279	780	265 258s	730	252
Water†	273	990	280s	—	—	—	259
Cetomacrogol 20%†	273	890	280	730	265s	720	257
P.E.G. 1500 10%†	273	1010	280s	—	—	—	259
P.E.G. 3000 10%†	273	1020	280s	—	—	—	259

* Identical results are obtained in ether saturated with water at pH 2.
† Containing HCl to give pH 1·9 to 2·4.
s = shoulder.
P.E.G. = Polyethylene glycol.

formula of surfactant from integrated signals (Donbrow, Molyneux & Rhodes, 1966) $CH_3(CH_2)_{14}CH_2(OCH_2CH_2)_{24}OH$. All changes in chemical shift were upfield.

Discussion

Jaffe & Orchin (1962) state that the amount of vibrational fine structure observed in the ultraviolet spectrum of a compound in a given solvent is related to the degree of interaction between solvent and solute. In general, the degree of interaction increases with increasing polarity of solvent. From these considerations it would be expected that the amount of fine structure observed in the three solvents water, ether and cyclohexane would increase in the order stated. However, from Fig. 1 it can be seen that more fine structure was observed in ether than cyclohexane. This effect may be attributed to dimerisation of benzoic acid in cyclohexane, the intermolecular reaction repressing fine structure. Spectral evidence of dimerisation of benzoic acid in cyclohexane has been obtained by Forbes & Knight (1959) and the spectra in ether were attributed to the formation of a weak hydrogen-bonded ether-benzoic acid complex. The fine structure in ether is similar to that observed earlier by Ungnade & Lamb (1952) in dioxane and also in very dilute solutions of benzoic acid in cyclohexane, the latter showing a progressive loss of fine structure with increase in concentration as the proportion of dimer increased.

In surfactant solutions of benzoic acid the following equilibrium exists:

$$HA_m \rightleftharpoons HA_w$$

where HA_m is the benzoic acid bound by the micelles and HA_w is the free acid in the water. Fig. 1 shows that the amount of fine structure measured in cetomacrogol solution at constant benzoic acid concentration increases with increasing concentration of surfactant. This is to be expected since increase in the concentration of surfactant will increase the amount of acid bound by the micelles, HA_m, and reduce the amount of unbound material, HA_w. The spectrum observed in any surfactant solution will depend upon the relative amounts of HA_m and HA_w. For the purpose of location of a substance within the micelle we were interested

in the spectrum of HA_m. It is known from previous studies of the benzoic acid-cetomacrogol system that in 20% cetomacrogol solution HA_m is about ten times as large as HA_w (Donbrow & Rhodes, 1964). Thus the spectrum obtained in the 20% surfactant solution could be corrected to obtain the micellar spectrum. Alternatively, when information about the values of HA_m and HA_w was not available, extrapolation from the spectra measured in various strength surfactant solutions to a limiting value representing 100% surfactant enabled the spectrum of HA_m to be obtained.

Though there was evidence of light scatter at lower wavelengths, the peaks shown in Fig. 1 were presumably not appreciably distorted by scatter, since they were reproduced at different absorption cell to photocell distances, in different instruments and at different path lengths.

From Fig. 1 it can be seen that the spectrum of micellar benzoic acid shows much less fine structure than that observed in ether; furthermore the minimum is displaced by 5 mμ (Table 1). The ether spectrum is not affected by saturation with water. It is therefore improbable that the benzoic acid forms an ether-like solution in the palisade layer. Again, the spectrum of benzoic acid in 10% aqueous polyethylene glycol 1500 or 3000 solutions (which have an oxygen content similar to that of 20% cetomacrogol) closely resembles its spectrum in water and does not resemble the micellar spectrum. Hence it is unlikely that there is a similar mode of binding of the benzoic acid to the ethylene oxide groups in the surfactant and the polymer. Since the spectra in ether and polyethylene glycol are entirely different, it is clear that the benzoic acid does not form an ether-like solution in the polyethylene glycol; however, this result could be reconciled with a low affinity of benzoic acid for the polyethylene glycol, particularly as the spectrum in polyethylene glycol resembles that in water (see also Donbrow & others, 1966). In any event the spectral evidence does not support the view that organic acids are wholly located in the palisade layer of the micelles of nonionic surfactants.

The micellar spectrum of benzoic acid is similar to its spectrum in cyclohexane. It is likely that the loss of fine structure accompanying dimer formation is caused by inhibition of vibrational motion (see Jaffe & Orchin, 1962), and that the vibration of the benzoic acid molecules in their solubilised state is also restricted. However the maxima in cyclohexane are displaced bathochromically 2–3 mμ and the absorption is enhanced by about 30% (Table 1). This probably indicates that the micellar benzoic acid is not wholly dissolved in the hydrocarbon core of the micelle but is, at least partially, in a medium of higher dielectric constant.

Further evidence, of value in locating the solubilised benzoic acid, is obtained from the nmr results. If the solubilised benzoic acid were located within, or at the exterior of, the palisade layer it would be expected that the changes in chemical shift of the surfactant protons would be restricted to those of the palisade layer. Similarly if the benzoic acid were incorporated wholly within the hydrocarbon nucleus it would be expected

that the change in chemical shift would be limited to the alkyl protons. From the data it can be seen that though both types of proton show Δ shifts, the Δ shift value is much larger for the alkyl protons (7 cps) than for the polyethylene oxide protons (3 cps). Since the samples were treated in a routine manner, the 3 cps shift is of uncertain significance but the 7 cps is probably significant.

We have previously shown potentiometrically that the uptake of benzoic acid by the micelles does not accord with the possibility of dimerisation occurring in the micelle (Donbrow & Rhodes, 1964), although the method is intrinsically capable of detecting dimerisation and indeed such dimerisation does occur in cetomacrogol dispersions of benzene containing liquid crystal phase (Rhodes & Donbrow, 1965). It is therefore concluded that the most likely location of the solubilised benzoic acid is at the junction of the hydrocarbon nucleus and palisade layer of the micelle, with the lipophilic benzene ring enclosed within the nucleus and the hydrophilic carboxylic acid group protruding into the palisade layer. Benzoic acid so located would lack mobility because of the presence of the polyethylene oxide chains of the surfactant molecules. This location could also allow formation of a hydrogen bond between the acidic hydrogen atom and the innermost ether oxygen atom. It is suggested that these effects may be the cause of the comparative lack of fine structure in the ultraviolet spectrum of micellar benzoic acid.

The uptake of benzoic acid on an interior surface of the micelle, accompanied by a reduction of mobility, fits in with an adsorption model for the solubilisation of this substance. It would therefore account for the observance of the Langmuir isotherm by this and similar systems, which we reported earlier.

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