Oxidation of Aldehydes Solubilized in Nonionic Surfactants I

Solubility of Benzaldehyde and Methylbenzaldehyde in Aqueous Solutions of Polyoxyethylene Glycol Ethers

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The solubilities of benzaldehyde and *p*-methylbenzaldehyde in aqueous solutions of polyoxyethylene glycol ethers of varying polyoxyethylene chain length have been measured at 25°. Solubility increases with surfactant concentration and is greater for benzaldehyde than *p*-methylbenzaldehyde. The start of the solubility curve neither corresponds to the critical micelle concentration (CMC) of the surfactant alone nor to that of the ternary system. On a molar basis, solubility increases with an increase in hydrophilic chain length but decreases if solubility is expressed in terms of the amount solubilized per ethylene oxide unit. The solubility of benzaldehyde in a lauryl derivative is the same as in a cetyl derivative of the same polyoxyethylene chain length, whereas the solubility of methylbenzaldehyde is greater in the surfactant with the longer hydrocarbon chain. From the solubility data and an examination of the ultraviolet absorption spectra in aqueous surfactant solutions and other solvents, it is suggested that the solubilization of benzaldehyde occurs in the polyoxyethylene region of the micelle, while *p*-methylbenzaldehyde is distributed between this region and the hydrocarbon interior.

SURFACTANTS are widely used in the preparation of emulsions and solutions; increased attention is being directed to the stability of these systems toward hydrolysis (1–6) and oxidation (7–13). For certain systems, the rate of reaction depends on the degree of saturation, where this is expressed as a ratio of the amount of reactant present to its solubility (5, 6, 12). This paper reports the solubilities of benzaldehyde and *p*-methylbenzaldehyde in nonionic surfactants of the polyoxyethylene ether type and examines the effect on solubility of variation in chain length of the polyoxyethylene and hydrocarbon groupings as a preliminary to oxidation studies.

EXPERIMENTAL

Materials.—Benzaldehyde (British Drug Houses, analytical reagent grade) and *p*-methylbenzaldehyde (Eastman Organic Chemicals, practical grade) were distilled at low pressure under oxygen-free nitrogen using a Towers fractional distillation unit fitted with automatic reflux ratio control. The aldehydes were packed in clear glass ampuls under oxygen-free nitrogen and stored protected from light in a refrigerator. The ampuls had been cleaned previously in concentrated sulfuric acid, washed in water, and dried. The absence of impurities and decomposition products in each aldehyde was confirmed by infrared spectroscopy in carbon tetrachloride and vapor-phase chromatography on a Celite-silicone column, using an argon ionization detector.

The nonionic surfactants used were Texofors A16, A24, A30, A60, and B23 (Glovers Chemicals Ltd.). Texofors in the A series are polyoxyethylene ethers

of cetyl alcohol, represented by the formula CH_3-$(CH_2)_{15}(O\cdot CH_2\cdot CH_2)_n\cdot OH$, where n is approximatey 16, 24, 30, or 60. Texofor B23 is a polyoxyethylene ether of lauryl alcohol, where n is approximately 23. The values of n as given were used in calculating the molecular weight. For convenience, the cetyl alcohol derivatives will be designated C16, C24, C30, and C60; similarly, the lauryl derivative will be designated L23. Some physical constants of the surfactants are given in Table I. Concentrated stock solutions were prepared, stored in the dark, and diluted as required. Double distilled water from an all-glass still was used throughout. Polyethylene glycols having molecular weights corresponding to those of the polyoxyethylene chain of each surfactant were prepared by mixing appropriate amounts of polyethylene glycol 600 and polyethylene glycol 4000 (Union Carbide Co.).

Measurement of Solubility of Aldehyde in Water.—A saturated solution of aldehyde in water at 25° was prepared. The amount of aldehyde was determined gravimetrically as the 2:4-dinitrophenylhydrazone, according to the method of Iddles and Jackson (14). Assays of different known concentrations of aldehyde in water gave 100% precipitation as the 2:4-dinitrophenylhydrazone.

Measurement of Solubilities of Aldehydes in Texofor Solutions.—Varying amounts of aldehyde were weighed into a series of 25-ml. graduated glass-stoppered cylinders containing the required concen-

TABLE I.—PHYSICAL CONSTANTS OF NONIONIC SURFACTANTS

Texofor	Designation	$n^{25°a}$	$d^{25°b}$	M.p.[c]	CMC$^{25° d}$ $M \times 10^{-3}$
A16	C16	1.448	1.093	37	6–7
A24	C24	1.449	1.123	38	8–10
A30	C30	1.451	1.155	48	16–18
A60	C60	1.455	1.191	58	32–40
B23	L23	1.449	1.148	41	100–160

[a] Abbe refractometer. [b] Displacement technique in dry *n*-heptane. [c] Micro melting point apparatus. [d] From surface tension measurements using the Du Nouy tensiometer.
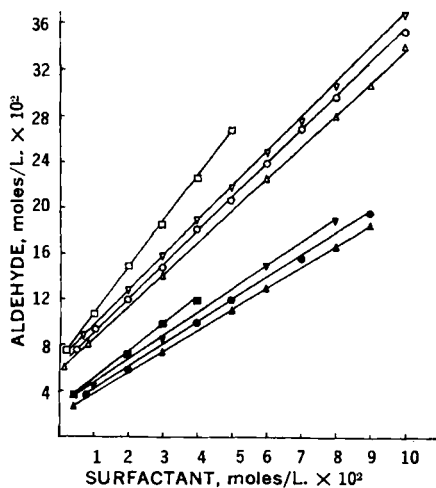
Fig. 1.—Solubilities of benzaldehyde and *p*-methylbenzaldehyde in aqueous solutions of polyoxyethylene glycol ethers of varying polyoxyethylene chain length at 25°. Open symbols, benzaldehyde; closed symbols, *p*-methylbenzaldehyde. Key: △, C16; ○, C24; ▽, C30; □, C60.

tration of Texofor. The cylinders were rotated in a thermostatically controlled water bath at 25 ± 0.01° for 24 hours. The end point was estimated visually and taken as the mean between a clear and cloudy dispersion.

Ultraviolet Spectra Measurements.—The ultraviolet spectra of benzaldehyde and *p*-methylbenzaldehyde in various solvents were determined with a Bausch & Lomb spectronic 505 recording spectrophotometer using short-path length cells.[1] Absorption by the solvent system was eliminated by using it in the comparison cell in all cases. Comparison between the various solvent systems was made on the basis of the relative positions of absorption maxima. Differences in the height of the curves are due to differences in solution concentration and path length.

RESULTS AND DISCUSSION

Solubilities of Aldehydes.—The water solubilities of benzaldehyde and *p*-methylbenzaldehyde at 25° were 6.55 Gm./L. (0.0617 M) and 2.27 Gm./L. (0.0189 M), respectively. The figure for benzaldehyde is considerably higher than previous literature values which range from 3.0 to 3.5 Gm./L. (15–18). The value in this report was therefore confirmed by a gas chromatographic technique (19). The solubilities of benzaldehyde and *p*-methylbenzaldehyde in surfactants C16, C24, C30, and C60 are shown in Fig. 1. Aldehyde solubilities are proportional to surfactant concentration and increase with the number of polyoxyethylene units in the surfactant molecule. The solubility of *p*-methylbenzaldehyde is less than that of benzaldehyde. Since each surfactant has the same hydrocarbon grouping, increase in aldehyde solubility on ascending the series C16 through C60 can be attributed to the increase in the number of polyoxyethylene units. Figure 2 shows the solubilities of benzaldehyde in solutions of poly-

ethylene glycols. Solubility increases with molar concentration and with increase in the molecular weight of the polyethylene glycol but is much less than in solutions of their surface-active derivatives. Polyethylene glycols are predominantly hydrophilic in character, and low solubilities in their solutions compared to surfactants may be due to the absence of micelles. Solubility in aqueous solutions of polyethylene glycols is thought to involve complex formation (20) and, although Kato (21, 22) has shown the presence of a micelle-like structure in aqueous solutions of a number of glycols, it would appear that the presence of micelles formed from molecules with both hydrophilic and hydrophobic properties is necessary for marked solubilization.

The solubilities of benzaldehyde and *p*-methylbenzaldehyde in low concentrations of C24 are shown in Fig. 3. There is a marked increase above the solubility in water in the region 1–10 × 10^{-3} M surfactant. This is well in excess of the CMC of C24 which, from surface tension measurements, was 8–10 × 10^{-6} M. Increase in solubility usually
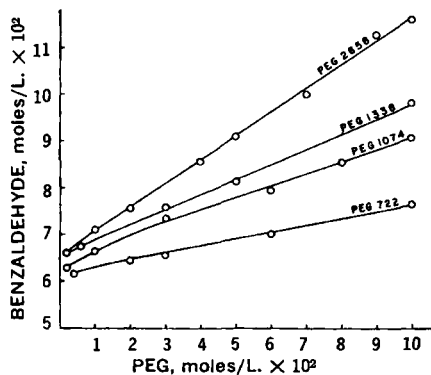

Fig. 2.—Solubility of benzaldehyde in aqueous solutions of polyethylene glycols (PEG) of varying molecular weight at 25°. In each case the number after PEG refers to the approximate molecular weight of a blend of PEG 600 and PEG 4000.
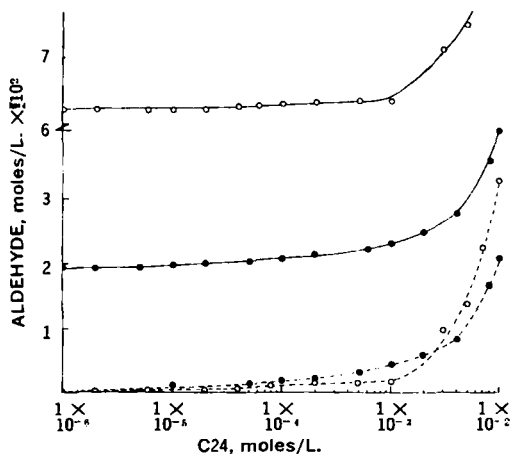

Fig. 3.—Solubilities of aldehydes in dilute aqueous solutions of C24 at 25°. Open symbols, benzaldehyde; closed symbols, *p*-methylbenzaldehyde. Key: - - -, corrected for water solubility; ———, uncorrected for water solubility.
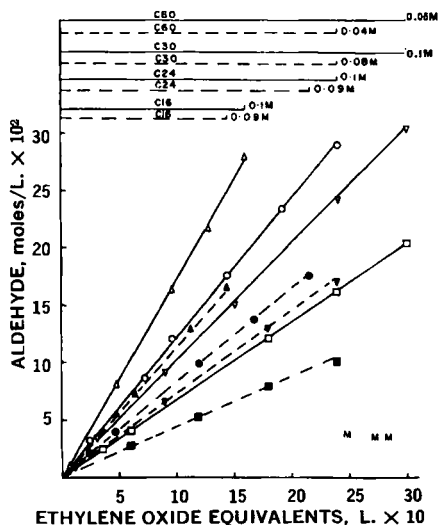
Fig. 4.—Solubilities of aldehydes in aqueous solutions of polyoxyethylene glycol ethers at 25° corrected for water solubilities, where the surfactant concentration is expressed as ethylene oxide equivalents per liter. Open symbols, benzaldehyde; closed symbols, *p*-methylbenzaldehyde. Key: △, C16; ○, C24; ▽, C30; □, C60.

begins at the CMC; for this reason, the onset of solubilization has been used as a method to estimate the CMC (23). A possible explanation for the discrepancy between the CMC and the start of the solubility curve is that the presence of aldehyde has increased the CMC. Both increases and decreases in the CMC of anionic and cationic surfactants have been found, depending on the nature and concentration of added solubilizate. These effects have been reviewed by Lawrence (24) and Hyde (25). Little evidence is available on the effect of solubilizates on the CMC of nonionic surfactants. Mulley and Metcalf (26) found that various solubilizates had little effect, even where strong interaction occurred between the solubilizate and nonionic surfactant. They suggested that large shifts in the CMC occur only where ionic effects are important, as shown by the effect of electrolytes (23, 27, 28). The CMC of solutions of C24 saturated with benzaldehyde was 32–40 × 10⁻⁶ *M*. This concentration is slightly greater than that of the surfactant alone but far less than the concentration of surfactant at which solubilization starts. It seems likely that the micelles must reach a certain degree of complexity before solubilization of benzaldehyde and *p*-methylbenzaldehyde can take place.

Figure 4 shows the solubility curves plotted as aldehyde concentration in moles per liter (corrected for water solubility) against surfactant concentration expressed as equivalents of ethylene oxide per liter. It is apparent from this method of expressing solubility that the efficiency of solubilization becomes less as the number of ethylene oxide units in the Texofor chain is increased. Goodhart and Martin (29) have reported a similar pattern for the solubilization of benzoic acid derivatives in nonionic surfactants. From light scattering (30–32) and vapor pressure measurements (33) several workers have shown that the micellar weight and the number

of surfactant molecules per micelle decreases as the ethylene oxide chain lengthens. It has been suggested that the origin of this effect lies in the increasing affinity of the monomer for water as the hydrophilic chain length increases, the hydrocarbon part of the molecule remaining constant. Furthermore, there appears to be little change in the radius of the micelle on increasing the number of ethylene oxide units. It appears that considerable curling of the monomer must occur when incorporated into the micelle, and this presumably takes place in the polyoxyethylene chain. Therefore, it seems likely that the decrease in efficiency of solubilization with an increase in the number of ethylene oxide units is associated with the accompanying decrease in micellar weight and number of surfactant molecules per micelle.

The effect of variation in hydrocarbon chain length of surfactant on solubilization was examined by comparing the solubilities in C24 and L23. From the solubility curves (Fig. 5) it is apparent that the solubility of benzaldehyde is not affected by variation in hydrocarbon chain length, while the solubility of *p*-methylbenzaldehyde is greater in C24, *i.e.*, the surfactant with the longer hydrocarbon chain. These results, together with the effect of variation in polyoxyethylene chain length on solubility, suggest that benzaldehyde is solubilized in the hydrophilic polyoxyethylene region of the micelle, while *p*-methylbenzaldehyde is distributed between both the hydrophilic and hydrophobic regions. Further evidence for these suggestions was obtained from a study of the ultraviolet absorption spectra of solutions of aldehydes in surfactants and other solvents.

Ultraviolet Absorption Spectra.—Riegelman and co-workers (34) have suggested that the ultraviolet spectrum of a solubilizate affords a sensitive method for determining its position within the micelle.

Spectra of benzaldehyde in various solvents are shown in Fig. 6. In solutions of C24 (curves 4–6) λmax. is at a wavelength longer than in *n*-heptane
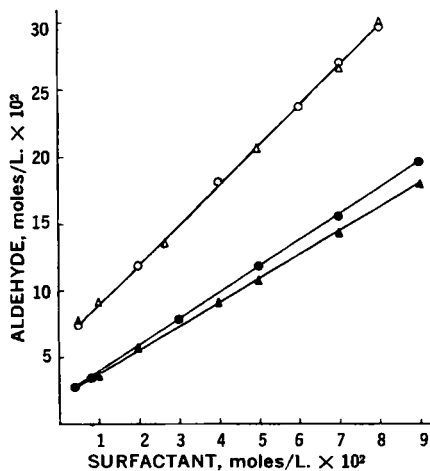

Fig. 5.—Effect of variation in hydrocarbon chain length of polyoxyethylene glycol ethers on the solubilities of benzaldehyde and *p*-methylbenzaldehyde at 25°. Open symbols, benzaldehyde; closed symbols, *p*-methylbenzaldehyde. Key: △, L23; ○, C24.

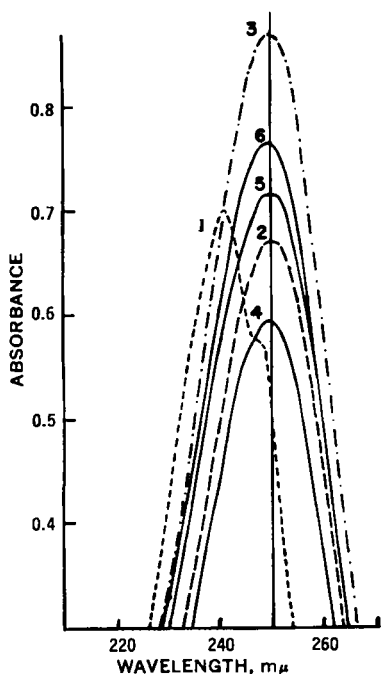Fig. 6.—Ultraviolet spectra of benzaldehyde in various solvents. Key: 1, heptane—0.00005 moles/L.; 2, water—0.00005 moles/L.; 3, PEG 1074 (0.02 M)—0.0685 moles/L.; 4, C24 (0.02 M)—0.00005 moles/L.; 5, C24 (0.02 M)—0.0685 moles/L.; 6, C24 (0.005 M)—0.0685 moles/L.
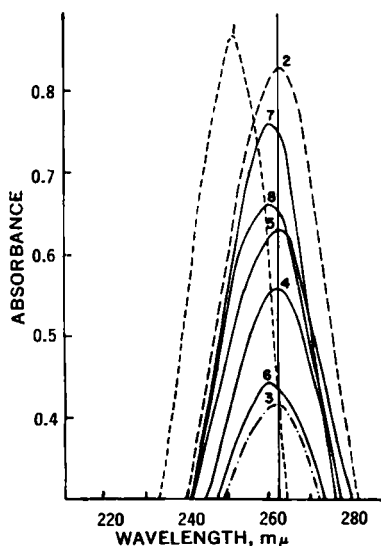

Fig. 7.—Ultraviolet spectra of p-methylbenzaldehyde in various solvents. Key: 1, heptane—0.00005 moles/L.; 2, water—0.00005 moles/L.; 3, PEG 1074 (0.02 M)—0.02 moles/L.; 4, C24 (1 × 10^{-7}M)—0.00005 moles/L.; 5, C24 (0.0002 M)—0.0210 moles/L.; 6, C24 (0.002 M)—0.0248 moles/L.; 7, C24 (0.02 M)—0.00005 moles/L.; 8, C24 (0.02 M)—0.02 moles/L.

(curve 1) and is identical to that in water (curve 2) and solutions of polyethylene glycol (curve 3); $\lambda_{max.}$ is not affected by the concentrations of benzaldehyde or surfactant (curves 4–6). Figure 7 shows the spectral curves of p-methylbenzaldehyde. In surfactant solutions below the CMC (curve 4) and also greater than the CMC but below the concentration at which solubilization begins (curve 5), $\lambda_{max.}$ is the same as in water (curve 2) and solutions of polyethylene glycols (curve 3). In the concentration range of surfactant at which solubilization starts (curve 6) and above this concentration (curves 7–8), $\lambda_{max.}$ for p-methylbenzaldehyde shows a shift of 2 mμ toward a shorter wavelength, *i.e.*, toward heptane (curve 1). These findings, together with the solubility data, support the view that solubilization of benzaldehyde in aqueous surfactant solutions occurs in the polar polyoxyethylene region of the micelle, while p-methylbenzaldehyde is located in both the polyoxyethylene region and in the hydrocarbon interior of the micelle. It appears that p-methylbenzaldehyde is taken up in the hydrocarbon interior from the start of solubilization since the surfactant concentration at which the shift in $\lambda_{max.}$ first occurs (curve 6, Fig. 7) coincides with the beginning of the solubility curve. Furthermore, the shift is found even when the aldehyde concentration is below its water solubility (curve 7), a demonstration that the aldehyde is preferentially soluble in the micellar pseudophase.

REFERENCES

(1) Riegelman, S., THIS JOURNAL, **49**, 339(1960).
(2) Nogami, H., *et al.*, *Chem. Pharm. Bull. Tokyo*, **8**, 1136 (1960).
(3) Nogami, H., Awazu, S., and Nakajima, N., *ibid.*, **10**, 503, 1158(1962).
(4) Mitchell, A. G., *J. Pharm. Pharmacol.*, **14**, 172(1962).
(5) *Ibid.*, **15**, 761(1963).
(6) *Ibid.*, **16**, 43(1964).
(7) Kern, C. J., and Antoshikiw, T., *Ind. Eng. Chem.*, **42**, 709(1950).
(8) Coles, C. L. J., and Thomas, D. F. W., *J. Pharm. Pharmacol.*, **4**, 898(1952).
(9) Patel, F. S. M., Kumpta, U. S., and Radhakrishna, M. V., *J. Sci. Ind. Res. India*, **14C**, 17(1955).
(10) Carless, J. E., and Nixon, J. R., *J. Pharm. Pharmacol.*, **9**, 963(1957).
(11) *Ibid.*, **12**, 348(1960).
(12) Carless, J. E., and Mitchell, A. G., *ibid.*, **14**, 46(1962)
(13) Carless, J. E., and Swarbrick, J., *ibid.*, **14**, 97T(1962).
(14) Iddles, H. A., and Jackson, C. E., *Ind. Eng. Chem. Anal. Ed.*, **6**, 454(1934).
(15) "International Critical Tables." Vol. 3, McGraw-Hill Book Co., Inc., New York N.Y., 1928, p. 391.
(16) "The Merck Index," 7th ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 128.
(17) Carless, J. E., and Nixon, J. R., *J. Pharm. Pharmacol.*, **12**, 340(1960).
(18) Swarbrick, J., Ph.D. thesis, London, England, 1964, p. 99.
(19) Mitchell, A. G., Wan, L. S. C., and Bjaastad, S. G., *J. Pharm. Pharmacol.*, in press.
(20) Higuchi, T., and Lach, J. L., THIS JOURNAL, **43**, 465 (1954).
(21) Kato, Y., *Chem. Pharm. Bull. Tokyo*, **10**, 771(1962).
(22) *Ibid.*, **11**, 1202(1963).
(23) Elworthy, P. H., *J. Pharm. Pharmacol.*, **12**, 293 (1960).
(24) Lawrence, A. S. C., and Stenson, R., *Proc. Intern. Congr. Surface Activity, 2nd, London*, 1, 388(1957).
(25) Hyde, A. J., and Lawrence, A. S. C., *Proc. Intern. Congr. Surface Activity, 3rd, Cologne*, A (No. 2) (1960).
(26) Mulley, B. A., and Metcalf, A. D., *J. Colloid Sci.*, **17**, 523(1962).
(27) Schick, M. J., *ibid.*, **17**, 801(1962).
(28) Becher, P., *ibid.*, **17**, 325(1962).
(29) Goodhart, F. W., and Martin, A. N., THIS JOURNAL, **51**, 50(1962).
(30) Nakagawa, T., Kuriyama, K., and Inoue, H., *J. Colloid Sci.*, **15**, 268(1960).
(31) Becher, P., *ibid.*, **16**, 49(1961).
(32) Elworthy, P. H., and MacFarlane, C. B., *J. Chem. Soc.*, **1962**, 537.
(33) Sirianni, A. F., and Coleman, R. D., *Can. J. Chem.*, **42**, 682(1964).
(34) Riegelman, S., *et al.*, *J. Colloid Sci.*, **13**, 208(1958).