Letters to the Editor

The solubility of benzaldehyde in water

SIR,—During investigations into factors controlling the oxidation of benzaldehyde solubilised in aqueous solutions of various polyoxyethylene glycol ethers we found the rate of reaction to depend mainly on the concentration of aldehyde in the micelles and not on the total concentration. To estimate the distribution of benzaldehyde between the micelles and true aqueous "phase" it was essential to know the solubility of benzaldehyde in water. In International Critical Tables (1928) the water-solubility of benzaldehyde is given as 3 g/litre at room temperature and in the Merck Index (1960) as 1 in 350 parts of water. The oxidation of benzaldehyde dispersed in aqueous solutions of surface-active agents has been investigated by Nixon (1958) and Swarbrick (1964) who estimated the water-solubility of benzaldehyde at 25° to be 3·49 and 3·5 g/litre respectively. We have found that the water-solubility is considerably higher than these values.

Benzaldehyde was distilled at low pressure under oxygen-free nitrogen using a Towers fractional distillation unit fitted with automatic reflux ratio control. The aldehyde was packed in ampoules under oxygen-free nitrogen and stored protected from light in a refrigerator. Samples were examined for the presence of impurities and decomposition products by infra-red spectroscopy and gas chromatography. Double distilled water from an all-glass still was used throughout.

Saturated solutions were prepared by shaking together an excess of aldehyde in water in stoppered cylinders in a water-bath thermostatically controlled at 25° ± 0·01°. Excess aldehyde was removed by filtration through Whatman No. 3 filter paper. The first portion of the filtrate was rejected. The amount of aldehyde in an aliquot of saturated solution was determined gravimetrically as the 2,4-dinitrophenylhydrazone according to the method of Iddles & Jackson (1934). The accuracy of the method was verified using known weights of benzaldehyde. An alternative method for removing excess aldehyde from the saturated solution was to centrifuge samples at a controlled temperature of 25° and then to remove a sample of saturated solution by means of a pipette. Both methods were satisfactory and gave concordant results.

The value for water-solubility obtained by the gravimetric method was checked by gas chromatography using methyl salicylate as an internal standard (Burchfield & Storrs, 1962). A Pye Panchromatograph equipped with a flame ionization detector was used as the gas chromatograph. The column was prepared by packing a 210 cm by 3 mm glass column with 25% Carbowax 20-M on 60–80 mesh Chromosorb W solid support. Operating conditions were as follows: column temperature, 200°; argon flow rate, 60 ml/min; detector voltage, 400 V.

TABLE 1. THE WATER-SOLUBILITY OF BENZALDEHYDE AT 25°

Method	Solubility, g/litre	Standard deviation*
Gravimetric	6·55	0·004
Gas chromatography	6·58	0·070

* 2 determinations on each of 3 saturated solutions.

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July 10, 1964

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The solubility of benzaldehyde in water as determined by refractive index measurements

SIR,—Mitchell Wan & Bjaastad (1964) have recently determined the solubility of benzaldehyde in water at 25° and found a value of 6·55 mg/ml, a figure considerably higher than the previous literature values which range from 3·0 to 3·5 mg/ml. As a result of this finding we have determined the solubility of benzaldehyde in water by measurement of the refractive index of a range of benzaldehyde dispersions.

The sample used was redistilled Analar benzaldehyde that had been stored, refrigerated, in glass ampoules under nitrogen in the dark. Varying concentrations of benzaldehyde were dispersed in freshly boiled and cooled distilled water; the air above the dispersions was then displaced with nitrogen and the sealed flasks shaken overnight in a water-bath at 25° ($\pm$0·5°). The dispersions were then left for a further 2–4 hr without shaking to allow sufficient separation of a clear supernatent in those dispersions containing benzaldehyde in excess of its aqueous solubility. This technique was used in preference to centrifuging, where the control of temperature was found to be inadequate, even with a temperature-controlled centrifuge. The refractive index of each benzaldehyde solution, in terms of instrument scale reading, was determined against water in the reference cell using a Hilger-Rayleigh interference refractometer (Model M154) maintained at 25° by circulating water from a thermostat bath. 1 cm cells were used throughout and the supernatent aqueous solutions of benzaldehyde, pipetted from the dispersions kept in the water-bath, were allowed to equilibrate in the instrument for 20 min. Duplicate readings, accurate to one scale division, were taken for each of the ten dispersions prepared. The whole procedure was then repeated using a second sample of benzaldehyde.

The solubility of benzaldehyde, taken as the intercept of the two straight lines shown in Fig. 1, is 6·9 to 7·0 mg/ml, as compared with the value of 6·55 mg/ml found by Mitchell using a gravimetric method confirmed by gas chromatography.

The refractive index method described herein has the advantage that it is independent of any coefficients or factors, involves no manipulative techniques