DISTRIBUTION OF SORBIC ACID IN OIL-WATER AND OIL-WATER-SURFACTANT OF DODECYL TRIMETHYL AMMONIUM-BROMIDE (DoTAB) SYSTEMS

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The influence of synthetic surfactant or emulsifier dodecyltrimethyl ammonium-bromide (DoTAB 0.4M) on the distribution of sorbic acid (2.5-40 mM) was studied in oil (non-aqueous phase) and water (aqueous phase). The study was conducted in two model systems, oil-water, and oil-water-DoTAB (pH 2, temp 25°C). in oil water maximum solubility of sorbic acid in water was 22-28%, while in oil water-DoTAB the distribution in the aqueous phase was increased to 74-80% due to the presence of surfactant micelles. Foods are multiphase system, where microorganisms exist in the aqueous phase and a large part of sorbic acid is distribute in non-aqueous phase. This investigation suggests that the presence of food emulsifiers in food can increase the distribution of sorbic acid in aqueous phase.

Key Words: Sorbic acid, Oil water surfactant, Dodecyltrimethyl ammonium bromide (DoTAB)

Introduction

Sorbic acid, one of the safest food preservative is added to foods for inhibition the growth of microorganismas (Luck 1976). It is a straight chain trans-trans unsaturated fatty acid (2, 4-hexadienoic acid) CH_8-CH=CH-CH-COOH having the molecular weight 112.13. Its solubility in water is lower than other solvents e.g. corn oil, ethanol, benzene and acetic acid and further decreases in the presence of dissolved food components (Sofos and Busta 1981). Most of the foods contain both aqueous and non-aqueous phases and sorbic acid is distributed more into non-aqueous phase. In such systems we need to increase the sorbic acid distribution in the aqueous phase where microorganisms exist.

Organic acid solubility in the aqueous phase is increased in the presence of surfactants (Wedzicha and Zeb 1989). This study was carried out to increase the distribution of sorbic acid in aqueous phase of multiphase food system. In first part of the work, the influence of synthetic emulsifier of dodecyltrimethyl ammonium-bromide (DoTAB) on the distribution of sorbic acid in oil-water model system was studied.

Materials and Methods

Unless otherwise stated, all reagents used were of Analar grade and were supplied by British Drug House (BDH) Ltd; Poole. Sunflower cooking oil was used.

Absorbance measurements were carried out using a Cecil C.E. 292 digital ultraviolet spectrophotometer. pH measurements were made on Jenway PHM-6 pH meter with a combined glass-calomel electrode.

DoTAB (0.4 M) solution was prepared in HCl solution (15 mM) and the pH 2 was adjusted with HCl solution (1 M) to maintain sorbic acid undissociated. Sorbic acid solution in oil was prepared by dissolving sorbic acid (80 mM) in sun-flower oil at 30°C.

Sorbic acid was dissolved in HCl solution (15 mM, pH2). Various volumes of this solution were diluted to 100 ml with the same concentration of HCl solution. The absorbance of the solution was measured at 263 nm and calibration curve was calibrated using the HCl solution (15 mM) as a blank.

Sorbic acid in oil-water system:

Solutions of HCl (15 mM, 50 ml) in duplicate were placed, in 100 ml Quick fit test tubes followed by oil (50 ml or 46 g) containing various concentrations of sorbic acid (2.5-40mM). The test tubes were closed and shaken for 5 days at 25±0.5°C on magnetic stirrer in a temperature controlled cabinet. They were transfered to a water-bath at the same temperature and held overnight to allow separation of the oil from the aqueous phase which was then carefully removed by suction. An aliquot of the aqueous phase was diluted with HCl (15 mM) and the sorbic acid concentration was measured at 263 nm.

Sorbic acid in oil-water-DoTAB system:

To 100 ml conical flasks containing magnetic fleas, DoTAB solution (0.4 M, pH 2, 25 ml) was added followed by oil (25 ml or 23 g) containing various concentrations of sorbic acid (2.5-40 mM). The flasks were placed on magnetic stirrer in a temperature controlled cabinet (25±0.5°C) and stirred gently to prevent emulsion formation. After 5 days the oil phase was carefully removed by suction, an aliquot of the aqueous phase

was diluted with HCl (15 mM), and the sorbic acid concentration was measured at 263nm.

Results and Discussion

Preservatives are added to foods, to prevent the growth of microorganisms. This effect requires that the preservative be absorbed by the organisms, and the chemical structure must be such as to allow passage through the microbial cell wall. The antimicrobial action of sorbic acid is pH-dependent, and attributed to the undissociated acid (Wedzicha *et al* 1990 and 1993). It is important for the preservative to have some solubility in aqueous and non-aqueous phases of foods. The pH of the experiment was adjusted to pH 2 to maintain sorbic acid undissociated. In oil-water at equilibrium sorbic acid will distribute as follows:

$$(HA)\ aq \rightleftharpoons (HA)\ oil$$

In the presence of surfactants or emulsifiers in the aqueous phase the molecules of sorbic acid in aqueous phase are in equilibrium with those dissolved within the micelles:
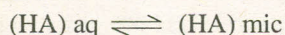
$$(HA)\ aq \rightleftharpoons (HA)\ mic$$

where (HA) aq, (HA)oil and (HA)mic denote undissociated sorbic acid in the aqueous, oil and micelles phases respectively. Emulsifiers which are also called surfactants or detergents, have both hydrophobic and hydrophilic properties and can form spherical molecular aggregates in aqueous media called "miccelles". The hydrophobic portions of these amphipathic molecules tend to aggregated to minimized contact with water molecules, where as the hydrophilic portions (which may be either charged or uncharged) remain in contact with aqueous phase at the surface (Geer *et al* 1971). The formation of micelles is highly dependent on the concentration of surfactants (Fendler and Fendler 1975). The concentration of surfactant at which micelles first appear in solution is termed the critical micelle concentration (CMC). The techniques used to measure CMC include the measurement of surface tension, conductivity, ability to solubilise certain dyes, viscosity, pH, light scattering, osmotic pressure and temperature coefficient of solubility.

Table 1 shows the critical micelle concentrations (CMC) of few emulsifiers. Micelles are transient species which form and break up very quickly, but an average spherical micelle might contain 30-100 surfactant molecules. When the surfactant concentration markedly exceeds the CMC, the shape gradually changes. It may elongate to cylindrical or lamellar structures. Spherical micelles can accommodate more organic acids than micelles having elongated or lamellar structures. Concentrated solutions of surfactant provide elongated struc-

Table 2
Distribution of undissociated sorbic acid [HA] in oil-water system

[HA] mM	[HA] oil mM	[HA]aq mM	%[HA]aq
2.5	01.8	0.70	28
5.0	03.63	1.37	28
10.0	07.58	2.42	24
20.0	15.30	4.70	24
30.0	23.11	6.89	23
40.0	31.44	8.56	22

[HA] oil and [HA]aq are the total concentrations of [HA] species in the oil and aqueous phases in mM, respectively. The pH of the aqueous phase was 2 and all measurements were at 25±0.5°C.

Table 3
Distribution of undissociated sorbic acid [HA] in oil-water-surfactant system

[HA] mM	[HA] oil mM	[HA]aq mM	%[HA]aq
2.5	0.65	01.85	74
5.0	1.31	03.69	74
10.0	2.40	07.60	76
20.0	4.40	15.60	78
30.0	6.37	23.63	79
40.0	8.11	31.89	80

The concentration of acid present in the oil phase and in aqueous phase, denoted by [HA] oil and [HA]aq respectively, at DoTAB (0.4 M) pH 2, 25±0.5°C. [HA] = Original concentration of sorbic acid in sunflower oil which was allowed to partition with an equal volume of aqueous phase containing surfactant.

Table 1
Critical micelle concentration (CMC) of synthetic surfactants or emulsifiers

Surfactant or Emulsifier	CMC
Dodecyl trimethyl ammonium bromide (DoTAB)	15 mM
Decyl trimethyl ammonium bromide (DTAB)	65 mM
Hexadecyl trimethyl ammonium bromide (HTAB)	0.92 mM
Sodium dodecyl sulphate (SDS)	8.1 MM

ture of micelles which is unable to solubilise organic acid (Corkil and Goodman 1969). The rate of certain organic reactions may increase in the presence of micelles (Cordes and Dunlap 1969).

The kinetics of nitrosamine formation was studied in the presence of micelle-forming surfactants of decyltrimethyl ammonium-bromide. The solubilities of different amines increased by this surfactant concentrations which were in the range 0.1-0.4 M. Amino acids containing long chain alkyl group were found more soluble than amino acids having branched chain alkyl group.

Source. Fendler and Fendler (1975), Becker (1967), the distribution of sorbic acid in oil-water system is shown in Table 1. Maximum distribution ratio of sorbic acid in aqueous phase is 28% Table 2. In oil-water-DoTAB system the distribution of sorbic acid in aqueous phase was increased to 80% Table 3. This is a useful investigation for food processors using sorbic acid as a chemical preservative in multiphase food products i.e. bakery items, certain meat and fish products, and confectionary and dairy products. These results suggest that emulsifiers can increase the distribution of sorbic acid in the aqueous phase of multiphase foods, and the shelf-stability of such foods, preserved by sorbic acid, can be further increased.

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