Equilibrium Vapor Pressure of Butylated Hydroxyanisole and Butylated Hydroxytolune in High Temperature Oil Solution

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ABSTRACT

The equilibrium partial pressure of butylated hydroxyanisole and butylated hydroxytoluene above their dilute oil solution in the frying temperature range (170-220 C) was determined. The system was found to follow Henry's law and to have an activity coefficient ranging, respectively, from 0.038-0.045 and from 0.036-0.042 (averages 0.042 and 0.039) for butylated hydroxyanisole and butylated hydroxytoluene. The extremely narrow ranges of γ suggest that the dominant effect of temperature upon the Henry coefficient, H, is through the vapor pressure of the pure substance. The equations for H (in mm Hg) as function of the absolute temperature T (in K) when antioxidant concentration expressed as molar fraction are: $H = 1.26 \times 10^8 \exp(-8.03 \times 10^3/T)$ for butylated hydroxyanisole, and $H = 1.55 \times 10^7 \exp(-7.02 \times 10^3/T)$ for butylated hydroxytoluene.

INTRODUCTION

Where oxidation is the primary cause of their deterioration (1-5), fats, oils, and fat containing foodstuffs can be stabilized to a certain extent by admixture of antioxidants. In frying processes, the antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), serve both to protect the oil during drying and to ensure a certain level of antioxidant in the product for its protection during storage.

Maintenance of the desired level of antioxidant in a frying bath is an important factor, but design parameters have been difficult to prescribe in the near absence of (inter alia) quantitative data on the evaporation loss of BHA and BHT under frying conditions. Evaluation of evaporative losses of the antioxidant requires data regarding the vapor pressure of BHA (and BHT) in equilibrium with antioxidant-oil solution at frying temperatures. The present study was undertaken with a view to determine the volatility of BHA and BHT above oil solution in the frying temperature range.

THEORETICAL ASPECTS

In low partial vapor-pressure systems (such as an antioxidant-oil solution), the gas phase is treated as an ideal gas (6), and the equilibrium relationship reads:

$$\bar{p} = \gamma p_0 x,$$

where $\bar{p}$ = partial vapor pressure of substance in solution, p_0 = vapor pressure of pure substance, x = molar fraction of substance, and γ = activity coefficient.

For a nonideal dilute solution, the product γp_0 represents the coefficient H in Henry's law, i.e. $\bar{p} = Hx$. For an ideal solution, $\gamma = 1$ and the relationship reduces to Raoult's law: $\bar{p} = p_0 x$.

EXPERIMENTAL PROCEDURES

Materials

Antioxidants: BHA and BHT, with the relevant Cox-type charts (log absolute pressure vs reciprocal absolute temperature) (Eastman Kodak, Zug, Switzerland) were used.

Oil: Commercial refined (additive-free) cottonseed oil with ca. mol wt 860 was used.

Equipment: Equipment used included the following: gas chromatograph (Packard model 340), and flame ionization detector. The column was 6 ft x 1/4 in. spiral filled with 10% DC-200. Carrier gas was N_2 80 ml/min. Temperatures were as follows: column, 160 C; detector, 200 C; inlet, 200 C; and outlet, 200 C.

Procedure

The analysis was carried out as described by Hartman and Rose (7), with slight modifications.

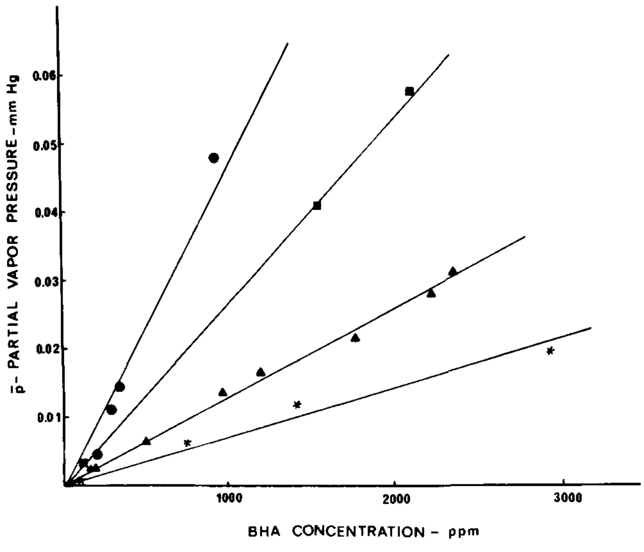

FIG. 1. Partial vapor pressure of butylated hydroxyanisole (BHA) in oil solution vs concentration. Temperature (C) = ● = 221, ■ = 200, ▲ = 180, and * = 172.

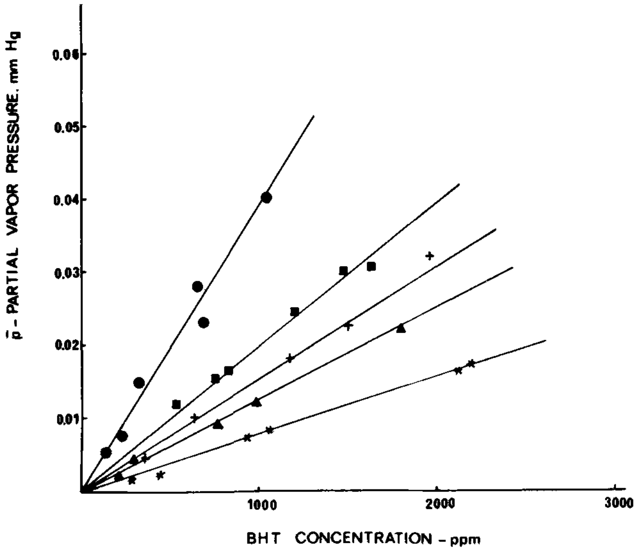

FIG. 2. Partial vapor pressure of butylated hydroxytoluene (BHT) in oil solution vs concentration. Temperature (C) = ● = 220, ■ = 200, + = 190, ▲ = 180, and * = 170.

TABLE I

Henry and Activity Coefficients for Butylated Hydroxyanisole (BHA) and Butylated Hydroxytoluene (BHT) in Dilute Oil Solution

	Temperature C (T)	Vapor pressure of pure substance $\left(\frac{p_0}{\text{mm Hg}}\right)$	Henry coefficient $\left(\frac{H}{\text{mm Hg}}\right)$	Activity coefficient
BHA	172	42	1.57	0.038
	180	60	2.72	0.045
	200	128	5.65	0.044
	221	250	9.83	0.040
BHT	170	56	2.00	0.040
	180	75	3.17	0.042
	190	100	3.95	0.039
	200	140	5.04	0.036
	220	250	9.95	0.040

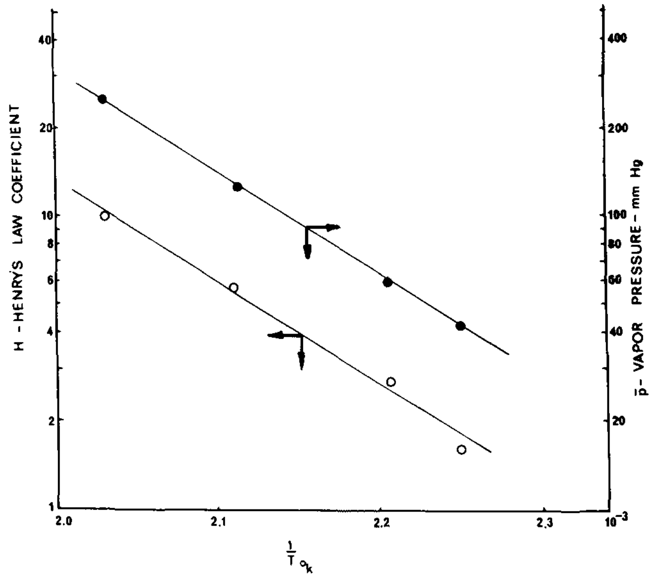

FIG. 3. Henry coefficient and partial vapor pressure of butylated hydroxyanisole (BHA) vs 1/T.

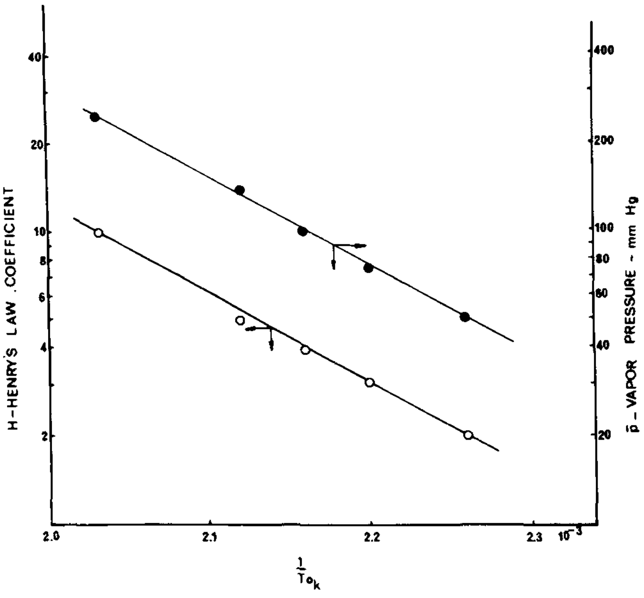

FIG. 4. Henry coefficient and partial vapor pressure of butylated hydroxytoluene (BHT) vs 1/T.

Samples (15 ml) of antioxidant solution was placed in a 200 x ϕ20 mm test tube. The tube was closed at the top end with a serum cup, through which the headspace was evacuated by means of a hypodermic needle to expedite a vapor-liquid equilibrium. The evacuated tube was immersed in a thermostatic (± 0.10 C) paraffin oil bath for 20 min, after which the headspace was restored to atmospheric pressure by means of the same needle. Headspace gas (1 ml) was withdrawn slowly with 5 ml a gas-tight Hamilton syringe and injected into the gas chromatograph. Simultaneously, 0.9 g oil was withdrawn and dissolved in 2.5 ml hexane; 1-5 μliter samples of the solution also were injected into the gas chromatograph oil. Headspace analysis was repeated 5 successive times at 5 min intervals (from the moment that headspace was restored to atmospheric pressure) and the amounts of BHA and BHT calculated through comparison with standards.

RESULTS AND DISCUSSION

The plots in Figures 1 and 2 show that, at constant temperature, the vapor pressure of the antioxidants, in equilibrium with their dilute oil solution, is linear with concentration. Lines through origin were obtained by least squares method. The slopes of the straight lines and the vapor pressures of the pure substances (BHA and BHT) yield the coefficients H and γ (Table I). The values of the latter coefficient range from 0.038-0.045 and 0.036-0.042, averaging 0.042 and 0.039, for BHA and BHT, respectively, and indicating a negative deviation from Raoult's law. The extremely narrow range of variation over the entire experimental temperature range suggests that the dominant effect of temperature upon the Henry coefficient is through the vapor pressure of the pure substance. This also is verified from Figures 3 and 4, where log H and the vapor pressures of the pure substances yield the same slopes when plotted against the reciprocal absolute temperature. These slopes can be used for determinating the latent heat of vaporization (found to be 16 and 14 Kcal/g mole for BHA and BHT, respectively. H can be evaluated for the practical frying temperature range either from the averages and the vapor pressure of the pure substance or from the following equations derived from Figure 3 and 4:

$$H = 1.26 \times 10^8 \exp(-8.03 \times 10^3/T) \text{ for BHA and}$$
$$H = 1.55 \times 10^7 \exp(-7.02 \times 10^3/T) \text{ for BHT,}$$

where T = temperature (K).

In conclusion, the vapor pressure of the antioxidant (BHA and BHT) above their dilute oil solution follows Henry's Law.

Henry's Law coefficient provided in this paper enables one to evaluate the evaporative losses of antioxidant in a frying system.

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