Some Variables Affecting Composition of Headspace Aroma

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Factors which influence the headspace concentration of volatile components in aqueous sucrose solutions were studied by gas chromatography. These include: type and concentration of the volatile; concentration of the sugar; the method by which the sample was prepared; and time of equilibration. Results indicate that while a "salting-out" effect occurs for acetone, a marked depression in headspace concentration of higher molecular weight compounds takes place when sugar, gelatin, or glycerol is added to dilute water solutions.

It is generally recognized that the composition of volatile components in the vapor phase above food is more closely related to aroma than the composition of these compounds in the food medium itself. Headspace analysis of food volatiles has consequently become a popular technique in flavor research. Since odorous volatile components normally exist in extremely low concentrations, their behavior is expected to follow Henry's law where the partial pressure of a solute above the solution is proportional to its molar concentration in the liquid. Buttery *et al.* (1969) used gas chromatography to study the volatilities of aldehydes, ketones, and methyl esters and showed that the higher molecular weight homologs of each series up to C_9 were actually more volatile in dilute water solutions than the lower homologs. This confirmed theoretical predictions made by these authors and by earlier workers (Butler *et al.*, 1935) according to the relation $p = p^0 \times N/N_s$ where p is the partial pressure of the solute, p^0 is the partial pressure of the solute in the pure state, N is the molar fraction of the soute, and N_s is the molar fraction of a saturated solution of that component. This equation also reflects the relationship between the volatility of a component in dilute solution and its solubility. Although most foods contain considerable quantities of water, prediction of the escaping tendency of volatile compounds from the food to the atmosphere above it is complicated by the presence in the food medium of several other ingredients (*e.g.*, proteins, carbohydrates, lipids, salts, and other volatile compounds). In a previous publication (Nawar, 1966), we presented experimental data which demonstrate certain aspects of the relationship between the concentration of a compound in the vapor phase and such factors as the type of medium in which it is dissolved, the degree of its solubility in the medium, its concentration in the liquid phase, its miscibility with other organic compounds in the mixture, and the presence of salts or sugars. More recently Nelson and Hoff (1968) studied partition coefficients of various compounds in water–lipid systems by determining Henry's constants for each compound in the single solvents.

The addition of inorganic salts to increase the vapor pressure of volatile compounds in dilute water solutions is a common procedure used in distillation techniques and in headspace analysis (Bassette *et al.*, 1962; Jennings, 1965; Nawar, 1966; Nelson and Hoff, 1968; Weurman, 1969). The effect of sugars on the volatility of organic compounds in dilute aqueous systems is more complex. Glucose caused some increase in vapor pressures, but the effect varied with different volatile concentrations (Nawar, 1966). In a similar study, Wientjes (1968) added relatively high concentrations of glucose, sucrose, fructose, and invert sugar to dilute aqueous solutions of various volatiles and analyzed the headspace by gas chromatography after equilibrating his samples at 30° C for 40 min. While the addition of sugar produced an increased partial vapor pressure for a number of components, a marked decrease resulted for others. Jennings (1965), for the first time, used radioactive detection methods to study the time required for vapor equilibration of dilute systems. He observed that for 5-ppm ethyl acetate solutions containing various levels of NaCl, vapor equilibrium required about 25 min at 25° C.

The purpose of the present work was to examine some of the factors which influence the headspace concentration of volatile compounds in aqueous solutions containing certain nonvolatile compounds.

EXPERIMENTAL

Samples were prepared in 125-ml flasks equipped with serum caps. The appropriate concentrations, based on wt of volatile/wt of water, were made with the amount of water maintained equal (40 ml) for all samples. Solutions containing sucrose, glycerol, or gelatin, together with controls containing only the volatile in water, were routinely held for 1 hr at 30° C ± 1° C before analysis. This was based on preliminary experiments which indicated that for the controls and under these experimental conditions the headspace concentration of the volatiles increased after sample preparation and reached a maximum in approximately 30 min. Headspace analysis was conducted by using glass syringes and injecting 3-ml aliquots of the headspace gas into a Perkin-Elmer gas chromatograph, Model 881, equipped with a 6-ft × $^1/_8$-in. silicone SE-30, 10% on Diatoport S, and a flame ionization detector. The concentration of a component in the headspace, expressed as microgram of volatile per milliliter of air, was determined by comparing the vapor glc peaks with a standard curve obtained from direct liquid injection of a series of standard solutions with different levels of concen-

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Table I. Volatilities of Methyl Ketones in Dilute Aqueous Solutions

	Present work		Other investigators	
Carbon no.	250 ppm μg/ml air	30° C Partition coefficient (× 10^{-3})	Buttery *et al.*, 1969 Partition coefficient, 25 °C (× 10^{-3})	Nelson and Hoff, 1968 Partition coefficient, 28° C (× 10^{-3})
3	0.64	2.5	1.6	1.3
4	0.76	3.0	1.9	
5	1.0	4.1	2.6	4.4
6	1.3	5.3		
7	1.6	6.2	5.9	
8	1.8	7.3	7.7	
9	2.6	10.	15.0	

Table II. Effect of Sucrose Concentration on the Volatilities (μg/ml air) of Various Compounds at 750 ppm[a] in Aqueous Solutions

		Headspace concentration		
% Sucrose[b]	Viscosity, cP	Acetone	Heptanone	Heptanal
0	0.8	1.8	5.1	5.1
20	1.5	1.9	4.9	4.4
40	4.3	2.1	4.0	4.1
60	33.8	2.2	1.8	1.4

[a] ppm volatile in water. [b] The appropriate amounts of sucrose added to the solution of the volatile in water to produce the specified concentrations.

trations. Air–water partition coefficients were determined as K = μg solute per ml air per μg solute per ml solution.

RESULTS AND DISCUSSION

The volatilities in water of a homologous series of methyl ketones, expressed in terms of both μg/ml air and air–water partition coefficients, are shown in Table I. For comparison, partition coefficient data obtained by other workers are given in the last two columns. The small differences in values obtained by different workers are probably due to the slightly different temperatures and techniques used, but the trend is essentially the same. The increase in the vapor concentration of these compounds in water solutions with increasing molecular weight is evident. It should be clear that the expression of volatilities as air–water partition coefficients is feasible only if the partition coefficients do not vary over the range of concentrations used. Although this is indeed the case in pure water solutions (Buttery *et al.*, 1969), considerable variations are observed if the solutions contain other compounds such as salts, sugar, or gelatin. It would, therefore, be more meaningful if the volatility of a food component is expressed in terms of μg/ml of air at given volatile concentrations in the food medium.

Table II shows the effect of adding various amounts of sucrose on the headspace concentration of different compounds in 750-ppm aqueous solutions. Several samples of each chemical in water were prepared and various quantities of the sugar added so as to produce solutions of varying sucrose concentrations but otherwise containing the same amount of water and volatile. The viscosity in centipoise is given for each of the sucrose solutions. It can be seen that while the concentration of acetone in the headspace is increased by adding sucrose, a marked depression in the headspace concentration of 2-heptanone and heptanal occurs with increasing sucrose concentrations. A "salting-out" effect appears to take place in the case of acetone. On the other hand, addition of sucrose seems to interfere in some manner with the escape of heptanone and heptanal molecules from solution.

In a different experiment the concentration of sucrose was maintained at 60% in all samples. Two methods, however, were used in preparing each sample. In one case the volatile was dissolved in water, and then sucrose was added as described above. In the other the sugar–water solution was prepared first and then mixed with the volatile. The composition of the sample (percents sugar, water, volatile) was identical in both cases. Two concentrations were used, *i.e.*, 750 and 75 ppm, based on the weight of volatile relative to that of water. The results are shown in Table III. Addition of sucrose to the water solution (column I) decreased the concentration of 2-heptanone in the headspace as it did in the previous experiment. However, when heptanone was incorporated in the sugar solution (column II), its headspace concentration was considerably higher than that of the control. This phenomenon is also observed, but to a lesser degree, in samples of 2-pentanone. In both cases the effect is more pronounced at the higher volatile concentration. Acetone and butanone behaved differently. Their headspace concentration increased regardless of the order in which sucrose was added. It should be pointed out that the addition of 60 g of sucrose to 40 ml of water gives a total volume of 77 ml. The observations made here, however, are not caused by the change in volume. All sucrose solutions had the same

Table III. Headspace Concentrations (μg/ml air) of Volatiles above Sucrose, Gelatin, and Glycerol Solutions

	Control volatile in H_2O	60% Sucrose		10% Gelatin		50% Glycerol	
		I[a]	II[b]	I	II	I	II
2-Heptanone							
750 ppm	4.7	1.4	16.0	3.9	5.5	1.8	2.0
75 ppm	0.4	0.2	0.7	0.3	0.4	0.2	0.2
2-Pentanone							
750 ppm	3.7	3.0	6.0	2.9	3.2	2.0	2.3
75 ppm	0.3	0.2	0.8	0.2	0.3	0.2	0.2
2-Butanone							
750 ppm	3.0	3.2	3.8				
75 ppm	0.3	0.3	0.4				
Acetone							
750 ppm	1.5	2.0	2.4	1.4	1.7	1.6	1.7
75 ppm	0.2	0.2	0.3	0.1	0.2	0.2	0.2

[a] I, Sucrose, gelatin, or glycerol added after dissolving the volatile in 40 ml of water. [b] II, Sucrose, gelatin, or glycerol dissolved in 40 ml of water and then mixed with the volatile.

volume but the effect on headspace concentrations varied with the type of volatile used (decrease for heptanone, increase for acetone) and with the order in which the sugar was added (decrease in I, increase in II—Table III). Furthermore, under the same conditions, different solids of varying water solubilities produce different effects on the headspace concentration of volatiles, suggesting that such effects are related to the interaction of the solids with water.

The relatively high headspace concentrations obtained when the sugar solutions were prepared before addition of the volatile (Table III, column II) may be due to the decreased solubility of the volatiles in sugar solutions or to the slower diffusion of these compounds in such systems. These values dropped significantly after 24 hr of equilibration at 30° C, while the values for the controls and for the samples in which the sucrose was added to the volatile-in-water solutions changed only slightly. For 2-heptanone, for example, at the 750-ppm level, the headspace concentrations after 24 hr were 4.0 μg/ml for the control, 1.5 μg/ml for the sample with sucrose added, and 2.1 μg/ml for the sample with the sucrose solution prepared before volatile addition. Although the headspace concentrations of 2-heptanone after 24 hr were still unequal in the two samples containing sucrose, both concentrations were considerably lower than that of the control, indicating a possible interaction or binding effect between the volatile and the sugar. On the other hand sucrose does not affect the headspace concentration in the absence of water. The headspace concentration in a flask containing 30 μg of heptanone and 60 g of sucrose was identical to that in a flask containing heptanone only. It appears, therefore, that the decrease in headspace concentration, upon addition of sucrose to aqueous volatile solutions, does not involve a direct interaction between sugar and volatile, but rather it occurs *via* interaction of the sugar with the water molecules.

The effects of gelatin and glycerol on the headspace concentration of volatiles are also shown in Table III. Although a "binding effect" upon addition of these agents is again obvious and seems to involve their interaction with water, the nature of such interaction is not as yet well understood.

ACKNOWLEDGMENT

The author thanks H. O. Hultin for helpful advice and Regina Whiteman for technical assistance.

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Received for review March 1, 1971. Accepted June 4, 1971. Presented at Symposium on Direct Vapor Analysis, Division of Agricultural and Food Chemistry, 160th National Meeting, ACS, Chicago, Ill., September 1970. This study was supported in part by a Heublein, Inc., grant.