

Food Volatiles

Volatilities of Aldehydes, Ketones, and Esters in Dilute Water Solution

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The volatilities in dilute water solution of some members of homologous series of alkanals, alkan-2-ones, and methyl alkanoates from C₃ to C₉ were studied experimentally by gas chromatography. The results confirm earlier theoretical predictions

by other workers that at 25° C. the higher molecular weight homologs of each series up to C₉ are actually more volatile in dilute water solutions than the lower molecular weight homologs.

Most fruits and vegetables are 50 to 90% water. Some understanding of the volatilities of organic compounds in these products might be obtained by consideration of the volatilities of these compounds in dilute water solutions. A review of the literature reveals very little published fundamental experimental information in this area especially in relation to compounds important in foods. Very significant work, however, was carried out over 30 years ago by Butler *et al.* (1935), who studied water solutions of the homologous series of alcohols from methanol to octanol. They found that the volatilities in the dilute water solutions gradually increased with increasing molecular weight. For the same mole concentration in dilute water solution at 25° C., octanol showed a predicted partial vapor pressure more than five times greater than methanol. However, they carried out direct studies only on C₁ to C₅ alcohols and predicted values for the C₆ to C₈ alcohols from the following relation,

$$p = p^\circ \times \frac{N}{N_s} \quad (1)$$

where p is the partial pressure of the solute above the solution, p° is the vapor pressure of the solute in the pure state, N is the molar fraction of the solute in the solution under consideration—*i.e.*, number of moles of solute per number of moles of H₂O—and N_s is the molar fraction of a saturated solution of that component. This equation was applicable only to compounds poorly miscible with water (less than ca. 10%).

Equation 1 is a form of Henry's law, $1/N_s$ being the factor correcting for the nonideality of the solution. It follows that for compounds with low water solubility $1/N_s$ corresponds to the activity coefficient γ of the material in water. Pierotti *et al.* (1959) determined the activity coefficients for a number of organic compounds in water, using a variety of methods. They also determined the vapor pressure, p° , for some of these compounds and so were able to calculate their volatilities in dilute water solution, which they expressed in terms of $p^\circ \times \gamma$. From such calculations these authors

predicted a similar increase in volatility with increasing molecular weight for dilute water solutions of homologous series of n -acids, n -alcohols, n -ketones, n -ethers, and n -paraffins for the range at least of C₁ to C₁₀.

Other work more related to food volatiles has been carried out by Burnett (1963), Burnett and Swoboda (1962), Nawar and Fagerson (1962), Nawar (1966), Nelson and Hoff (1968), and some of the present authors (Buttery *et al.*, 1965).

Determination of the concentrations of slightly soluble organic materials, within a usable quantitative accuracy, is difficult because of complicating adsorption effects and the interference of impurities. The present work was undertaken to determine experimentally the volatilities of aldehyde, ketone, and ester homologs, using techniques where adsorption effects are minimized and the specific method of gas-liquid chromatography (GLC).

EXPERIMENTAL

Materials. The organic compounds were obtained from reliable commercial sources or synthesized by well established methods. They were purified by gas-liquid chromatography (GLC) before use.

Gas Chromatography. The column used was a 500-foot \times 0.03-inch I.D. stainless steel capillary coated with silicone SF-96(100) containing 5% Igepal CO 880. Column temperature was varied (50° to 150° C.) depending upon the compound being studied. The carrier gas was nitrogen saturated with water vapor. The detector was flame ionization. Attached to the gas chromatograph was a stainless steel gas-sampling valve of the conventional O-ring type (Viton O-rings), except that it was enclosed in a small oven which kept the valve, sample loop, and all connections at 160° to 170° C. The outlet tube (160° to 170°) from the sample valve led through a small volume silicone rubber septum GLC injector (160° to 170°) and then to the column.

The complete system from the beginning of the gas-sampling valve to the inlet of the column was silanized with hexamethyldisilazane before the study, to lessen adsorption effects.

Method. A measured volume of the sample was dissolved by adding it to odor-free distilled water made up to the mark in a graduated flask and shaking as much as necessary over about one-half hour. The solu-

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bility of the material was checked by allowing it to stand a short while and then observing the surface of the water in the narrow neck of the flask. This method was found to be sensitive for the detection of even very small amounts (less than 0.0005 ml. in 1 liter of water) of undissolved organic compound. Solubilities were determined more accurately for nonanal, undecan-2-one, and methyl octanoate in the following way. A small volume of water was saturated by stirring with the compound for several hours. The saturated solution was then centrifuged and the lower aqueous layer separated from any undissolved compound. The concentration was then determined by comparison of the GLC peak areas from the saturated solution with those of standard solutions of that compound in hexane.

For the determination of the partition coefficient a concentration was chosen which was well below the saturation point (usually 5 to 200 p.p.m.). After the material was completely dissolved, 100 ml. of the solution was placed in an 8-ounce (ca. 250-ml.) Teflon bottle closed with a cap equipped with a connection for 0.04-inch I.D. Teflon capillary tubing. The bottle was then placed in a 25° C. constant temperature bath for 30 minutes or more to equilibrate. Solution samples (1 to 10 μ l.) were taken from the bottle and injected into the GLC apparatus through the silicone rubber septum injector. Vapor samples were introduced into the GLC apparatus by connecting an 18-inch length of Teflon capillary tube (0.04-inch I.D.) from the GLC gas-sampling valve to the Teflon bottle and then transferring the sample to the valve by squeezing the flexible bottle. This forced the vapor through the sampling tube of the valve, which was then activated. The volume of vapor introduced was corrected for the difference in temperature of the valve and that above the solution. Immediately (1 to 5 seconds) after the introduction of the vapor sample a volume of water equal to that used for the solution sample was injected through the silicone rubber injector, so that both vapor and solution samples passed through the column under closely similar conditions. Solution and vapor samples were injected alternately, so that a change in the concentration of the solution due to removal of vapor would be compensated. The air-water partition coefficient was determined as

$$K = \frac{\text{weight of solute per ml. of air}}{\text{weight of solute per ml. of solution}} \text{ at } 25^{\circ} \text{ C.} \quad (2)$$

The GLC peak area of the solution and vapor peaks were measured by the method of peak height by peak width at $\frac{1}{2}$ peak height. Using peak areas the above equation becomes

$$K = \frac{\text{area of vapor peak} \times \text{volume of solution injected}}{\text{area of solution peak} \times \text{volume of vapor injected}} \quad (3)$$

GLC peak area to weight conversion factors cancel out. For each compound this was calculated as the average of four to 10 determinations.

Vapor Pressures. Vapor pressures were determined at 25° C. for nonanal, undecan-2-one, and methyl

octanoate in the following way. The pure compound (10 ml.) was placed in a dry 8-ounce Teflon bottle and equilibrated in a 25° C. water bath. The procedure for transferring the vapor sample from the Teflon bottle to the GLC apparatus then followed exactly that described above for the solution.

The concentration of the compound in the vapor was determined by comparing the vapor GLC peaks to those obtained by injecting a standard solution of the compound in hexane.

RESULTS AND DISCUSSION

The results found for the homologous series of aldehydes, ketones, and esters are listed in Table I and shown diagrammatically in Figure 1.

The volatilities have been expressed in terms of the air-water partition coefficient, which is a useful factor for rapid calculation of an unknown concentration in one medium, when the concentration is known in the other. The results of Butler *et al.* (1935) for alcohols are included in Figure 1 for comparison. The results found are in general agreement with the trends predicted by Pierotti *et al.* (1959). There is a gradual increase in volatility for the higher molecular weight homologs, with alcohols having the lowest volatilities, ketones intermediate, and esters and aldehydes somewhat higher. For equal concentrations in water, nonanal is more than 100 times as concentrated in the vapor as ethanol (Table I) and approximately eight times as concentrated as propanal. From this point of view we might expect higher homologs to have some advantages in efficiency as odorants when we are considering largely aqueous foods. Table I and Figure 1 predict a reverse order of elution from a gas chromatography column using water as a stationary phase. This has been observed by Phifer and Plummer (1966), who showed that in gas chroma-

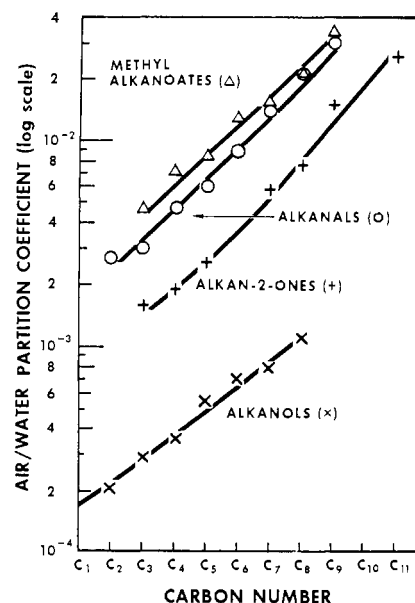


Figure 1. Plots of air-water partition coefficients at 25° C. for homologous series against carbon number

Table I. Air-Water Partition Coefficients for Homologous Series of Aldehydes, Ketones, Esters, and Some Alcohols at 25° C.

Compound	Air-Water Partition ^a Coefficient at 25° C.
Acetone	$1.6 \pm 0.2^b \times 10^{-3}$
Butan-2-one	$1.9 \pm 0.2 \times 10^{-3}$
Pentan-2-one	$2.6 \pm 0.2 \times 10^{-3}$
Heptan-2-one	$5.9 \pm 0.6 \times 10^{-3}$
Octan-2-one	$7.7 \pm 0.4 \times 10^{-3}$
Nonan-2-one	$15 \pm 0.8 \times 10^{-3}$
Undecan-2-one	$26 \pm 7 \times 10^{-3}$
Acetaldehyde	$2.7 \pm 0.5^b \times 10^{-3}$
Propanal	$3.0 \pm 0.1 \times 10^{-3}$
Butanal	$4.7 \pm 0.3 \times 10^{-3}$
Pentanal	$6.0 \pm 0.1 \times 10^{-3}$
Hexanal	$8.7 \pm 0.6 \times 10^{-3}$
Heptanal	$11 \pm 1 \times 10^{-3}$
Octanal	$21 \pm 4 \times 10^{-3}$
Nonanal	$30 \pm 4 \times 10^{-3}$
Methyl acetate	$4.7 \pm 0.3^b \times 10^{-3}$
Methyl propionate	$7.1 \pm 0.5 \times 10^{-3}$
Methyl butyrate	$8.4 \pm 0.1 \times 10^{-3}$
Methyl pentanoate	$13 \pm 3 \times 10^{-3}$
Methyl hexanoate	$15 \pm 2 \times 10^{-3}$
Methyl octanoate	$32 \pm 5 \times 10^{-3}$
Butanol	$3.6 \pm 0.4^b \times 10^{-4}$
Hexanol	$7.0 \pm 0.6 \times 10^{-4}$
Octanol	$10 \pm 0.6 \times 10^{-4}$

^a Weight of compound per ml. of air/weight of compound per ml. of water at 25° C.

^b Standard deviation.

tography separation of the homologous series of alcohols from methanol to pentanol, pentanol was eluted first and methanol eluted last.

Addition of salts to aqueous solutions is known to enhance the volatility of dissolved organic compounds. A recent study of aldehyde, ester, and alcohol volatilities above saturated aqueous sodium sulfate solution by Nelson and Hoff (1968) showed relative trends similar

to that in Figure 1, although the volatilities of all compounds were, as expected, many times greater than those for pure water solutions.

Variation of Volatility with Concentration. The air-water partition coefficients were determined for 2-heptanone and hexanal over a wide range of concentrations up to the point of saturation (Figure 2). The variation of these coefficients is within experimental error over almost a 1000-fold change in the concentrations of these two compounds and does not change appreciably as saturation is approached. This fact is related to the expression (Equation 1) used by Butler *et al.* (1935). This can be readily understood, if it is considered that at the saturation point some minute amount of undissolved compound is present; therefore the partial vapor pressure would be the same as that of the pure material. At half this saturation concentration the partial pressure is half the vapor pressure of the pure material, and so on. If the compound is poorly soluble, there is little interaction of the solute molecules with each other.

Comparison of Experimental and Predicted Volatilities. Butler *et al.* (1935) expressed the volatility in terms of p/N values. These values are related to the air-water partition coefficient (K) used in the present work by a simple conversion factor,

$$K = \frac{p}{N} \times 0.97 \times 10^{-6} \quad (4)$$

As mentioned above for the less soluble alcohols, Butler *et al.* (1935) calculated p/N values from the vapor pressure of the pure material (p°) and the solubility (N_s). In a similar way the p/N values can be calculated from p° and the activity coefficient. Unfortunately, accurate vapor pressures and solubilities are available for only relatively few compounds. Activity coefficients for a fairly wide variety of compounds are available from the work of Pierotti *et al.* (1959). Vapor pressures and solubilities were determined in the present work for the highest molecular weight members of the homologous series studied. For non-

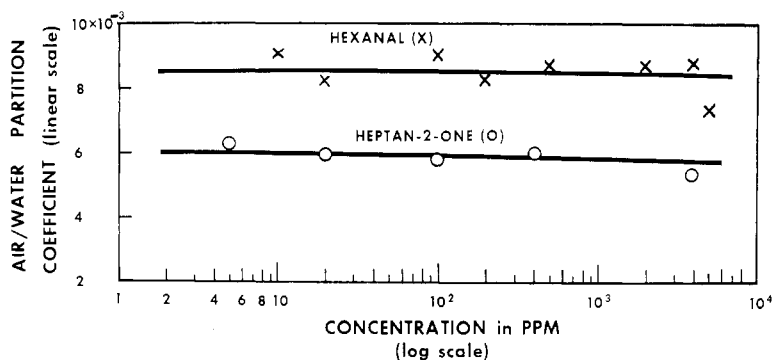


Figure 2. Variation of air-water partition coefficient found for hexanal and heptan-2-one at different concentrations up to point of saturation

Hexanal became saturated at 5000 p.p.m. (0.5%) and heptan-2-one at 4000 p.p.m. (0.4%)

Table II. Comparison of Air to Water Partition Coefficients at 25° C. Found in the Present Work with Both Calculated and Experimental Coefficients of Other Workers

Compound	Present Work		Other Authors	
	Exptl.	Calcd.	Exptl. ^{a, b}	Calculated ^{a, c, d, e}
Acetone	1.5×10^{-3}		1.6×10^{-3}	1.67×10^{-3}
Octan-2-one	7.7×10^{-3}			8.3×10^{-3}
Undecan-2-one	26×10^{-3}	28×10^{-3}		
Acetaldehyde	2.7×10^{-3}			3.6×10^{-3}
Propanal	3.0×10^{-3}			4.4×10^{-3}
Butanal	4.7×10^{-3}			5.2×10^{-3}
Nonanal	30×10^{-3}	34×10^{-3}		
Methyl propionate	7.1×10^{-3}			7.1×10^{-3}
Methyl butyrate	8.4×10^{-3}			10×10^{-3}
Methyl octanoate	32×10^{-3}	34×10^{-3}		
Butanol	3.6×10^{-4}		3.49×10^{-4}	3.50×10^{-4}
Hexanol	7.0×10^{-4}			6.3×10^{-4}
Octanol	10×10^{-4}			9.9×10^{-4}

^a Butler *et al.* (1935).

^b Burnett (1963).

^c Pierotti *et al.* (1959).

^d Jordan (1954).

^e Seidell (1941).

anal, $p^\circ = 0.39$ mm., $N_s = 12.2 \times 10^{-6}$ mole of nonanal per mole of H_2O (96 grams per 10^6 grams of H_2O); for undecan-2-one, $p^\circ = 0.064$ mm., $N_s = 2.22 \times 10^{-6}$ (21 grams per 10^6 grams of H_2O); for methyl octanoate, $p^\circ = 0.38$ mm., $N_s = 11.2 \times 10^{-6}$ (98 grams per 10^6 grams of H_2O).

Comparisons of calculated and experimental air-water partition coefficients are shown in Table II. In general the agreement is satisfactory among calculated, previous experimental, and present experimental coefficients.

Reliability of Results. To measure the small concentration of a particular compound in the atmosphere above an aqueous solution it is necessary to have a sensitive, quantitative, and specific method of detection. Probably one of the best techniques used for this purpose is that of Jennings (1965), who studied air-water equilibria using isotopically labeled organic compounds and measured the concentration by radioactive detection methods. The biggest drawback of this technique, however, is the limited variety of commercially available isotopically labeled organic compounds. Also the method may not necessarily be specific, as small traces of radioactive impurities could interfere.

Gas chromatography is more specific and with flame ionization detection both sensitive and quantitative over a wide range. It is, however, less direct than the radioactive isotope method. The sample has to be transferred from the container used for bringing about the equilibrium to the GLC apparatus. In this transferral, and in the GLC apparatus itself, adsorption can occur which would interfere with the absolute accuracy of the measurement. The equilibrium could also be affected by adsorption on the walls of the container used for holding the solution.

There are two approaches to minimizing adsorption. The first is to use containers with walls constructed of materials with low adsorption properties for the compounds under study, such as Teflon. The second is to heat the container walls. In the present work the authors used a Teflon bottle to contain the solution and transferred the vapor from this bottle, through Teflon tubing, to a heated (160° to 170° C.) silanized, stainless steel, gas-sampling valve fitted with Viton O-rings. A heated gas-sampling valve was first used for this type of study by Burnett (1963).

Another complicating adsorption effect is that of the GLC column and apparatus, between the point of injection of the sample and the detector. Free organic acids are particularly susceptible to adsorption by the column. This effect also is dependent on the amount of sample injected; comparatively large samples are not affected as much as very small samples. In the present work the partition coefficients were determined by Equation 3. Using GLC peak areas of both solution and vapor, area-weight conversion factors cancel out. The volume of the solution was chosen so that the peak area of the solution peak was of the same order of size as the peak area of the vapor. This meant that roughly equal quantities of the sample traveled through the column for vapor and solution samples and that the adsorption factors were similar and tended to cancel out in Equation 3. The carrier gas was also saturated with water, which would keep adsorption by the column to a minimum.

The present system was tested for reliability by comparison of the figures obtained in the present work with those of Butler *et al.* (1935) and Burnett (1963) for butanol and acetone and with the predicted values of

Butler *et al.* (1935) for hexanol and octanol (Table II).

In some earlier work (Buttery *et al.*, 1965), glass syringes were used to transfer the vapor sample to the GLC apparatus. The degree of adsorption for hexanal and propanal by the syringe was measured and found to be negligible. However, the adsorption of surfaces is greater the higher the boiling point of the organic compound. Thus, although it is negligible using a glass syringe for hexanal (b.p. 129°), the adsorption for nonanal (b.p. 190°) as calculated in the present work can be about 80%. The earlier results with syringes then agreed reasonably well with the present work for the C₃ to C₆ aldehydes but were several times lower for nonanal.

Adsorption by syringes is misleading, however, because even though there is adsorption, sampling with a syringe for a single component can be adequate for relative quantitative measurements of the concentrations in a vapor, probably because for each compound the adsorption by the syringe might be expected to be approximately proportional to its concentration and so the amount left for injection would be proportional to the original concentration, at least over a limited range of concentration.

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LITERATURE CITED

- Burnett, M. G., *Anal. Chem.* **35**, 1567 (1963).
Burnett, M. G., Swoboda, P. A. T., *Anal. Chem.* **34**, 1162 (1962).
Butler, J. A. V., Ramchandani, C. N., Thompson, D. W., *J. Chem. Soc.* **1935**, 280.
Buttery, R. G., Guadagni, D. G., Okano, S., *J. Sci. Food Agr.* **16**, 691 (1965).
Jennings, W. C., *J. Food Sci.* **30**, 445 (1965).
Jordan, T. E., "Vapor Pressure of Organic Compounds," Interscience, New York, 1954.
Nawar, W. W., *Food Technol.* **20**, 115 (1966).
Nawar, W. W., Fagerson, I. S., *Food Technol.* **16**(11), 107 (1962).
Nelson, P. E., Hoff, J. E., *J. Food Sci.* **33**, 479 (1968).
Phifer, L. H., Plummer, H. K., *Anal. Chem.* **38**, 1652 (1966).
Pierotti, G. J., Deal, C. A., Derr, E. L., *Ind. Eng. Chem.* **51**, 95 (1959).
Seidell, A., "Solubilities of Organic Compounds," Van Nostrand, New York, 1941.

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