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Effectiveness of water-air and octanol-air partition coefficients to predict lipophilic flavor release behavior from O/W emulsions

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ABSTRACT

Flavor release from food matrices depends on the partition of volatile flavor compounds between the food matrix and the vapor phase. Thus, we herein investigated the relationship between released flavor concentrations and three different partition coefficients, namely octanol-water, octanol-air, and water-air, which represented the oil, water, and air phases present in emulsions. Limonene, 2-methylpyrazine, nonanal, benzaldehyde, ethyl benzoate, α-terpineol, benzyl alcohol, and octanoic acid were employed. The released concentrations of these flavor compounds from oil-in-water (O/W) emulsions were measured under equilibrium using static headspace gas chromatography. The results indicated that water-air and octanol-air partition coefficients correlated with the logarithms of the released concentrations in the headspace for highly lipophilic flavor compounds. Moreover, the same tendency was observed over various oil volume ratios in the emulsions. Our findings therefore suggest that octanol-air and water-air partition coefficients can be used to predict the released concentration of lipophilic flavor compounds from O/W emulsions.

1. Introduction

The flavor perception (taste) of foods is an important criterion for consumers when purchasing food. Upon the consumption of foodstuffs, flavor compounds are released from the food matrix into the vapor phase and are bound to the olfactory receptors. As foods are composed of many different components (i.e., lipids, polysaccharides, proteins, etc.) the release of flavor from any particular food can be influenced by various interactions, such as chemical and structural interactions, among others (Guth & Rusu, 2008). For example, the protein β-lactoglobulin interacts with flavor compounds through hydrophobic interactions to influence flavor release (Pelletier, Sostmann, & Guichard, 1998; Sostmann, Bernal, Andriot, & Guichard, 1997). A number of carbohydrates and salts also interact with flavor compounds in a similar manner (Friel, Linforth, & Taylor, 2000). In contrast, lipids present in foodstuffs decrease the vapor pressure of many lipophilic flavor compounds and result in the retention of flavor compounds in foods (Seuvre, Phillippe, Rochard, & Voilley, 2007). Indeed, the lipid phase is the main component involved in the retention of lipophilic flavor compounds in food components (Roberts, Pollien, & Watzke, 2003; Philippe et al., 2003).

Lipids generally exist in foods as emulsions, which are mixtures of two immiscible phases with emulsifiers. In the presence of emulsifiers, one phase is dispersed in another phase in the form of droplets. In the context of lipids, the amount of lipids present in an emulsion can change the texture and taste of the substances (Shamil, Wyeth, & Kilcast, 1991; Malone, Appelqvist, & Norton, 2003), and as such, variation in the volume ratio of lipids in emulsions is an important method for modifying flavor release. In general, the greater the lipid content in an oil-in-water (O/W) emulsion, the more lipophilic flavor compounds are retained in the emulsion (Bayarri, Taylor, & Hort, 2006), thus resulting in a decreased flavor intensity (Frank, Appelqvist, Piyasiri, & Delahunty, 2012). To prepare foodstuffs of particular textures, emulsions are often used, and as such, emulsion techniques are required during food processing to prepare the required oil and water mixtures. For example, mayonnaise, whipped cream and milk are O/W emulsions. Indeed, for these products, the perceived flavor is particularly important to consumers, and so the prediction of flavor release behavior from emulsions is useful during the development of processed foods.In O/W emulsions, it is considered that flavor compounds are transferred from oil droplets to a water (aqueous) phase prior to release from the water phase into an air (vapor) phase. Thus, to predict the flavor release behavior of such compounds, partition coefficients are often used, which are defined as the ratio of a compound concentration between two phases

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under equilibrium (Meynier, Lecoq, & Genot, 2005). In general, the values of partition coefficients depend on the chemical functional groups present and the lengths of the carbon chains in the compound (Buttery, Guandagni, & Ling, 1973). Octanol-water partition coefficients (logPow) are the most general index used to represent the lipophilicity of chemical compounds. Indeed, the relationship between the concentration of flavor compounds released from emulsions and their corresponding logPow values has been studied in detail (Druaux & Voilley, 1997; Rabe, Krings, & Berger, 2004; Benjamin, Leus, & Everett, 2011). In contrast, the water-air partition coefficient (logPwa) represents the volatility (from water) of flavor compounds. However, the determination of logPwa values experimentally is challenging because many flavor compounds are lipophilic and exhibit poor solubility in water. In addition, in O/W emulsions, both the oil phase and the emulsifiers can inhibit flavor release, while some emulsifiers can interact with flavor compounds in the water phase or the interfaces of O/W emulsions (Chen, Guo, Wang, Yin, & Yang, 2016; Lee, Liu, Wong, & Liu, 2017). As such, the oil phase present in O/W emulsions can improve the retention of flavor compounds compared to the retention by emulsifiers (Roberts et al., 2003). It was considered that many lipophilic flavor compounds are released into an air phase from the oil droplets through the water phase. We therefore considered that an octanol-air partition coefficient (logPoa) could be employed to predict the flavor release behavior from O/W emulsions. For the purpose of this study, three partition coefficients, namely logPow, logPwa and logPoa, will be examined. These three coefficients are related as outlined in Eq. (1):

$$\text{logPow} + \text{logPwa} = \log\left(\frac{c_o}{c_w} \times \frac{c_w}{c_a}\right) = \log\left(\frac{c_o}{c_a}\right) = \text{logPoa} \quad (1)$$

where *Co*, *Cw*, and *Ca* are the concentrations of the volatile compound in the oil, water, and air phases, respectively under equilibrium. In addition, an air-emulsion partition coefficient (logPae) has also been reported in the literature (Harrison, Hills, Bakker, & Clothier, 1997; Meynier et al., 2005), with the various partition coefficients being related as outlined in Eq. (2):

$$P_{ae} = \frac{1}{\left(\left(\frac{\Phi_c}{P_{aw}}\right) + \left(\frac{\Phi_d}{P_{oa}}\right)\right)} \quad (2)$$

where P_{ae} is the partition coefficient between air and the emulsion, Φ_c is the mass fraction of the continuous phase, Φ_d is the mass fraction of the dispersed phase, P_{aw} is the partition coefficient between air and the continuous phase, and P_{oa} is the partition coefficient between air and the dispersed phase. In this study, water was employed as the continuous phase and canola oil was employed as the dispersed phase. This allowed us to predict the concentration of flavor compounds released into the headspace from O/W emulsions according to Eq. (2).

In flavor release simulations, where flavor compounds bear the same chemical functional groups, the released concentrations of the flavor compounds correlate with the lipophilicity of the flavor compounds. Indeed, it was previously reported that the released concentrations of ester and ketone groups from O/W emulsions correlated with the length of carbon chains (i.e., lipophilicity) regardless of droplet size and fat volume in the O/W emulsions (Frank et al., 2012). However, there are thousands of different types of food flavoring compounds possessing diverse chemical structures. As such, it is difficult to predict the concentrations of released flavor compounds even when their molecular structures are known. We therefore chose to investigate the concentration of different structural flavor compounds released from various O/W emulsions containing a range of oil contents. We will then move on to examine and compare the correlation between the experimental data and the three calculated partition coefficients, i.e., logPea, logPwa and logPoa. The overall aim of this investigation is to examine whether the logPoa and logPwa values are useful for predicting the released concentrations of flavor compounds from O/W emulsions. We expect that the results of this study will provide a novel method for simulating flavor release from O/W emulsions without the requirement to calculate logPea values.

2. Materials and methods

2.1. Materials

Eight flavors were examined in this study, namely limonene (≥97%), nonanal (≥95%), 2-methylpyrazine (≥99%), benzaldehyde (≥99%), and ethyl benzoate (≥99%), which were purchased from Sigma Aldrich (Gillingham, UK). Benzyl alcohol (≥99%) and octanoic acid (≥99%) were purchased from Nacalai Tesque (Kyoto, Japan), and α-terpineol (≥98%) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The partition coefficients (logPow, logPwa, and logPoa) of the eight flavors are shown in Table 1. These flavors were dissolved in ethanol (≥99.5%, Nacalai Tesque, Kyoto, Japan) to produce stock solutions of 1 vol%. Decaglycerol monolaurate (ML750) was employed as a surfactant and was supplied by Sakamoto Yakuhin Kogyo (Osaka, Japan). Finally, canola oil (J-oil mills, Inc., Tokyo, Japan) was purchased from a local shop.

2.2. Sample preparation

ML750 (1.0 g/L) was dissolved in distilled water by stirring for 3 h at 300 rpm. Canola oil (1, 5, 10, or 20 vol%) was then added to the aqueous ML750 solution, and the resulting mixture was homogenized for 2 min at 5000 rpm using an ultrafast digital homogenizer (AHG-160D, AS ONE, Osaka, Japan) to prepare the coarse emulsions. The droplet sizes of the coarse emulsions droplet size were reduced by passing through a Shirasu Pores Glass (SPG) membrane with a pore size of 10.0 μm (SPG Technology Co. Ltd., Miyazaki, Japan). This resulted in the preparation of monodispersed emulsions (Shimoda et al., 2011). The sample emulsions were then added to glass vials (50 mL) and the appropriate stock solutions were dissolved individually in the sample emulsions. Each flavor was dissolved in the various sample emulsions at a concentration of 100 ppm, and the emulsions were sealed with Teflon film and stored at 4 °C over 12 h with stirring at 350 rpm.

2.3. Static headspace analysis

The headspace concentrations of the volatile flavor compounds were measured using a gas chromatograph (GC-14B, Shimadzu Co., Kyoto, Japan) equipped with a DB-WAX capillary column (30 m × 0.32 mm i.d., 0.5 μm film thickness, Agilent Technologies Inc., Santa Clara, CA) and coupled with a flame ionization detector

Table 1
Octanol-water, water-air, and octanol-air partition coefficients (logPow, logPwa, and logPoa, respectively) of the various flavor compounds employed herein.

Flavor compound	logPow[1]	logPwa[1]	logPoa[2]
2-Methylpyrazine	0.21	4.04	4.25
Limonene	4.38	-0.11	4.27
Benzaldehyde	1.48	2.96	4.44
Nonanal	3.27	1.52	4.79
Ethyl benzoate	2.64	2.52	5.16
Benzyl alcohol	1.10	4.86	5.96
α-Terpineol	3.28	3.30	6.58
Octanoic acid	3.05	4.43	7.48

[1] Calculated using the *EPI* suite.
[2] Calculated using Eq. (1).