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Effect of additives on volatility of aroma compounds from dilute aqueous solutions

Eva Baránková, Vladimír Dohnal*

Department of Physical Chemistry, University of Chemistry and Technology, 166 28 Prague 6, Czech Republic

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ABSTRACT

Volatility of fragrance and flavor substances from food and cosmetic products or intermediates is influenced by admixtures of various nonvolatile substances which occur in these basically aqueous matrices naturally or are added on purpose. For control of the production process and formulation of a final product, it is important to know how such admixtures affect the air–water partitioning of aroma substances. In this work, using an effective headspace gas chromatography method, we studied the effect of salts (NaCl, $NaHCO_3$), saccharides (glucose, sucrose), macrocyclic polysaccharides (α-cyclodextrin, β-cyclodextrin), polyalcohols (ethylene glycol, glycerol) and protein denaturants (urea, guanidine hydrochloride) on the air–water partition coefficient of two isomeric esters ethyl butanoate and butyl ethanoate as typical representatives of aroma substances. The strongest effect was observed for cyclodextrins (aroma retention by inclusion complexation) and for inorganic salts (aroma release by salting-out). For other additives, a weaker salting-in (denaturants, ethylene glycol) or salting-out (saccharides, glycerol) was found. The dependence of these effects on the additive concentration was in all cases well correlated by Setschenow equation and for cyclodextrins also by the 1:1 complex formation model. Determination of the temperature dependence of these effects gave a useful insight into the thermodynamics of the ester–cyclodextrin inclusion binding. Considerations of guest–host size matching supported by simple molecular modeling proved useful to rationalize different binding affinities observed for individual ester–cyclodextrin pairs and suggest their possible binding modes.

1. Introduction

The presence of flavor and fragrance substances in food and cosmetic products determines their sensorial properties, deciding thus about their consumer acceptability. For rational control of the olfactory and gustatory perception knowledge of aroma partitioning between air and aqueous medium is essential. The air–water partition coefficient, however, depends on the composition of the aqueous matrix; it is affected in both positive and negative direction by various nonvolatile admixtures which occur in these matrices naturally or are added on purpose. Strong salting-out effects, typical especially for inorganic salts, can be utilized for separation of a given aroma from the aqueous matrix. Strong salting-in effects, typical for macrocyclic polysaccharides, can be on the other hand employed for retention of a given aroma and its protection against thermal or chemical degradation. Although studies examining the effect of nonvolatile substances on volatility of aqueous aroma compounds are quite abundant in the literature [1–8], published results have sometimes qualitative rather than quantitative character.

The goal of this work is to obtain accurate quantitative information on the effects of various food-relevant admixtures (additives, modifiers) – salts, saccharides, polyalcohols, protein denaturants, and cyclodextrins (CDs) – on volatility of two isomeric esters, ethyl butyrate and butyl acetate, from their dilute aqueous solutions. The selected volatile organic compounds are important representatives of the fruit aroma and occur naturally as well as in artificial flavors and fragrances. Experimental methodology for the study uses headspace gas chromatography and has been developed in this laboratory recently [9]. The effects of the additives on air–water partition coefficient of the aroma substances are correlated by Setschenow equation and for cyclodextrins also analyzed in terms of a complex formation model. Thermodynamic approach and simple molecular modeling are employed to rationalize differences in strength and mode of binding for individual ester–CD pairs.

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* Corresponding author at: Department of Physical Chemistry, University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czech Republic. Tel.: +420 220 444 297.

E-mail addresses: dohnalv@vscht.cz, Vladimir.Dohnal@vscht.cz (V. Dohnal).

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2. Theory

2.1. Headspace gas chromatography (HSGC) method

The HSGC method is based on static gas–liquid equilibration of a solution in a vial and subsequent analysis of the vapor by gas chromatography. Mass balance considerations for the solute distribution between the gas and the liquid phase lead to [10]

$$c_1^{\mathrm{L}} = \frac{c_1}{1 + K_{\mathrm{GL}}\beta} \tag{1}$$

where c_1 is the solute concentration in the solution loaded into the vial, c_1^{L} is the solute concentration of the equilibrium liquid phase, $\beta = V_{\mathrm{G}}/V_{\mathrm{L}}$ is the headspace-to-liquid volume ratio of the vial, and K_{GL} is the gas–liquid partition coefficient. This latter quantity generally used to describe the partitioning of a volatile solute between the gas and the liquid phase is defined as

$$K_{\mathrm{GL}} = \frac{c_1^{\mathrm{G}}}{c_1^{\mathrm{L}}} \tag{2}$$

Assuming proportionality between the GC response A_1 and the solute gas phase concentration c_1^{G} one gets

$$A_1 = k \times c_1^{\mathrm{G}} = k \times K_{\mathrm{GL}} c_1^{\mathrm{L}} = k \times \frac{K_{\mathrm{GL}} c_1}{1 + K_{\mathrm{GL}}\beta} \tag{3}$$

where k is the proportionality constant. In analogy, for the same stock solution of the solute but without additive added (superscript 0) and the same vial loading (β) one may write

$$A_1^0 = k \times c_1^{\mathrm{G}0} = k \times K_{\mathrm{GL}}^0 c_1^{\mathrm{L}0} = k \times \frac{K_{\mathrm{GL}}^0 c_1^0}{1 + K_{\mathrm{GL}}^0\beta} \tag{4}$$

Combining Eqs. (3) and (4) yields after rearrangement

$$\frac{K_{\mathrm{GL}}}{K_{\mathrm{GL}}^0} = \frac{A_1}{A_1^0} \times \frac{c_1^0}{c_1} \times \frac{1}{1 + K_{\mathrm{GL}}^0\beta[1 - (A_1/A_1^0)(c_1^0/c_1)]} \tag{5}$$

Eq. (5) is a basic relation enabling one to determine explicitly the effect of added additive on the solute's gas–liquid partition coefficient from the HSGC measurement. It should be noted that the first term (A_1/A_1^0) on the right-hand side of Eq. (5) is dominant one, while the other two terms have a character of corrections which can be under certain circumstances even negligible. The second term (c_1^0/c_1) corrects for the change of the solute concentration caused by the modifier addition and can be evaluated from

$$\frac{c_1^0}{c_1} = (1 + m_3 M_3)\frac{\rho^0}{\rho} \tag{6}$$

where m_3 is the molality of the added modifier and M_3 its molar mass, ρ^0 the density of pure water, and ρ the density of the modifier solution. The third term on the right-hand side of Eq. (5) is a relatively small vapor-space mass-balance correction which tends to be negligible for small values of K_{GL}^0 and/or A_1/A_1^0 ratios close to unity. In cases where the mass balance correction is essential, K_{GL}^0 must be known from a separate VLE experiment and β determined on the basis of the vial loading. An important advantage of the present HSGC procedure is the fact that it requires no calibration of GC response.

2.2. Dependence of gas–liquid partition coefficient on modifier concentration

The effect of modifier on K_{GL} varies with the concentration of added modifier. To describe this concentration dependence, a simple empirical equation due to Setschenow has been often used in the literature. In this work, we employed the Setschenow equation in the following form

$$\log\frac{K_{\mathrm{GL}}}{K_{\mathrm{GL}}^0} = K_{\mathrm{S}} \times \frac{m_3}{m_{\mathrm{st}}} \tag{7}$$

where K_{S} is the Setschenow constant, m_3 is the molality of the added modifier, and $m_{\mathrm{st}} = 1\ \mathrm{mol\ kg^{-1}}$ is the standard molality.

Strong salting-in effects characteristic for cyclodextrins result from the ability of these macrocyclic substances to encapsulate solutes into their cavity [11]. As the inclusion complex formation decreases the concentration of free solute molecules in the solution and thus also their concentration in the vapor phase, K_{GL} well senses this binding. Assuming 1:1 complex formation and experiments conducted under an excess of cyclodextrin, the following equation for the variation of K_{GL} with CD concentration can be derived [9]

$$\frac{K_{\mathrm{GL}}^0}{K_{\mathrm{GL}}} - 1 = K \times \frac{c_3}{c_{\mathrm{st}}} \tag{8}$$

where K is the equilibrium constant of the solute–CD binding, c_3 is the molar concentration of the added modifier, and $c_{\mathrm{st}} = 1\ \mathrm{mol\ dm^{-3}}$ is the standard concentration.

3. Experimental

3.1. Materials

The chemical samples used for measurements are specified in Table 1. They were used without further purification. The water content in cyclodextrins was determined by the coulometric Karl Fischer titration and taken into account in the preparation of sample solutions. Water was distilled and subsequently treated by a Milli-Q Water Purification System (Millipore, USA).

3.2. Apparatus and procedure

An automatic headspace sampler Turbomatrix HS40 (Perkin-Elmer) connected to an Agilent 6890 Plus GC equipped with a flame ionization detection was employed for the measurements. Nitrogen served as a carrier and sampling gas. The temperature of the headspace sampler oven (i.e., the experimental temperature) was calibrated using a Pt-100 resistance thermometer (Testo Model 950) the sensor of which was inserted in an ad hoc dummy aluminum vial placed in the sampler oven. The standard

Table 1
Specification of chemicals used in this work.

Compound	Source	Mass fraction purity
Ethyl butanoate	Merck	>0.98
Butyl ethanoate	Penta, Czech Rep.	0.992
Sodium chloride	Lachema, Czech Rep.	0.999
Sodium hydrogen carbonate	Lachema, Czech Rep.	0.99
Sucrose	Lachema, Czech Rep.	0.998
Glucose	Fluka	0.995
Ethylene glycol	Fluka	0.995
Glycerol	Penta, Czech Rep.	0.995
Urea	Lachema, Czech Rep.	0.995
Guanidine hydrochloride	Fluka	0.99
α-Cyclodextrin	CycloLab Hungary	>0.98, water content[a] 0.1103
β-Cyclodextrin	CycloLab Hungary	>0.98, water content[a] 0.1394

[a] Determined by KF titration.