Thermodynamic study of two different chewing-gum bases by inverse gas chromatography

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Abstract

This work describes the physico-chemical characterisation of two different chewing gum bases and the interactions with the incorporated flavour molecules using inverse gas chromatography as a specific technique. Ethyl butyrate, limonene, 1-octanol and *cis*-2-hexenal were injected to calculate the partition coefficients, the activity coefficients and the Henry's constants at infinite dilution and 298 K. The partition coefficients, activity coefficients and Henry's constants showed a difference between the two gum bases, but the excess molar heat of mixing (ΔH_m) showed an incompatibility for the flavour compounds in both gum bases. Finally, the determination of the solubility parameter of the gum bases by two methods showed that the two gum bases have similar solubility parameters at 298 K.
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Keywords: Thermodynamic parameters; Chewing gum; Food analysis; Inverse gas chromatography; Activity coefficients; Aroma compounds

1. Introduction

Chewing gum manufacturers are intensively working on the ingredient composition (formulation) of gum bases to achieve specific texture properties and better flavour impact and lastingness. An increasing number of patents were submitted about these topics and efforts are continuously underway to improve them. The characterisation of flavour gum base interactions is still under investigation and only a few scientific papers have been published in this specific field. Inverse gas chromatography (IGC) is a technique widely used in polymer science to characterise from a physico-chemical point of view pure polymers and polymer blends [1–3]. As chewing gum bases can be considered as polymer blends, IGC could be used to characterise chewing gum bases and their interactions with flavour molecules. Thermodynamic parameters such as partition coefficients, activity coefficients, Henry's constants, excess molar heat of mixing and solubility parameters were determined using volatile compounds with well-known physico-chemical properties. The main flavour retention mechanism is the liquid–liquid interaction between the gum and the flavour molecules.

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2. Preparation and composition of chewing gums

The process of producing chewing gum is basically a blending operation that uses a horizontal sigma blade mixer. The mixer is equipped with a circulating water-heated jacket (50–60 °C). Sweeteners are mixed with the pre-heated chewing gum base (the temperature of the gum base is between 50 and 55 °C). The mixing time is typically about 12–15 min for a 1-kg laboratory batch. Flavours are incorporated in a range from 0.5 to 2.0% at the last 3–5 min of the process. A non-exhaustive list of ingredients used for chewing gum bases is given in Table 1.

To better understand the interactions, De Roos [4] listed physico-chemical parameters such as partition coefficients adding kinetic parameters to improve the model. Lee [5] gave a list of equations from which the partition coefficients and diffusion coefficients could be calculated without any experimental data. These parameters were then used to predict drug delivery in chewing gums. A list of patents showed how to select the chewing gum ingredients as a function of their solubility parameter to obtain the desired properties [6,7]. The use of inverse gas chromatography to determine thermodynamic parameters characterising gum bases and their interactions with flavour molecules can be considered as an interesting analytical technique in food science, especially for chewing gum. It could help to better understand the flavour release phenomena from chewing gums.

3. Inverse gas chromatography and food science

IGC is an analytical technique widely used to study surface properties of adsorbents, cellulose, starches or other polymers. The interest for IGC in food science is increasing in particular when a humidity control is available. The chewing gum polymers give the opportunity to transfer IGC methodology into food science. Gas–liquid chromatography (GLC) was used for the determination of solubility parameters of synthetic polymers such as poly(dimethylsiloxane) and poly(methylmethacrylate) [3,8]. Price and Guillet and co-workers [3,9–13] were the pioneers in the physico-chemical interpretation of GLC data from polymers. Pawlisch [14], Macris [15] and Danner and co-workers [16,17] used GLC for purposes going from thermodynamic parameters to diffusion coefficient by capillary IGC. In food science, King and List [18] used GLC to study the interactions of several volatile compounds in soybean oil. Boutboul [19], Delarue and Giampaoli [20], and Boutboul et al. [21] were able to characterise the type of interactions (London, Van der Waal's, dipole–dipole or H-bonding) between starch and several flavour molecules. Gauthier et al. [22] showed that attractive or repulsive forces could be calculated from IGC data. Benczédi and Tomka [23–25] calculated thermodynamic parameters characterising water–starch interactions by IGC and developed an equation calculating the solubility parameter of starch using only water as solvent. Starting from the actual GLC knowledge in food science, this present work focused in the study of two different chewing-gum bases and their interactions with flavour molecules by the determination of thermodynamic parameters.

4. Material and methods

Inverse gas chromatograph was a model 6890 instrument from Agilent (Palo Alto, CA, USA), modified by Surface Measurement System (London, UK). Flame ionisation detection (FID) and thermoconductivity detection were installed in series allowing organic compounds and water to be detected. Helium was used as a carrier gas at flow-rates varying from 5 to 25 ml/min. The relative humidity (RH) was set to 0%. The glass columns were 20, 55

Table 1
Ingredients composition of a chewing-gum in %

Ingredient	Sugar gum (%)		Sugarless gum (%)	
	Chewing	Bubble	Chewing	Bubble
Gum base	19.4	16.8	25.0	26.0
Corn syrup	19.8	22.4	–	–
70% Sorbitol	–	–	15.0	17.0
Sugar	59.7	59.7	–	–
Glycerol	0.5	0.3	6.5	6.5
Water	–	0.3	–	–
Sorbitol	–	–	52.3	49.3
Flavour	0.6	0.5	1.2	1.2
Total	100.0	100.0	100.0	100.0

and 210 cm long with 3 mm I.D. All injections were performed manually at infinite dilution (constant retention times at low sample amount). Methane or air can be used as a non-retained compound. To set the right experimental temperature range, a thermal analysis with a differential scanning calorimeter (DSC7 from Perkin-Elmer, Shelton, CT, USA) was used to determine the melting point (mp) or glass transition temperature (T_g) of the gum bases. A thermogravimetric analyser (TGA7 from Perkin-Elmer) was also used to determine the gum load in the packed column. A Nova1000 instrument (Quantachrome, Germany) was used to determine the density of the gum bases. The alkanes C_5 to C_{12}, toluene, ethyl acetate, acetone and Chromosorb G AW/DMCS 60–80 mesh were at min. 99% purity from Sigma–Aldrich and the four flavour molecules from a tutti-frutti aroma (ethyl butyrate, limonene, 1-octanol and *cis*-2-hexenal) were sourced within Firmenich. Finally, the two unflavoured and unsweetened gum bases containing 25% poly(vinyl acetate) (gum A) and 25% poly(isobutylene) (gum B) were supplied by Cafosa (Barcelona, Spain).

4.1. Preparation of the packed column:

The standard method used to coat polymers on DMCS treated inert supports is well described by many authors [2,10]. Toluene at 70 °C was found to be a good solvent for chewing gum base and columns with 10% (w/w) and 20% (w/w) chewing-gum bases were prepared.

4.2. Retention volumes

Eqs. (1) and (2) give the definition of the two fundamental retention volumes:

$$V_n = jF(t_r - t_m) \qquad \text{Net retention volume (ml)} \qquad (1)$$

$$V_g^o = \frac{jF(t_r - t_m)}{w} \cdot \frac{273.15}{T_c}$$

Specific retention volume (ml/g)   (2)

$$K_p = \frac{V_g^0 \rho_g T_c}{273}$$

Partition coefficient between gum and carrier gas

by mass fraction (−)   (3)

The specific retention volumes were determined at 333, 343, 353, 363, 373 and 383 K and the $\ln(V_g^o) = f(1/T)$ linear regression was used to extrapolate the specific retention volume at 298 K. The partition coefficients were then calculated at 298 K using Eq. (3) [26].

4.3. Activity coefficient and Henry's constant at infinite dilution

At infinite dilution, the following equation can be considered (Eq. (4)):

$$p_i = \Omega_i^\infty P_i^0(T) \, x_i \qquad (4)$$

$$He = \Omega_i^\infty P_i^0(T) \qquad (5)$$

Price [3,9], Guillet [13], DiPaola-Baranyi [10,27] and Patterson [28] defined the activity coefficient by mass fraction (Ω_i) (Eq. (6)), volume fraction (γ_i) (Eq. (7)) and the Flory–Huggins interaction parameter $(X_{1,2})$ (Eq. (8)) for a polymer with infinite molecular mass as followed:

$$\ln(\Omega_1^\infty) = \ln\left(\frac{273.15R}{V_g^0 P_1^0 M_1}\right) - \frac{P_1^0}{RT}(B_{11} - V_1^0) \qquad (6)$$

$$\ln(\gamma_1^\infty) = \ln\left(\frac{\rho_2}{\rho_1}\right) + \ln\left(\frac{273.15R}{V_g^0 P_1^0 M_1}\right)$$

$$- \frac{P_1^0}{RT}(B_{11} - V_1^0) = X_{1,2}^\infty + 1 \qquad (7)$$

$$X_{1,2}^\infty = \ln(\gamma_1^\infty) - 1 \qquad (8)$$

4.4. Excess molar heat of mixing

To complete the calculation of thermodynamic parameters for flavour gum base interactions, the molar heat of solution can be calculated using Eq. (9) and the excess molar heat of mixing using Eq. (10):

$$\Delta H_s = -\frac{R\partial(\ln(V_g^0))}{\partial(1/T)} \qquad (9)$$

$$\Delta H_m = \Delta H_v + \Delta H_s \qquad (10)$$

where $\Delta H_m =$ excess molar heat of mixing (J/mol), $\Delta H_v =$ molar heat of vaporisation (J/mol), and $\Delta H_s =$ molar heat of solution (J/mol).

A $\Delta H_m < 0$ indicates a compatibility or presence of attractive forces (interactions) between the solute and the polymer (solubilisation or plastification). A $\Delta H_m > 0$ suggests an incompatibility or presence of repulsive forces between the solute and the polymer (phase separation). A $\Delta H_m = 0$ suggests an athermal process where the driving force of the solute–polymer mixing is entropy.

4.5. Solubility parameter

Polymers can be characterised by a thermodynamic parameter defined as followed (Eq. (11)):

$$\delta_i = \left(\frac{E_i^v}{V_i}\right)^{1/2} = \left(\frac{\Delta H_i^v - RT}{V_i}\right)^{1/2} = (\text{c.e.d.})^{1/2} \quad (11)$$

where δ_i = solubility parameter ($i = 1$ solute, $i = 2$ polymer) (MPa$^{1/2}$), E^v = energy of evaporation (kJ/mol), H^v = enthalpy of evaporation (kJ/mol), and c.e.d = cohesive energy density.

This parameter can be easily determined experimentally for molecules with well-defined enthalpies of evaporation, which is not the case for most polymers. DiPaola-Baranyi et al. [27] developed Eq. (11) and was able to determine by linear regression the solubility parameter of a polymer by IGC (Eq. (12)) at a defined temperature. Benczédi et al. [23,24] found a method to determine solubility parameters using only one solute at different temperatures (Eq. (13)). The limitation of Eq. (13) is the necessity to know all the constants at the experimental conditions (temperature and pressure) limiting the number of solvent molecules:

$$\left(\frac{\delta_1^2}{RT} - \frac{X_{1,2}^\infty}{V_1^0}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{X_s^\infty}{V_1^0}\right) \quad (12)$$

$$\delta_2(T) = \delta_1(T) - \left[\frac{\partial(X_{1,2}^\infty/V_1)}{\partial(1/T)}\right] \quad (13)$$

5. Results and discussion

The differential scanning calorimetry (DSC) measurements showed that the two gum bases are in the rubbery state at ambient temperature (T_g gum A = 283.9 K and T_g gum B = 291.1 K). The lowest experimental temperature was set to 333 K. A

significant density difference exists between the two gum bases (1.216 g/ml for gum base A and 1.043 g/ml for gum base B) due to the different gum base formulations. The calculation of the specific retention volume (V_g^o) needs the exact weight of gum base in the column. The calcination method by thermogravimetric analysis (TGA) was used in this work and the results are summarised in the Table 2.

The calcination shows that the gum base is well coated on the inert support and not demixed during the solvent evaporation or the drying step. After packing different columns (20, 55 and 210 cm long) and injecting volatile compounds, the optimal condition can be set as followed:

(1) Relative humidity of the system = 0%
(2) Temperature range = from 333 to 383 K (GLC conditions)
(3) Flow rate = from 5 to 25 ml/min.
(4) Gum base loading = 20%
(5) Column length = 55 cm

The experiments were divided in two parts: a first part concerning the determination of the thermodynamic parameters characterising the flavour–gum interactions and a second part characterising the gum base by the determination of the solubility parameter.

5.1. Flavour–gum base interactions

Using the optimised experimental conditions, the partition coefficients, activity coefficients and Henry's constant by mass fraction were calculated at infinite dilution and at 298 K. The results are summarised in Table 3.

The results show significant differences for the four flavour molecules in the two gum bases. The partition coefficients, activity coefficients and Henry's constants are higher for the four molecules

Table 2
Determination of the exact gum base loading in the packed columns

Stationary phase	Mass loss (%)	Exact loading (%)
Chromosorb G, 60–80 mesh	1.9	0
Gum base A, 10%	9.9	8.0
Gum base A, 20%	17.7	15.8
Gum base B, 10%	10.4	8.5
Gum base B, 20%	17.0	15.1

Table 3
Partition coefficients, activity coefficients and Henry's constant by mass fractions at 298 K

flavour	Partition coefficient (−)		Activity coefficient (−)		Henry's constant (kPa)	
	Gum base A	Gum base B	Gum base A	Gum base B	Gum base A	Gum base B
Ethyl butyrate	747.2	1119	45.8	26.9	40.1	23.6
cis-2-Hexenal	2197	2962	38.3	20.9	6.47	3.53
1-Octanol	6851	13 390	37.4	14.3	4.61	1.76
Limonene	4273	13 680	42.4	9.74	21.4	4.92

in the gum base A meaning a higher tendency to leave the gum base, i.e. a lower compatibility with the gum base A. For limonene, the activity coefficient in the gum base A is four times higher compared with the gum base B. The calculation of the molar heats of solution and the excess molar heats of mixing will complete the thermodynamics of flavour–gum base interactions. Table 4 summarised these results.

The addition of the molar heat of vaporisation and the molar heat of solution gives the excess molar heat of mixing. Positive values suggest an incompatibility or presence of repulsive forces between the flavour molecules and the gum bases. The gum base B showed a less incompatibility than the gum base A, but it can be assumed that the flavour molecules are mainly incorporated as droplets in the two gum bases. Neither solubilisation nor plastification of the gum bases occurred with the investigated flavour compounds. The high values obtained for the activity coefficients and Henry's constants can be correlated

with the positive excess enthalpies of mixing. Looking at the composition of the two gum bases, the gum base containing 25% of poly(isobutylene) seems to have more affinity for the four flavour compounds than the gum base B containing 25% of poly(vinyl acetate). From these thermodynamic results, predictions of the flavour release from chewing gum bases could be done, but it was not the main topic of this paper.

5.2. Solubility parameter of the two gum bases

The solubility parameter allows a characterisation of the gum base from a thermodynamic point of view. For polymers having no defined molar heats of vaporisation, indirect ways have to be considered. One of the most common ways to determine the solubility parameter is the group contribution method, but it has some important limitations such as the reduction of the polymer to a single molecular species. IGC is an alternative method taking into

Table 4
Molar heat of solution and excess molar heat of mixing of the flavour molecules in the gum bases A and B at 298 K

	Molar heat of vaporization (kJ/mol) exp. temp.: 343 K	Molar heat of solution (kJ/mol)		Excess molar heat of mixing (kJ/mol)	
		Gum base A	Gum base B	Gum base A	Gum base B
Ethyl butyrate	+40.0	−31.0	−34.8	+9.0	+5.2
cis-2-Hexenal	+46.5	−33.6	−36.7	+12.9	+9.8
1-Octanol	+64.2	−32.3	−40.5	+31.9	+23.7
Limonene	+55.0	−28.8	−41.0	+26.2	+14.0
Pentane	+23.5	–	−27.4	–	−3.9
Hexane	+28.7	−20.0	−30.6	+8.7	−1.9
Heptane	+33.9	−24.6	−34.6	+9.3	−0.7
Octane	+38.2	−30.0	–	+8.2	–
Nonane	+43.2	−34.6	–	+8.6	–
Acetone	+28.1	−14.3	−29.7	+13.8	−1.6
Ethyl acetate	+32.4	−19.7	−32.8	+12.7	−0.4
Toluene	+35.5	−27.3	−36.4	+8.2	−0.9

account the interaction between the polymer and the selected volatile compounds under GLC. IGC can be a very interesting method when apolar polymers are investigated. The calculation of the solubility parameters using Eqs. (12) and (13) gave similar results (17.2 and 18.6 MPa$^{1/2}$ for gum base A, 15.2 and 16.1 MPa$^{1/2}$ for gum base B). These results show that the two gum bases are apolar and the London forces are responsible for the interactions.

6. Conclusions

This work shows how IGC can be used to study thermodynamic parameters characterising flavour–chewing gum as well as gum base solubility parameters. These thermodynamic parameters are then used to better understand the physico-chemical properties of a flavoured gum. Partition coefficients, activity coefficients and Henry's constants show the affinity of flavour molecules for gum bases, molar heat of solution shows the compatibility of flavour molecules with gum bases predicting a solubilisation of the flavour or plastification of the gum base. This compatibility or incompatibility of a flavour molecule in gum base could cause a change in the flavour release. A high compatibility can be correlated to a slow release or lastingness where an incompatibility gives a flavour impact without lastingness. In the case of chewing gums, it exists several solutions for flavour impact while lastingness is still under investigations.

Finally, the solubility parameter allows a characterisation of the gum bases without taking into account any flavour interactions. In this work, the two gum bases show an apolar character.

IGC is a very interesting technique to better understand and predict physico-chemical properties of flavoured gum bases.

References

[1] J.S. Aspler, D.G. Gray, J. Polym. Sci. 21 (1983) 1675.
[2] Z.Y. Al Saigh, Int. J. Polym. Anal. Charact. 3 (1997) 249.
[3] G.J. Price, J.E. Guillet, J. Solut. Chem. 6 (1986) 605.
[4] K.B. de Roos, Flavour Sci. Technol. (2002) 355.
[5] W.W. Lee, Pharm. Technol. On-Line (2001) 1.
[6] J. Bronislaw, Patent WO 99/44436, 1999.
[7] P. Schmiedel, M. Jekel, Patent EP01/08279(C03K), 2002.
[8] A.J. Ashworth, G.J. Price, Macromolecules 19 (1986) 358.
[9] G.J. Price, J.E. Guillet, J. Solut. Chem. 16 (1987) 605.
[10] G. DiPaola-Baranyi, J.E. Guillet, Macromolecules 11 (1978) 228.
[11] J.E. Lipson, J.E. Guillet, in: R.B. Seymour, G.A. Stahl (Eds.), Macromolecular Solutions. Solvent–Property Relationships in Polymers, Pergamon Press, New York, 1980.
[12] D.G. Gray, J.E. Guillet, Macromolecules 7 (1974) 244.
[13] J.M. Braun, J.E. Guillet, Adv. Polym. Sci. 27 (1976) 107.
[14] C.A. Pawlish, PhD thesis, University of Massachusetts, Amherst, MA, 1985.
[15] A. Macris, MS thesis, University of Massachusetts, Amherst, MA, 1979.
[16] I. Hadj Romdhane, R.P. Danner, AIChE J. 39 (1993) 625.
[17] I. Hadj Romdhane, R.P. Danner, J.L. Duda, Ind. Eng. Chem. Res. 34 (1995) 2536.
[18] J.W. King, G.R. List, J. Am. Oil Chem. Soc. 67 (1990) 1.
[19] A. Boutboul, Dissertation, Paris XI Orsay, 2001.
[20] J. Delarue, P. Giampaoli, J. Agric. Food Chem. 48 (2000) 2372.
[21] A. Boutboul, P. Giampaoli, A. Feigenbaum, V. Ducruet, Food Chem. 71 (2000) 387.
[22] H. Gauthier, A.-C. Coupas, P. Villemagne, R. Gauthier, J. Appl. Polym. Sci. 69 (1998) 2195.
[23] D. Benczédi, I. Tomka, F. Escher, Macromolecules 31 (1998) 3055.
[24] D. Benczédi, I. Tomka, F. Escher, Macromolecules 31 (1998) 3062.
[25] D. Benczédi, Trends Food Sci. Technol. 9 (1999) 1.
[26] P.G. Demertzis, M.G. Kontominas, in: D.R. Lloyd, T.C. Ward, H.P. Schreiber (Eds.), Inverse Gas Chromatography: Characterization of Polymers and Other Material, ACS Symposium, Washington, DC, 1989, p. 77.
[27] G. DiPaola-Baranyi, J.E. Guillet, J.E. Klein, H.E. Jeberin, J. Chromatogr. 166 (1978) 349.
[28] D. Tewari, Y.B. Schreiber, H.P. Patterson, Macromolecules 3 (1971) 356.