

Surface characterization of okra hydrocolloid extract by inverse gas chromatography (IGC)



Maria Dimopoulou^{a,b}, Christos Ritzoulis^{a,*}, Costas Panayiotou^b

^a Department of Food Technology, ATEI Thessaloniki, 57400 Thessaloniki, Greece

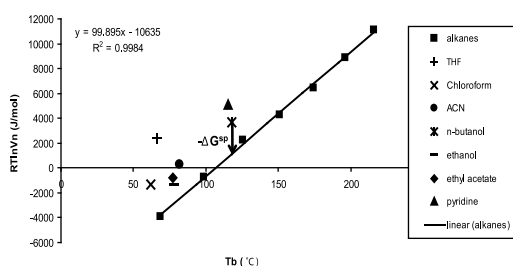
^b Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

HIGHLIGHTS

- Okra hydrocolloid extract was studied using inverse gas chromatography (IGC).
- The thermodynamic components of the adsorption were calculated.
- The okra extract matrix is Lewis amphoteric with predominantly basic character.
- The above are discussed in conjunction with data from other analytical methods.

GRAPHICAL ABSTRACT

Energy of adsorption of n-alkanes and polar probes versus their boiling temperatures on the surface of okra extract, at 40 °C.



ARTICLE INFO

Article history:

Received 3 July 2014

Received in revised form

23 September 2014

Accepted 24 September 2014

Available online 4 November 2014

Keywords:

Okra

Hydrocolloid

Inverse gas chromatography (IGC)

Thermodynamic properties

Surface characterization

ABSTRACT

An extensive surface characterization of okra hydrocolloid extract was conducted by means of inverse gas chromatography (IGC) at infinite dilution in three temperatures (40, 50, 60 °C). The specific retention volume of 14 solvents, used as probes, was utilized for the assessment of the surface energy, the free energy of adsorption, as well as the relevant enthalpy and entropic component. The contribution to the surface energy of okra extract decreases with increasing temperature. Furthermore, surface characterization demonstrated that the okra extract matrix is Lewis amphoteric with predominantly basic character, as confirmed by the acidity and basicity constants K_A and K_B , respectively. The above were discussed in conjunction with X-ray diffractometry (XRD), size exclusion chromatography (SEC–MALLS/UV), and Fourier transform infra-red spectroscopy (FTIR) data.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Abelmoschus esculentus, formerly known as *Hibiscus esculentus*, is a plant of the Malvaceae family. It is an integral part of the diet of Africa and India as well as of other countries with a worldwide production estimated close to 7 million metric tons, grossing close

to an estimated US\$ 4.4 billion in 2010 [1]. Okra fruit is a staple food in India, in several African countries, in the middle East and in southeastern Europe, however, investigations on its composition, functional and nutritional properties are limited in the literature [2–4].

Of primary interest is the thick and slimy texture of okra aqueous extracts; this is mostly due to their polysaccharide content. Okra gum extract, as discussed above, is a food-originating, low-cost hydrocolloid with a potential as a thickening agent/rheology modifier [5–7], and as an emulsifier of acidic foods [8]. The above

* Corresponding author. Tel.: +30 2310013379; fax: +30 2310013369.

E-mail addresses: critzou@food.teithe.gr, critzoulis@yahoo.co.uk (C. Ritzoulis).

pinpoint the need of a thorough physico-chemical characterization of its surface properties. To the best of the authors' information, no such study exists in the literature. The aim of the present work is the utilization of inverse gas chromatography (IGC) for the surface characterization of this material in thermodynamic terms.

Inverse gas chromatography is a powerful tool for the thermodynamic characterization of materials [8]. This technique has been employed for the characterization of a variety of organic materials such as copolymers [10–12], polymer blends [13], hyperbranched polymers [14,15], pharmaceutical materials [16], powders [17,18], crude oils [19], nanomaterials [20], fibers [21], and some non-food carbohydrates [22,23].

Furthermore, IGC has proved to be useful in development of cellulose/plastic composites over the past decades [24–32]. Data have been reported on the change of surface energy following the surface modification of cellulosic fibers by coating and solution grafting with various chemicals [24–33]. A number of recent works have indicated that significant changes in surface energy were made by surface modification of cellulosic fibers with maleic anhydride functionalized polypropylene (MAPP). The treated fibers showed surface energy values close to that of thermoplastics [24,34,35]. Also similar results have shown the surface coating and/or grafting of fibers with polystyrene, phthalic anhydride, silanes, and plasma treatment [24].

Concerning polymeric materials, IGC can contribute to the estimation of two main groups of properties, namely (i) a polymer's surface parameters, for example its surface free energy and its acid–base character; (ii) its bulk properties, such as the polymer's solubility parameter and Flory–Huggins interaction parameters. IGC experiments are based on the calculation of the net retention volume, V_N , of a series of test probes as they move through a chromatographic column filled with the material under study (here okra mucilage). V_N is affected by the working temperature, and the polymer's glass transition temperature (T_g): It is generally agreed that the surface characterization of a polymer should be conducted at temperatures lower than its T_g ; while its thermodynamic characterization should be conducted above the T_g [36]. Retention volumes measured below the polymer's T_g result from the adsorption of the probes on the surface of the stationary phase (the material under study), while above the T_g they result from the sum of surface and of bulk sorption [9,36].

IGC can, according to the above, be used as to assess thermodynamic quantities such as the energy, enthalpy, and entropy of adsorption of the polar probes on the surface of okra mucilage, the dispersive component of the surface energy, and the Lewis acidity and basicity constants of the polymer. The results can contribute to understanding the mass transfer between okra fruit and its aqueous environment during processing, cooking, and digestion. Prior to reporting the experimental work, the basic theoretical background will be summarized in the next section.

1.1. Theoretical background

In a typical IGC experiment, a series of probes of known properties are injected into the packed column, either at infinite dilution or at finite concentrations [9]. At infinite dilution, where the probe–probe interactions can be considered to be negligible, the system being dominated by stationary phase–probe interactions [22]. Gases such as air [9,36] or methane [9,10,16,36,37] can be used as a non-retained marker. This serves the calculation of the column dead time. As mentioned previously, IGC experiments revolve around the measurement of the net retention volume, V_N , which, for a given probe, is the volume of the carrier gas required to

sweep out this injected probe from the column and is calculated by [22,37]:

$$V_N = \frac{T}{T_F} j F_M \left(1 - \frac{p_W}{P'} \right) (t_R - t_M) \quad (1)$$

where t_R and t_M are the retention times of the probe and of marker, respectively, F_M is the carrier gas flow rate at ambient pressure P' and at temperature T_F . T is the temperature of the column, p_W is the vapor pressure of water at T_F and j is the James and Martin factor. This is used in order to correct the gas carrier compressibility, and is defined as [16,14b]:

$$j = 1 - \frac{P_i - P_o}{2P_o} \quad (2)$$

where P_i and P_o are the inlet and outlet pressures.

1.2. Surface properties

1.2.1. Dispersive interactions

The dispersive component of a solid body's surface energy, γ_s^d can be determined with the Dorris and Gray method [38]:

$$\gamma_s^d = \left(\frac{1}{4\gamma_{CH_2}} \right) \left(\frac{-\Delta G^{CH_2}}{N\alpha_{CH_2}} \right)^2 \quad (3)$$

where N is the Avogadro's number, ΔG^{CH_2} is free energy of the adsorption of one single methylene group of a cross-sectional area α_{CH_2} . In Equation (3) γ_{CH_2} is the surface energy of a solid body constituted solely of methylene groups. The adsorption free energy of a single methylene group is given by [22]:

$$\Delta G^{CH_2} = -RT \ln \left(\frac{V_{n+1}}{V_n} \right) \quad (4)$$

where V_{n+1} and V_n are the retention volumes of n -alkanes comprising of $n+1$ and n carbon atoms, respectively. If a plot of the $RT \ln V_N$ values of a series of n -alkanes versus the number of their carbon atoms is linear, the slope of this line is equal to a single methylene group's free energy of adsorption ΔG^{CH_2} [22].

1.2.2. Specific interactions

Probes that can interact with the column matrix with forces other than dispersive ones, can be used as to study the non-dispersive (specific) interactions with the stationary phase. When a polar probe is injected in the column, it interacts with the material under study by both dispersive and specific interactions. Here "specific" includes all non-dispersive types of interactions such as hydrogen bonding, polar, or ionic forces among others [9,22]. As the total free energy of adsorption can be considered equal to the sum of a specific and a non-specific component, the contribution of specific interactions to the free energy of adsorption, ΔG^{sp} , can be calculated as the difference between the total free energy of adsorption, ΔG^{ads} , and the dispersive component of this free energy ΔG^d . According to Brookman and Sawyer [39], ΔG^{sp} can be calculated by means of plotting ΔG (or $RT \ln V_N$) values against the boiling temperatures (T_b , in °C) of the injected probes. The n -alkane series leads to a linear plot, which constitutes a reference straight line for the dispersive interactions. The contribution of specific interactions to the free energy of adsorption, ΔG^{sp} , corresponds to the vertical distance between the ΔG^{ads} value and the reference line according to the following equation:

$$(-\Delta G^{sp}) = (-\Delta G^{ads}) - (-\Delta G^{ref}) = RT \ln \left(\frac{V_N}{V_{N,ref}} \right) \quad (5)$$

where V_N is the net retention volume of the polar probe and $V_{N,ref}$ is the net retention volume of a hypothetical alkane with the same boiling point as that of the polar probe.

Download English Version:

<https://daneshyari.com/en/article/592281>

Download Persian Version:

<https://daneshyari.com/article/592281>

[Daneshyari.com](https://daneshyari.com)