



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Study of the temperature effect on the acid-base properties of cellulose acrylate by inverse gas chromatography at infinite dilution

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ARTICLE INFO

Article history:

Received 19 May 2018

Received in revised form 2 July 2018

Accepted 4 July 2018

Available online xxx

Keywords:

Adsorption

Specific enthalpy

Lewis acid and base constants

Amphoteric constant

Surface energy

Hamieh's model

ABSTRACT

Inverse gas chromatography (IGC) at infinite dilution was used to characterize the surface and interfacial properties of polymers, oxides or polymers adsorbed on oxides. In this paper, the dispersive component of the surface energy of CA was calculated following the molecular models of the surface areas of n-alkanes proving the presence of two linear zones with two different slopes in the temperature intervals and indicating a change in the structure of CA groups. The acid-base properties in the Lewis terms of cellulose acrylate were determined. One proved that the specific enthalpy and entropy of interaction of polar probes are functions of the temperature. The application of Hamieh's model allows to the determination of the acid-base constants K_A and K_D and the amphoteric constant K of cellulose acrylate surface. It was proved that the constants K_A , K_D and K of cellulose acrylate strongly depend on the temperature. This study allowed us to determine the probability w of the specific adsorption of polar probes on the cellulose acrylate surface. This probability parameter also depends on the temperature.

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1. Introduction

It is well known that cellulose is the most abundant naturally polymer on earth. Cellulose is used as natural resource, to produce polymer hydrogels due to its excellent biodegradability and biocompatibility [1,2]. Chiappone et al. [3] and Nair et al. [4] studied the physicochemical, mechanical and ionic properties of cellulose/acrylate, its derivatives and its adhesion on polymers. Bajpai et al. [5] prepared and studied an antibiotic drug Minocycline (Mic) loaded cellulose nano-whiskers (CNWs) / poly(sodiumacrylate) hydrogel films for their drug releasing capacity in physiological buffer solution (PBS) at 37 °C. It was proved some fair anti-fungal and antibacterial properties [6].

Acrylates were used for polymerization on cotton and cellulose [7,8] and improved the properties of these natural products [9]. Other functionalized palm celluloses via graft-copolymerization were studied in order to obtain interesting physico-chemical properties and to improve mechanical properties compared [10–13].

Cellulose is a nontoxic, renewable resource and very abundant. By chemical modification of cellulose, new characteristics can be obtained, e.g., improved solubility in various solvents [14]. The modified cellulose will lead to many industrial applications, more particularly in paint, food, and pharmaceutical industry [15]. Keshawy et al. [14] prepared natural modified biodegradable oil sorbents containing segments that act as targeted sites for biodegradation. By using cellulose derivatives, they prepared a crosslinked copolymer of hydroxypropyl cellulose acrylate/octadecyl acrylate as the oil sorbent.

However, because of the non-solubility of cellulose and some difficulties related to the melting processes, only several cellulose derivatives with less hydrogen bonding can be processed. Most of these commercially interesting derivatives are chemically modified from the native cellulose in heterogeneous reaction mixtures [16]. One of these cellulose derivatives is the cellulose acrylate that was synthesized and used for its more interesting properties. Many authors in literature used the inverse gas chromatography (IGC) technique to determine the surface physicochemical properties of polymers [17–29] and cellulose and its derivatives [30–34].

The surface properties, the acid-base properties in Lewis terms and the second order transition temperatures of some important polymers were studied in literature [17,18]. Zhao et al. [8] studied the solubility parameter of cellulose acrylate (CA) by using inverse

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gas chromatography at infinite dilution, in order to find out some solvents or mixed solvents, which solubility parameter was close to that of the synthesized CA in order to dissolve it into homogeneous solution. Hamieh et al. [22–25] determined the surface properties of poly(α -n-alkyl) methacrylates, and proved an important effect of the length of lateral chain on the thermal properties of such polymers in their bulk phase or when adsorbed on silica or alumina, by using IGC technique at infinite dilution.

In this paper, we proposed to determine the acid-base properties of Cellulose acrylate by using inverse gas chromatography (IGC) technique at infinite dilution and Papirer's approach [35–38] and Hamieh's model [39–42].

We used different n-alkanes molecules and polar organic molecules. The polar molecules were used to determine the specific interactions between CA and these probes. The retention time obtained by this technique was proved to be a primordial experimental parameter to characterize the surface properties of the cellulose derivative CA. An important effect of the temperature on the acid-base constants of CA were highlighted and proved in this study.

In the next section, we will summarize the theory and models of the inverse gas chromatography at infinite dilution (IGC-ID). We applied it in the experimental part to determine the specific interactions and acid-base constants of CA.

2. Theory and methods

Inverse gas chromatography was revealed to be an excellent surface technique, used for thirty years, to determine surface phenomena, glass transitions and acid-base properties of solid materials [17–20]. The IGC technique was advantageously applied to determine the change, as a function of temperature, of the surface properties of solid materials or nanomaterials, polymers, oxides or polymers adsorbed on oxides. Model organic molecules of known properties are injected in the column containing the solid. The retention times of these molecules, measured at infinite dilution, allow us to determine the interactions between the model polar or non-polar molecules and the solid substrates, by supposing that there is no lateral interaction between the probe molecules themselves.

2.1. Retention volume

The net retention volume V_n was calculated from:

$$V_n = jD_c(t_R - t_0) \quad (1)$$

where t_R is the retention time of the probe, t_0 the zero retention reference time measured with a non-adsorbing probe such as methane, D_c the flow rate and j a correction factor taking into account the compression of the gas [43]. D_c and j are respectively given by the following expressions:

$$D_c = D_m \frac{T_c}{T_a} \frac{\eta(T_c)}{\eta(T_a)} \quad (2)$$

and

$$j = \frac{3}{2} \frac{\left(\frac{\Delta P + P_0}{P_0}\right)^2 - 1}{\left(\frac{\Delta P + P_0}{P_0}\right)^3 - 1} \quad (3)$$

where D_m is the measured flow rate, T_c the column temperature, T_a the room temperature, $\eta(T)$ the gas viscosity at temperature T , P_0 the atmospheric pressure and ΔP the pressure variation.

2.2. Specific interactions

The free energy of adsorption ΔG° of n-alkanes on the solid substrates is given by the following fundamental equation of IGC technique:

$$\Delta G^\circ = RT \ln V_n + C \quad (4)$$

where R is the ideal gas constant, T the absolute temperature and C a constant depending on the reference state of adsorption. The free energy of adsorption ΔG° contains the two contributions relative to the dispersive and specific interactions. In the case of n-alkanes, ΔG° is equal to the free energy of adsorption corresponding to the dispersive interactions ΔG^d only.

To calculate the specific interactions between the solid substrates and polar probes, several methods were used in the literature [35,36,39–42]. Two approaches are presented in the next sections.

2.3. Fowkes approach

Specific interactions can be determined by applying the well-known relationship of Fowkes which gives at the same time the dispersive component of the surface energy of solids γ_s^d by using the geometric mean of the dispersive components (exponent d) of the surface energy of the probe γ_l^d and the solid γ_s^d :

$$\Delta G^\circ = \Delta G^d = NaW_a = 2Na(\gamma_l^d \gamma_s^d)^{1/2} \quad (5)$$

Where W_a is the energy of adhesion, N is Avogadro's number and a the surface area of one adsorbed molecule of the probe.

For polar molecules, the specific interactions are added to the dispersive interactions:

$$\Delta G^\circ = 2Na(\gamma_l^d \gamma_s^d)^{1/2} + \Delta G^{sp} \quad (6)$$

By plotting $RT \ln V_n$ as a function of $2Na(\gamma_l^d)^{1/2}$ of n-alkanes, it is possible to deduce, from the slope of the straight line, the value of dispersive component γ_s^d of the surface energy of the solid. If γ_l^d , γ_s^d and a the cross section of an adsorbed molecule, are known, it is possible to calculate the contribution to the free energy of adsorption of the Lewis acid–base surface interactions ΔG^{sp} by using Eq. (6) [44].

2.4. Critique to the method based on Fowkes equation

However, the true values of the surface area of organic molecules adsorbed on a solid substrate are not known with a good accuracy, especially because of the change of molecule positions when approaching a solid surface at certain temperature. The problem will be more complicated when the temperature increases; in such case, we cannot neglect the effect of the thermal agitation on the surface areas of adsorbed molecules. In a previous study, Hamieh et al. [45] proved the effect of the temperature on the surface area of n-alkanes and polar molecules. In this study, we proposed various theoretical models giving the molecular areas of n-alkanes: geometrical model, cylindrical molecular model, liquid density model, BET method, Kiselev results and the two-dimensional Van der Waals model by using its constant b that depends on the critical temperature and pressure of the liquid. The Redlich–Kwong equation transposed from three-dimensional space to two-dimensional space [39,41] was also used to calculate the areas of organic molecules. Table 1 summarizes the different surface area values for the used n-alkanes using the various molecular models.

All above proposed theoretical models were experimentally tested by using inverse gas chromatography at infinite dilution coupled to the dynamic contact angle technique. Hamieh et al. [45] showed the areas a (T) of polar molecules adsorbed on Polyte-

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