

Surface characterization of chitin by inverse gas chromatography

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Abstract

The surface properties of a chitin (degree of deacetylation was 33.6%) were quantificationally analyzed by inverse gas chromatography (IGC) in this work. Four *n*-alkanes (C_5 , C_6 , C_7 , and C_8) were chosen as apolar probes to characterize the dispersive component of free energy. Trichloromethane ($CHCl_3$), acetone, ether and tetrahydrofuran (THF) were chosen as polar probes to detect the Lewis acid–base parameters. It was found the dispersive component of free energy was 37.58, 42.12, 45.70, and 51.69 mJ/m² at 40, 50, 60, and 70 °C, respectively. The Lewis acidic number K_a was 0.0793, and the basic number K_b was 0.7936. The result means the chitin is a Lewis basic polymer.

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1. Introduction

Chitin and its *N*-deacetylation derivative, chitosan, are important natural polysaccharides. Among the most widespread natural polysaccharides, such as cellulose, starch, chitin and lignin, chitin and its primary derivative chitosan are special in that they have acetamide and amino groups (Kurita, 2001). These groups give chitin and chitosan many special chemical and biological characteristics, including biocompatibility, biodegradability, nontoxicity, antibacterial properties, heavy metal ion chelation ability, gel-forming properties, hydrophilicity, ease of chemical modification and remarkable affinity to proteins. Owing to these advantages, chitin and chitosan have been widely utilized in controlled release, bioartificial organs, biosensors, tissue engineering, water treatment, membrane separation, food industries, etc. (Krajewska, 2005; Kumar, 2000; Kurita, 2001).

Chitin is obtained at a relatively low cost from the shells of shellfish, such as crabs and shrimps, the wastes of the seafood processing industry. It consists of 2-acetamido-2-

deoxy- β -D-glucose through a β (1 \rightarrow 4) linkage. Fig. 1 is the chemical structure of chitin. However, the composition and properties of chitin may vary due to different original materials and manufacture processes (Kurita, 2001).

Among the properties characterizing a polymer material, surface properties are significant. The specific properties of a polymer material depend strongly on its surface energy and specific interaction forces. Specific interactions may be in the form of hydrogen bonding, charge transfer complexes, acid–base type interactions, dipole moments and electron acceptor–donor complexes. Nowadays, the Lewis acid–base concept for describing surface properties is increasingly accepted, which suggests that the totality of specific interactions may be viewed as Lewis acid–base forces (Mukhopadhyay & Schreiber, 1995; Santos & Guthrie, 2005; Sun & Berg, 2003). The usual techniques for measuring surface acid–base parameters are isoelectric point, indicator dye adsorption, X-ray photoelectron, calorimetry and inverse gas chromatography (IGC). However, the surface acid–base properties obtained by different methods generally cannot be compared directly each other. For polymer materials, IGC technique is more often used to characterize the surface Lewis acid–base properties than the other methods (Mukhopadhyay & Schreiber, 1995; Santos & Guthrie, 2005; Sun & Berg, 2003). To our

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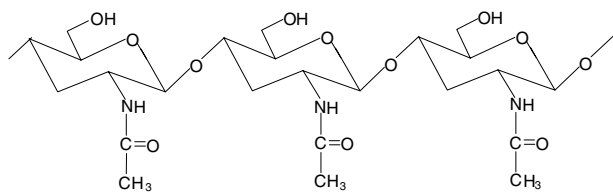


Fig. 1. Chemical structure of chitin.

knowledge, the surface Lewis acid–base properties of chitin is still not measured.

In this study, IGC was used to characterize quantitatively the Lewis acid–base properties and the dispersive component of surface free energy of a chitin. The K_a and K_b values, which describe the Lewis acidity and basicity of the chitin surface were calculated.

2. Inverse gas chromatography

IGC is an inversion of conventional gas chromatography. The main difference between GC and IGC is that the interested species is the polymer material acting as the stationary phase in IGC column. Probe solvents with known properties are injected in the column and the retention times of these probes are measured at infinite dilution. The interactions between the probe solvents and the polymer material are calculated from the retention times, and the surface properties of the polymer are determined.

The dispersive component of surface free energy γ_s^d of polymeric stationary phase is measured when n -alkanes are as probes. The assumption is that only dispersive interactions exist between n -alkanes and polymer. γ_s^d is obtained from the net retention volume according to Eq. (1) (Santos, Fagelman, & Guthrie, 2002; Santos & Guthrie, 2005):

$$-\Delta G_a = RT \ln(V_n) = 2N_A a (\gamma_s^d)^{0.5} (\gamma_1^d)^{0.5} + K' \quad (1)$$

where ΔG_a is the total free energy of adsorption of probe, R is the gas constant, T is the temperature of column, V_n is the net retention volume, N_A is the Avogadro number, a is the surface area of n -alkanes, γ_1^d is the dispersive surface free energy of n -alkanes, K' is a constant related to the reference gas pressure and the reference surface pressure. From a plot of ΔG_a vs. $a(\gamma_1^d)^{0.5}$ for the n -alkane probes, the value of γ_s^d is calculated with the slope. The net retention volume V_n is calculated according to Eq. (2) (Santos et al., 2002; Santos & Guthrie, 2005):

$$V_n = (t_r - t_0)FCJ \quad (2)$$

where t_r is the retention time of probe solvent, t_0 is the retention time of non-interacting probe, F is the flow rate of carrier gas, C is a correction factor, allowing for the vapor pressure of water at the temperature of bubble flow meter used to determine the flow rate of carrier gas by the following expression:

$$C = 1 - P_{H_2O}/P_0 \quad (3)$$

where P_{H_2O} is the saturated vapor pressure of water at ambient temperature, P_0 is the atmospheric pressure. J is

the James–Martin compression correction term determined as follows:

$$J = \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (4)$$

where P_i is the inlet pressure of carrier gas.

The Lewis acid–base properties are calculated from ΔG_a^s , the contribution to the free energy of adsorption by Lewis acid–base (specific) interactions when polar (specific) solvents are injected into the chromatographic column, the expression is (Santos et al., 2002; Santos & Guthrie, 2005):

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s \quad (5)$$

where ΔG_a^d is the dispersive contribution to the total free energy of adsorption, which is determined with n -alkanes. ΔG_a^s results from the distance between the $RT \ln(V_n)$ value of polar solvent and the straight n -alkane line.

The enthalpy of specific interactions ΔH_a^s , is calculated according to the following expression (Santos et al., 2002; Santos & Guthrie, 2005):

$$\Delta G_a^s = \Delta H_a^s - T\Delta S_a^s \quad (6)$$

where ΔS_a^s is the specific entropy of adsorption. ΔH_a^s results from the slope of the plot of $\Delta G_a^s/T$ vs. $1/T$.

The Lewis acid number K_a and Lewis base number K_b are calculated according to Eq. (7) (Santos et al., 2002; Santos & Guthrie, 2005):

$$-\Delta H_a^s = K_a \times DN + K_b \times AN^* \quad (7)$$

where DN and AN^* are the Gutmann's Donor and modified Acceptor number of polar solvents, respectively. Plotting $-\Delta H_a^s/AN^*$ vs. DN/AN^* , gives K_a as the slope, and K_b as the intercept.

3. Experimental

3.1. Materials

Chitin was purchased from Shanghai Chemical Reagent Ltd., China. The degree of deacetylation (DD) of the chitin was determined by elemental analysis using a Euro EA3000 Elemental Analyzer. The DD value was calculated from the following equation (Kasaai, Arul, & Charlet, 2000):

$$DD = \left(1 - \frac{C/N - 5.145}{6.816 - 5.145} \right) \times 100 \quad (8)$$

where C/N is the percent ratio of carbon and nitrogen in chitin. The DD value of the chitin was 33.6%.

For the IGC analysis, the apolar n -alkanes probes were n -pentane (C_5), n -hexane (C_6), n -heptane (C_7), and n -octane (C_8). The polar probes were trichloromethane ($CHCl_3$), acetone (Acet), ether and tetrahydrofuran (THF). They were analytical grade solvents and purchased from Tianjin Kermel Chemical Reagents Development Centre, China. Methane was used as the non-interacting probe, which was prepared in our laboratory. The characteristics of probe solvents are listed in Table 1.

Table 1

Characteristics of the probe solvents (Hamieh & Schultz, 2002; Hegedus & Kamel, 1993; Jandura et al., 2002; Kamdem, 1993; Perruchot et al., 2006; Santos & Guthrie, 2005)

Probe	a (Å ²)	γ_1^d (mJ/m ²)	$a(\gamma_1^d)^{0.5}$ (Å ² (mJ/m ²) ^{0.5})	AN^* (kJ/mol)	DN (kJ/mol)
<i>n</i> -C ₅	46.1	16.0	184	—	—
<i>n</i> -C ₆	51.5	18.4	221	—	—
<i>n</i> -C ₇	57.0	20.3	257	—	—
<i>n</i> -C ₈	63.0	21.3	291	—	—
CHCl ₃	44.0	25.9	224	22.7	0.0
Acet	42.5	16.5	173	10.5	71.4
Ether	47.0	15.0	182	5.88	80.6
THF	45.0	22.5	213	2.1	84.4

3.2. IGC instrument

The instrument was a GC-900A gas chromatograph (Shanghai TianPu Analytical Instrument Ltd., China), equipped with a flame ionization detector (FID). Nitrogen was used as the carrier gas. The flow rate was 10.5 ml/min, measured from the end of the column with a soap bubble flow meter. The injector and FID were heated to 130 °C. The probe solvents were injected manually, using a 1.0 µL Hamilton syringe. The injection volumes were 0.1 µL.

The column was a stainless steel tube (0.5 m length, 2.56 mm i.d.). It was washed with acetone prior to use. The chitin was crushed and dried at 120 °C for 40 h before using. 1.4577 g sieved chitin powder (80–100 mesh) was packed into the column. The column was conditioned at 90 °C and fast carrier gas flow rate (20 ml/min) for 12 h prior to measuring. The IGC experiments were performed at 40, 50, 60, and 70 °C.

4. Results and discussion

Fig. 2 shows the plot of $\ln V_n$ vs. the inverse of the column temperature for *n*-alkanes and polar probes. The

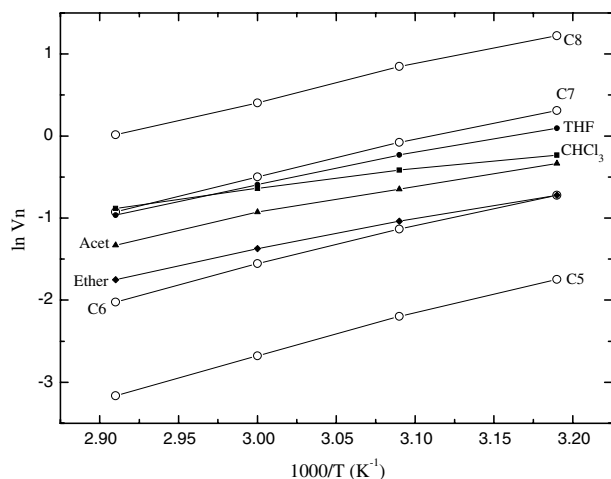


Fig. 2. Plot of $\ln V_n$ vs. $1000/T$ for the probes.

linear relationships of the plots are well. From the values of net retention volumes of the probes, the surface properties of chitin are determined.

4.1. Dispersive component of surface free energy γ_s^d of the chitin

According to Eq. (1), the dispersive component of surface free energy γ_s^d of the chitin is calculated from ΔG_a ($RT \ln V_n$) of *n*-alkanes for every temperature. Fig. 3 shows the plots of $(RT \ln V_n)$ vs. $a(\gamma_1^d)^{0.5}$ for the *n*-alkanes at different temperatures. The results are listed in Table 2. It shows the dispersive component of surface free energies increase with the increasing temperatures.

Generally, surface free energy of a solid material decreases when temperature increases. So, the results of Table 2 seem to contradict the law. However, the data in Table 2 are only the *dispersive component* of surface free energies, instead of the total free energies which are the sum of dispersive components and Lewis acid–base components. The total free energies depend on the chosen probe solvents by IGC method.

4.2. Lewis acid–base parameters K_a and K_b of the chitin

Fig. 4 shows the calculation of the free energy of adsorption by Lewis acid–base interactions ΔG_a^s for the polar probes adsorbed on the chitin at 60 °C. Table 3 lists the data of ΔG_a^s measured at the overall temperatures.

According to Eq. (6), the enthalpy of specific interactions ΔH_a^s for every polar probe are calculated from the free energy of specific interactions listed in Table 3. The results are listed in Table 4.

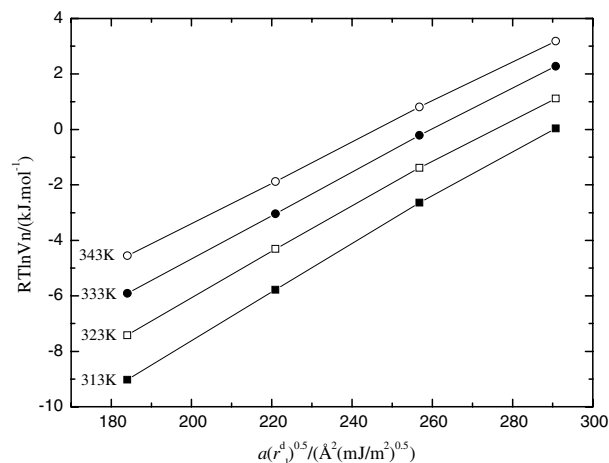


Fig. 3. Surface free energy of adsorption vs. $a(\gamma_1^d)^{0.5}$ for *n*-alkanes.

Table 2

Dispersive component of surface free energy γ_s^d (mJ/m²) of the chitin

	Temperature (K)			
	313.2	323.2	333.2	343.2
Chitin	37.58	42.12	45.70	51.69

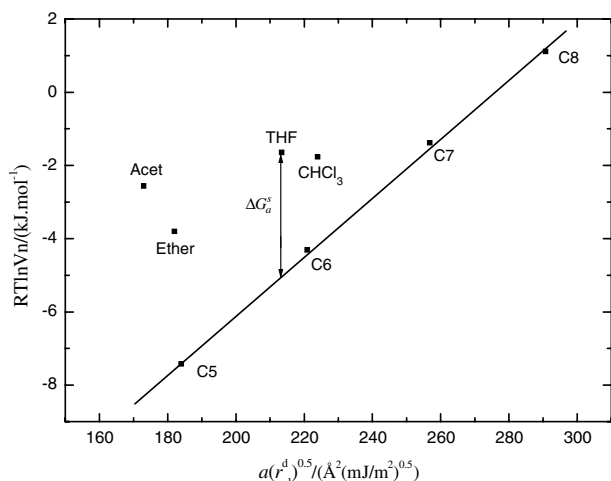


Fig. 4. Free energy of adsorption vs. $a(r_1^d)^{0.5}$ for *n*-alkanes and polar probes at 333.2 K.

Table 3

Free energy of adsorption by Lewis acid–base interactions ΔG_a^s (kJ/mol)

	Temperature (K)			
	313.2	323.2	333.2	343.2
CHCl ₃	1.088	1.754	2.425	3.107
Acet	4.582	5.108	5.773	6.231
Ether	2.908	3.353	3.802	4.256
THF	2.712	3.070	3.398	3.775

Table 4

Enthalpy of specific interactions ΔH_a^s (kJ/mol)

Probes	CHCl ₃	Acet	Ether	THF
ΔH_a^s	−19.72	−13.12	−10.99	−8.28

Then, the Lewis acid–base numbers are calculated according to Eq. (7). Fig. 5 shows a plot of $-\Delta H_a^s/AN^*$ vs. DN/AN^* for the polar probes. The linear correlation for the four polar probes is fine. The Lewis acidic number K_a is calculated from the slope, and the basic number K_b is

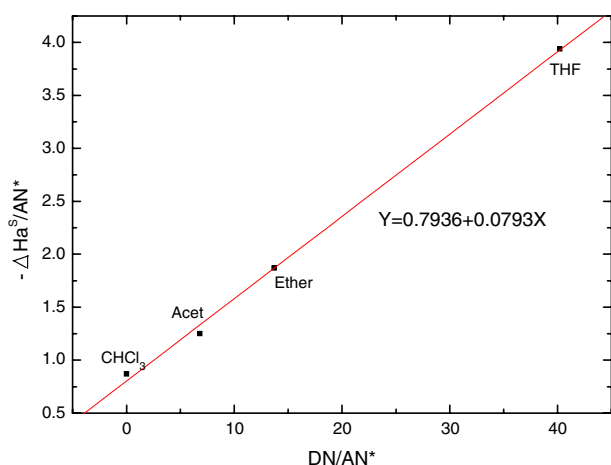


Fig. 5. Determination of K_a and K_b for the surface Lewis acid–base of the chitin.

Table 5

K_a and K_b of the chitin

K_a	0.0793	± 0.0027
K_b	0.7936	± 0.0573

calculated from the intercept. The last values are listed in Table 5.

The result in Table 5 shows clearly that this kind of chitin (degree of deacetylation was 33.6%) is a Lewis basic polymer, the acidity is very weak. The basicity comes from its amino groups. Therefore, the chitin is inclined to adsorb acidic molecules. In Table 4, the smallest enthalpy of specific interaction is trichloromethane, because trichloromethane is an acidic molecule from its AN^* and DN (Table 1).

5. Conclusions

The surface properties, dispersive component of surface free energy and Lewis acid–base of a chitin (degree of deacetylation was 33.6%) were quantificationally determined by IGC method in this work. The dispersive component of surface free energies increase from 37.58 mJ/m² at 313.2 K to 51.69 mJ/m² at 343.2 K. The Lewis acidic number K_a and the basic number K_b are 0.0793 and 0.7936, respectively. The result indicates the chitin is a Lewis basic polymer.

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