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Van der Waals parameters, refractive indices and dispersion equation of pectin

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The refractive indices of water solutions and films from apple and citric pectin with concentration 1 and 2% are measured at two wavelengths $(\lambda_1 = 532\text{nm}, \lambda_2 = 632.8\text{nm})$ with a laser refractometer. The Van der Waals parameters – the characteristic frequency ω and dispersion coefficient *C* are determined from the refractive indices of the films. The results show that the dispersion coefficient *C* lies in the range 0.292 - 0.295 and the characteristic frequency varies between $2.8.10^{16}\ rad/s$ and $3.1\times10^{16}\ \text{rad}/\text{s}$ for these polysaccharides. From the latter facts it is clear that the dispersion coefficients of apple and citric pectin are higher than those of the phospholipids (C lies in the range 0.27 to 0.28) but lower than those of the proteins (C lies in the range 0.309 to 0.317).

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1. Introduction

Pectin is a polysaccharide interesting for investigations since its derived products are widely used in the canning industry as well as in the production of sugar products and soft drinks. Apart from the food industry, pectin is widely used in cosmetics, the textile industry and medicine in the production of anti-ulcer medicaments and antidotes for serious poisoning with heavy metals; also it is used as a styptic. [1-4]. Pectin is used in the production of jelly-bons, jelly desserts and jelly vegetable salads.

The aim of this study is to verify the applicability of the Nir method for polysaccharides, in order to determine the Van der Waals parameters for the different types of pectin as well as to investigate the dependence of these values on the pectin concentration.

2. Experimental

2.1 Sample preparation

In this work, pectin films and their solutions have been investigated refractometrically. For this purpose polysaccharides – apple and citric pectin – are dissolved in water.

Different concentrations have been used in order to obtain film thickness varying from $7\mu\text{m}$ to $45\mu\text{m}$. Thin films were obtained for each of the studied biopolymers upon glass substrates. The films were dried at $20^\circ C$.

2.2 Instrumental

The refractive indices of the pectin water solutions and their films were measured by laser refractometer at temperature $t = 18^\circ\text{C}$ for two wavelengths - $\lambda_1 = 532\text{nm}$ and $\lambda_2 = 632.8\text{nm}$. The optical scheme of the refractometric block and its principle of action have been described in [5]. The refractive indices of the samples have to be calculated according to the following relation:

$$n = N\sin[A_1 \pm \arcsin\left(\frac{\sin\alpha_{cr}}{N}\right)], \tag{1}$$

where A_1 and N are respectively the refracting angle of the prism and its refractive index. In our investigation, the prism was made from heavy flint-glass TF-4 with a refracting angle $A_1 = 65^\circ$. The prism's refractive indices were $N_1 = 1.748$ and $N_2 = 1.735$ at $\lambda_1 = 532\text{nm}$ and $\lambda_2 = 632.8\text{nm}$ respectively. A profound analysis of the uncertainty of the refractive index has been presented in [6]. In our case the experimental error was about 2×10^{-4}.

The density of the water pectin solutions was determined picnometrically. For this purpose, the picnometer with the studied or the standard liquid sample were placed in a metal housing and its temperature was kept constant by a thermostat. We have also measured the intrinsic viscosity $[\eta]$ of the apple and citric pectins. These data have been used to determine the molecular weight (M) of the studied biopolymers. Numerical values of this quantity are necessary for calculation of important optical constants like the static polarizability and molecular refraction.

2.3 Theoretical background

The Van der Waals force F can be found using the parameters ω and C; respectively characteristic frequency and dispersion coefficient. The force per unti area between two planar surfaces, separated by a distance d, can be expressed in the following manner [7]:

$$F = -\frac{A}{6\pi d^3}, \qquad (2)$$

where A is the Hamaker's constant, given by the equation [8]:

$$A = A_{12} + A_{00} - A_{10} - A_{20} \qquad (3)$$

and $$A_{ik} = \frac{27}{32}\hbar\frac{C_i C_k \omega_i \omega_k}{\omega_i + \omega_k}, \qquad (4)$$

where $\hbar$ is Plank's constant divided by 2π, the subscripts 1,2 and 0 refer to the left hand surface, right hand surface and the volume between the surfaces. C_i (or C_k) and ω_i (or ω_k) are respectively the dispersion coefficient and characteristic frequency of the substance of which surface i (or k) is composed.

The indicated parameters (ω and C) can be obtained from the following equation, which is given in [9-10]:

$$\frac{n^2-1}{n^2+2} = \frac{C\left[1-\left(\omega_1/\omega\right)^2\right]}{\left[1-\left(\omega_1/\omega\right)^2\right]^2 + \left(\gamma\,\omega_1/\omega^2\right)^2}, \qquad (5)$$

where ω_1 is angular frequency , n is the refractive index of the pure substance (e.g. the pectin film) and γ is the damping coefficient.

3. Results and discussion

The refractive indices of thin films of apple and citric pectin and their solutions were measured by laser refractometer using the method of the disappearing diffraction picture. The data are present in Table 1. The thickness of the film was measured with a "Mitutoyo" digital micrometer (experimental error ± 1μm).

Table 1. Refractive indices of films and solutions from pectin.

Type	$\begin{pmatrix} d_0 \\ \pm 1 \end{pmatrix}$ μm	phase	$n_1 \pm 2\times10^{-4}$ $\lambda_1 = 532$nm	$n_2 \pm 2\times10^{-4}$ $\lambda_2 = 632.8$nm
1% apple pectin	9	Liquid	1.3337	1.3317
		Film	1.5089	1.5061
2% apple pectin	45	Liquid	1.3351	1.3326
		Film	1.5093	1.5070
1% citric pectin	7	Liquid	1.3335	1.3324
		Film	1.5056	1.5028
2% citric pectin	30	Liquid	1.3340	1.3326
		Film	1.5096	1.5071

The table shows that the thickness of 1% pectin films is less than 10 μm. Such thin films cannot be investigated using conventional refractometers. It can be seen that the refractive indices of films from apple pectin with lower concentration $(C = 1\%)$ differ considerably from these of films from citric pectin with the same concentration. However, such a conclusion cannot be made for the same types of pectin at higher concentrations.

We can neglect the damping coefficient γ in the suggested relation (5). In this way, the expression is reduced to:

$$\frac{n^2-1}{n^2+2} = \frac{C}{1-\left(\omega_1/\omega\right)^2} \qquad (6)$$

By using this formula and the refractive indices of the films, given in Table 1, we calculated Wan der Waal's parameters - C and ω. The results are presented in Table 2.

Table 2. Van der Waals parameters of different types of pectin

Type	$\omega\times10^{-16}$, rad/s	Dispersion coefficient C
1% apple pectin	2.8	0.294
2% apple pectin	3.1	0.295
1% citric pectin	2.8	0.292
2% citric pectin	3.0	0.295

From this table, it is evident that the dispersion coefficient C of the pectin lies in the narrow range 0.292 to 0.295, and the characteristic frequency (ω) changes from 2.8×10^{16} rad/s to 3.1×10^{16} rad/s. The data obtained for the parameters ω and C of the polysaccharide were compared with data available in sources of reference on phospholipids, sugars and proteins. It was established that the value of the dispersion parameter C, obtained for the polysaccharide pectin, is lower than that of the sugars (C lies in the range 0.317 to 0.332) [11] and for the proteins (C lies in the range 0.309 to 0.324) [12] and higher than the value specified for the phospholipides (C lies in the range 0.27 to 0.28) [11].

It has to be pointed out that the Van der Waals forces are less sensitive to the values of the characteristic frequency ω, which appears in the expression (4) in the first order, and more sensitive to the dispersion parameter C. The investigation we have carried out to obtain the Van der Waals' parameters is more precise than the ones of Nir [12] for phospholipids and proteins. In this study, the refractive index of the pectin film is directly measured, it is not calculated through the partial specific volume according to the formula of Lorenz-Lorenz:

$$\frac{n_1^2-1}{n_1^2+2} = \left(C\bar{v}\right)\frac{n^2-1}{n^2+2} + \left(1-C\bar{v}\right)\frac{n_2^2-1}{n_2^2+2} \qquad (7)$$

where n_1 is the refractive index of the solution at the angular frequency of incident light ω_1, n and n_2 are the refractive indices of the solute and solvent, $\bar{v}$ is the partial specific volume and C is the concentration in $\mathrm{g/cm^3}$.

In this work, reological and picnometric investigations were carried out. They were used for obtaining important physical parameters, for calculating the optical polarizability of the pectin films. The molecular weight (M) was determined from the data for the intrinsic viscosity $[\eta]$ according to the method proposed by Owens [13]. Results for M and $[\eta]$ are given in Table 3.

Table 3. Reological data for apple and citric pectin.

Type	$[\eta]$, dlg^{-1}	molecular weight- M (Owens)
Apple pectin	3.60	61000
Citric pectin	2.12	41000

The density of the solid phase was calculated by the formula (8), which is proved in [14]:

$$\frac{\left(n_1^2-1\right)\left(n^2+2\right)}{\left(n_1^2+2\right)\left(n^2-1\right)}=\frac{d_1}{d} \tag{8}$$

This formula gives the connection between the refractive indices of the solution (n_1) and the film (n) and their densities, respectively d_1 and d. The density of the liquid phase was determined picnometrically. The data for d_1 and d are presented in Table 4.

Table 4. Densities of the liquid and solid phases for apple and citric pectin.

Type	d_1, $kg.m^{-3}$ measured by picnometer	d , $kg.m^{-3}$ calculated from (7)
1% apple pectin	1002.4591	1452.16
2% apple pectin	1005.8106	1456.78
1% citric pectin	1003.0103	1445.78
2% citric pectin	1006.3618	1458.31

The optical polarizability (α) of pectin films were evaluated by the following equation, suggested in [15], using some data from Tables 3 and 4.

$$R=\frac{n^2-1}{n^2+2}\frac{M}{d}=2.52.10^{24}\alpha\ , \tag{9}$$

where R, n, d are the molecular refraction, refractive index and density of the pectin films, respectively and M is the molecular weight of the polysaccharide. The obtained results are presented in Table 5.

Table 5. Optical constants of pectin films.

Type	$\alpha, cm^3, \times 10^{21}$	
	$532nm$	$632.8nm$
1% apple pectin	4.98	4.95
2% apple pectin	4.96	4.95
1% citric pectin	3.34	3.33
2% citric pectin	3.34	3.32

It is clear that the optical polarizability (α) does not depend on the pectin concentration, weakly depends on the wavelength, but differs considerably according to the type of pectin – apple and citric.

4. Conclusions

The Van der Waals parameters, i. e. the parameters required in the calculation of the Van der Waals interaction, are the dispersion equation coefficient C and characteristic frequency ω.

The results obtained in the present work show that a two-wavelength laser refractometer is suitable not only for Van der Waals parameter determination, but also for obtaining information about the dispersion characteristics of thin film samples.

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