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On the Molecular Weight of Pectic Substances and its Relation to Their Gel Strengths

I. N. Panchev, N. A. Kirtchev, Chr. G. Kratchanov & T. Proichev

Higher Institute of Food and Flavour Industries, 26 Lenin Blvd., Plovdiv, 4002, Bulgaria

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ABSTRACT

A study has been made on the possibility of determining the molecular weight M_w*, the second virial coefficient* A_2 *and the radius of gyration by measuring the light scattering of pectin aqueous solutions. The experimental data were processed on a computer by using an algorithm, accounting for the effect of microgel formations in the pectic solution. A tendency towards a decrease in* M_w *when decreasing the degree of esterification for a certain type of pectin was established and was confirmed by the change in the intrinsic viscosity* $[\eta]$*. This fact is explained by degradation during deesterification.*

The dependence of the gel strength of the pectic preparations on their degree of esterification, molecular weight M_w *and purity (p%) was also studied as well as the dependence of the gel strength on the intrinsic viscosity* $[\eta]$*, the degree of esterification and the purity p%. The passive multifactor experiment method was used to obtain regression models which were tested for an optimum in the factors influencing the gel strength. The optimal value for the degree of esterification was obtained at 57–58% which confirmed the view that within this range the pectin macromolecules possess maximum conformational flexibility.*

INTRODUCTION

Pectic substances (PS) find application in the food industry most often as gelling components. Therefore, various aspects of the gel strength (GS) of pectic substances have been studied but for a number of reasons considerable problems still exist in this respect. Above all there are specific difficulties in determining the characteristics of the PS due to their composition, origin and methods of extraction as well as to the variety of existing methods for the quantitative evaluation of the GS. In order to assess and predict the properties of pectic substances it is necessary to

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know the molecular weight of the pectic substances, the degree of esterification of the carboxyl groups and the way in which they are distributed along the entire length of the pectin macromolecule (Bettelheim, 1970; Rees, 1972; Nelson, 1977; Pilnik, 1980; Biemiller, 1986). Despite the opinion, widely accepted in the literature, that the increase in the molecular weight of the pectic substances results in an increase in their gel strength, this remains a controversial issue and the methods for solving it are still to be found. This is due on the one hand to the heterogeneous composition of the pectic substances which include neutral sugars and ballast substances, and on the other hand to the marked ability of the pectic substances as linear polymers with a semisolid chain to form aggregates (microgels) in aqueous solutions (Sorochan *et al.*, 1971; Jordan & Brant, 1978; Senkievitch *et al.*, 1979; Berth *et al.*, 1982; Plashchina *et al.*, 1985). The experiments for determining the characteristics of the pectic substances according to their molecular composition consist mainly in applying the classical methods of ultracentrifugation, osmometry and viscosimetry (Glikman & Orlov, 1951; Smidsrod & Haug, 1971; Berth *et al.*, 1977, 1980; Fishman *et al.*, 1986) as well as light scattering (Sorochan *et al.*, 1971; Smith & Stainsby, 1977; Jordan & Brant, 1978; Senkievitch *et al.*, 1979; Berth *et al.*, 1982; Plashchina *et al.*, 1985). The basic problem in interpreting the light scattering data to determine M_w is how to eliminate the contribution of the microgel formations to the intensity of light scattering $\Delta R(\theta)$. To solve this problem some authors (Smith & Stainsby, 1977) apply the method of enzyme disaggregation of the pectin aggregates, others (Robinson *et al.*, 1982) suggest the use of aqueous solutions containing carbamide, taking into account the destructive impact of carbamide on the hydrogen bonds responsible for the formation of microgels. Kratochvil (1982) suggests as a solution to this problem the use of experimental data obtained at scattering angles larger than 50°. Plashchina *et al.* (1985) combine the light scattering method with ultracentrifugation.

The aim of the present work was to study the opportunity for determining M_w of pectic substances by the method of light scattering and to interpret quantitatively the relationship between the gel strength, M_w, the degree of esterification and purity of pectic substances.

MATERIALS AND METHODS

The pectins used in the experiments were obtained from apples, grapefruit, lemon and orange peels, carrots, sunflower heads, etc., by the methods proposed by Kirtchev *et al.*, (1988). The gel strength of the pectic preparations was determined by the Tarr–Baker method on standard 65% jellies (Baker, 1926). The degree of esterification (DE) and the polyuronic acid content were determined titrimetrically (Owens *et al.*, 1952). The solutions used to determine M_w were prepared by leaving the necessary amount of pectin to swell in water for 24h and then stirring it until the pectin was fully dissolved. The initial solutions had a 0·5% concentration of pectin and contained 0·15 M NaCl to make possible the screening of the electrostatic repulsion of $COOH^-$ groups according to the methods given in Smidsrod & Haug (1971). After dialysis was carried out at +4°C for 48 h through a cellophane membrane to the solvent, the initial solution was centrifuged for 90 min at 17 000 revolutions per minute in a JANETCKY 24 lab. centrifuge. The solvent and the solution were dedusted using Millipore membrane filters with a pore diameter of 0·45 μm and 0·22 μm. The initial pectic solution was prepared in the cuvette for measuring the light scattering and the concentrations were determined by weight and by measuring the refractive index with a laboratory interferometer manufactured by Carl Zeiss Jena in 1973.

The intensity of light scattering of the working solutions and of the solvent were measured within the 40 to 150° range on a FPS-3M automatic nephelometer manufactured in the Academy of Sciences of the USSR in 1975, using a light wavelength of $\lambda = 546{\cdot}1$ nm. The nephelometer was calibrated with spectroscopically pure benzene and the light scattering intensity value of benzene at 90°C $R^{B}_{90} = 16{\cdot}3 \times 10^{-5}$ cm^{-1} was used for the calculations in accordance with Eskin (1986).

The increment of the refractive index $\mathrm{d}n/\mathrm{d}c$ for pectic solutions was determined from the analytical formula of $n = f(C\%)$ by the method of least squares, running the LIN programme borrowed from Johnson (1980) on a SM-4 computer. In accordance with the results given in Prochazka *et al.* (1983) for solutions containing aggregate (microgel) formations the function of light scattering is expressed by the equation

$$\frac{KC}{\Delta R(\theta)} = \frac{A_0 + A_1\, C + (B_0 + B_1 C)x + (C_0 + C_1 C)x^2}{1 + (D_0 + D_1\, C)x} \tag{1}$$

where C is the concentration of the polymer, g cm^{-3}; x is $\sin^2(\theta/2)$; $\Delta R(\theta)$ is the intensity of light scattering for an angle θ and; K is an optical constant calculated from the equation

$$K = \frac{2\pi^2 n_0}{N_A \lambda^4}\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \tag{2}$$

in which n_0 is the refractive index of the solvent; $\mathrm{d}n/\mathrm{d}c$ is the increment of the refractive index; N_A is the Avogadro number and; λ is the wavelength (nm). A_0, A_1, B_0, B_1, C_0, C_1, D_0, D_1 are experimental constants

$$\left(A_0=\frac{1}{M_w};\ \frac{A_1}{2}=A_2\right)$$

A_2 is the second virial coefficient

$$\lim_{\theta \to 0}\frac{\mathrm{d}(KC/\Delta R(\theta))}{\mathrm{d}(\sin^2(\theta/2))}=B_0-A_0D_0=k'\langle\overline{r_z^2}\rangle/(3M_w) \tag{3}$$

$$K'=\frac{16\pi^2 n_0{}^2}{\lambda^2} \tag{4}$$

$\langle r_z^2\rangle^{1/2}$ is the radius of gyration of the macromolecule

$$B_0=K'(\langle\overline{r_{z1}^2}\rangle+\langle\overline{r_{z2}^2}\rangle)/3M_w) \tag{5}$$

$$C_0=K'^2(\langle\overline{r_{z1}^2}\rangle\cdot\langle\overline{r_{z2}^2}\rangle)/(9M_w) \tag{6}$$

where $\langle\overline{r_{z1}^2}\rangle^{1/2}$ is the radius of gyration of the macromolecule after excluding the effect of the microgel formations in the solution and $\langle\overline{r_{z2}^2}\rangle^{1/2}$ is the radius of gyration of the microgel formations. The coefficients of eqn. (1) were calculated using experimental data for light scattering of the solutions for the particular kind of pectin by optimizing the objective function

$$\mathrm{CELF}=\sum_{i=1}^{n}\sum_{j=1}^{m}(Z_{ij}^{t}-Z_{ij}^{e})^2=>\min \tag{7}$$

where

$$Z_{ij}^{t}=\frac{(X_1+X_2Y_{1i})+(X_3+X_4Y_{1i})Y_{2j}+(X_5+X_6Y_{1i})\ Y_{2j}^2}{1+(X_7+X_8Y_{1i}Y_{2j})} \tag{8}$$

in which Y_{1i} is the concentration C, g cm^{-3}; $Y_{2j}=\sin^2(\theta/2)$; $i=1, 2 \dots n$ is the number of the concentration C; $j=1, 2 \dots m$ is the number of the angle θ; $X_1=A_0$; $X_2=A_1$; $X_3=B_0$; $X_4=B_1$; $X_5=C_0$; $X_6=C_1$; $X_7=D_0$; $X_8=D_1$. Z_{ij}^e are the experimental values for $(KC/\Delta R(\theta))$ and Z_{ij}^t are the theoretical values for $(KC/\Delta R(\theta))$ calculated after the model of Brandt (1970). The minimum of the function CELF $(X_1, X_2 \dots X_8)$ and the values of the unknown constants were found using the modified simplex method of Nelder and Midl (Himmelblau, 1972). The program realization of the method was carried out using the PANLP program written in FORTRAN which is an adaptation of the FLEXSI program borrowed from Himmelblau (1972) and compiled for the particular problem on an SM-4 computer.

The viscosimetric measurements of the studied pectic solutions were made at 25°C using a VPZ-3 capillary viscosimeter of the Ubbelohbe type in accordance with the methods proposed in Tverdohlebova (1981). The characteristic viscosity $[\eta]$ was calculated on the basis of Huggins' equation

$$\frac{\eta_{cp}}{C} = [\eta] + K_{\mathrm{H}}[\eta]^2 C \tag{9}$$

where η_{cp} is the reduced viscosity of the solutions; C is the concentration and; K_{H} is Huggins' constant. This was done using the REO program compiled by the authors and written in FORTRAN on the basis of the MNK algorithm which was run on a SM-4 computer.

To find the regression dependence of the gel strength of the studied pectins and the parameters influencing its value, a standard computer program for multiple regression written in FORTRAN IV and taken from IBM (1970) was used. The program was run on a SM-4 computer. The statistical evaluation of the regression coefficients and the adequacy tests of the model were made using the statistical criteria of Student and Fisher in accordance with Brandt (1970). The study of the gel strength maximum in accordance with the obtained mathematical model was carried out using a simplex method of optimization (Himmelblau, 1972).

RESULTS AND DISCUSSION

Tables 1, 2 and 3 give the experimental results for the studied pectins of apples, orange peels and celery, respectively. These experimental data are the average values of three parallel measurements. The data show that as a result of the acid deesterification of the initial pectic preparations the molecular weight M_{w} and the intrinsic viscosity ($[\eta]$) decrease with a decrease in the degree of esterification. The respective values of $\langle r_{z2}^2\rangle^{1/2}$ and $\langle r_{z2}^2\rangle^{1/2}$ also decrease while the values of $\langle r_{z1}^2\rangle^{1/2}$ decrease only slightly. This is most probably due to the disaggregation of the microgel formations in the pectin preparations. The values of $\langle r_{z2}^2\rangle^{1/2}$ and $\langle r_z^2\rangle^{1/2}$ are much greater than $\langle r_{z1}^2\rangle^{1/2}$ and indicate that in aqueous pectic

TABLE 1
Experimental Results for Pectins from Apples

No.	*Degree of esterification (%)*	$M_w \times 10^5$ *(D)*	$A_2 \times 10^3$ (m^3 *mol* kg^{-2})	$\langle \overline{r_{z1}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_{z2}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_z^2} \rangle^{1/2}$ *(nm)*	$\psi(\alpha) \times 10^3$	$[\eta]$ (*dl* g^{-1})	*GS (°TB)*	*Purity (%)*
1	74·3	1·43	0·72	75	403	468	0·47	2·55	178	58·1
2	68·8	1·29	0·75	70	248	258	0·32	2·35	196	74
3	61·7	1·24	0·74	70	278	287	0·29	2·26	229	77·1
4	59·3	1·17	0·73	69	233	244	0·25	2·24	226	75·3
5	56·4	0·91	0·77	68	297	311	0·15	1·79	201	78

TABLE 2
Experimental Results for Pectins from Orange Peels

No.	*Degree of esterification (%)*	$M_w \times 10^5$ *(D)*	$A_2 \times 10^3$ (m^3 *mol* kg^{-2})	$\langle \overline{r_{z1}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_{z2}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_z^2} \rangle^{1/2}$ *(nm)*	$\psi(\alpha) \times 10^3$	$[\eta]$ (*dl* g^{-1})	*GS (°TB)*	*Purity (%)*
1	69·5	1·42	0·73	70	351	367	0·40	2·51	187	76·6
2	68·1	1·34	0·73	71	266	275	0·35	2·47	202	78·7
3	63·2	1·19	0·74	71	254	263	0·30	2·43	222	74·4
4	55·1	1·04	0·72	68	242	251	0·18	1·98	226	80
5	53·1	0·79	0·73	65	249	268	0·09	1·57	192	79

solutions there is an association of macromolecules. The values of the function $\psi\ (\alpha) = 0{\cdot}75\ M_w^2{\cdot}A_2\ \langle\overline{r_{z1}^2}\rangle^{3/2}$ calculated in accordance with Plashchina *et al.* (1985), indicate the poor tendency of the macromolecules to swell and a considerable stability in relation to conformational transformations unlike flexible macromolecules showing Gaussian behaviour.

The second virial coefficient (A_2) for all pectins studied does not show significant alterations with the changes in the degree of esterification. The low positive values of A_2 conform to the fact that the solvent used is one of the best for the natural polymer under consideration. As for the gel strength, the changes occurring along with the change in the degree of esterification cannot be classified as monotonously decreasing. There is a complex dependence of the gel strength both on the degree of esterification and on the M_w. Besides the apple, orange and celery pectins (Tables 1, 2 and 3) the study also included pectins of different origin obtained from different initial samples by means of acid deesterification. The numerous values of the GS, M_w and DE as well as the difficulties in comparing the data with respect to their GS brought about the need to look for a formal mathematical model providing a functional connection between the studied parameters and gel strength of the form GS $= F(x_1, x_2 \ldots x_n)$ type where $x_1, x_2 \cdots x_n$ are independent variables whose effect, according to data both from experiments and from the literature, can be considered definitely established. The dispersion analysis of the effect of $\langle\overline{r_{z1}^2}\rangle^{1/2}, \langle\overline{r_{z2}^2}\rangle^{1/2}, \langle\overline{r_z^2}\rangle^{1/2}$, A_2 showed a lack of a sufficiently well grounded regression relationship between the effect of these factors and the GS values. The model did not include the factor distribution of the carboxyl groups in the pectin molecule because acid deesterification was applied in obtaining the studied pectins which guaranteed statistically uniform distribution of the carboxyl groups. The method of the passive multifactor experiment (Afifi & Azen, 1979) was used to study the effect of the DE, M_w and the purity $p\%$ (polyuronic acid content) on the GS values. The separate independent factors $x_1 = \text{DE}\%$, $x_2 = M_w$ and $x_3 = p\%$ for the over 60 pectins which were studied changed within the following ranges:

$$29{\cdot}5\% \leqslant x_1 \leqslant 74{\cdot}3\%$$
$$1{\cdot}7 \times 10^4 \leqslant x_2 \leqslant 1{\cdot}74 \times 10^5\ \text{D}$$
$$57{\cdot}4\% \leqslant x_3 \leqslant 91{\cdot}6\%$$

The results of the dispersion analysis of the multiple regression dependence GS $= F$ (DE%, M_w, $p\%$) are given in Tables 4 and 5. The evaluation of the significance of the regression model coefficients and its adequacy was made using the statistical criteria of Student and Fisher. In

TABLE 3
Experimental Results for Pectins from Celery Roots

No.	*Degree of esterification (%)*	$M_w \times 10^5$ *(D)*	$A_2 \times 10^3$ *(m^3 mol kg^{-2})*	$\langle \overline{r_{z1}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_{z2}^2} \rangle^{1/2}$ *(nm)*	$\langle \overline{r_z^2} \rangle^{1/2}$ *(nm)*	$\psi(\alpha) \times 10^3$	*[η]* *($dl\,g^{-1}$)*	*GS* *(°TB)*	*Purity* *(%)*
1	60·1	1·73	0·79	128	489	523	0·37	2·97	218	90·4
2	54·6	1·31	0·78	126	471	501	0·20	2·38	224	90·6
3	44·2	1·18	0·74	124	451	495	0·147	2·19	215	90·9
4	36·8	1·15	0·81	122	445	497	0·145	2·15	184	91·6
5	32·3	1·10	0·82	120	442	489	0·130	2·13	112	91·4
6	29·6	1·00	0·91	99	321	362	0·06	1·92	112	91·2

TABLE 4

Statistical Data on the Model of Multiple Regression Dependence of the Gel Strength on the DE%, M_w and the Purity of Pectic Preparations of Various Origin

Variable	*Average values*	*Standard deviations*	*Partial correlation coefficients*	*Regression coefficients*	*Standard errors of regression coefficients*	*Calculated t values*
X_1	54·46	12·4	0·672	18·77	2·157	8·7
X_2	$1{\cdot}03\times10^{5}$	$0{\cdot}406\times10^{5}$	−0·6452	$0{\cdot}5118\times10^{-3}$	$3{\cdot}862\times10^{-2}$	1·325
X_3	77·05	14·11	0·9922	5·315	0·6645	7·999
X_1^2	$3{\cdot}116\times10^{3}$	$1{\cdot}278\times10^{3}$	0.6422	−0·1558	0·02226	−7·002
X_2^2	$12{\cdot}27\times10^{9}$	$8{\cdot}352\times10^{9}$	0·8412	$-0{\cdot}1963\times10^{-8}$	$0{\cdot}2289\times10^{-9}$	0·8576
$X_1.X_2$	$5{\cdot}993\times10^{6}$	$3{\cdot}195\times10^{6}$	0·7488	$0{\cdot}4167\times10^{-4}$	$0{\cdot}9721\times10^{-5}$	4·287
$X_1.X_2.X_3$	$4{\cdot}346\times10^{8}$	$2{\cdot}058\times10^{8}$	0·609	$-0{\cdot}496\times10^{-6}$	$0{\cdot}9208\times10^{-7}$	−5·387
Dependent values	189·5	42·37	—	—	—	—

Coefficient of multiple correlation $R_M = 0{\cdot}9295$.

$$y = 18{\cdot}77X_1 + 0{\cdot}5118\times10^{-3}X_2 + 5{\cdot}315X_3 - 0{\cdot}1558X_1^2 - 0{\cdot}1968\times10^{-8}X_2^2 + 0{\cdot}4167X_1.X_2 - 0{\cdot}496\times10^{-6}X_1.X_2.X_3 - 819.3 \quad (10).$$

TABLE 5

Dispersion Analysis of Multiple Regression Dependence GS = F(DE%, M_w, p%)

Source of dispersion	*Sum of squares*	*Degrees of freedom*	*Average squares*	*F-criterion*
Regression	$0{\cdot}698\times10^{5}$	7	$0{\cdot}9972\times10^{4}$	Experimental 34·45
Deviation from regression	$0{\cdot}11\times10^{5}$	38	$0{\cdot}2894\times10^{3}$	$F_{\text{theor.}}(7;38) = 4{\cdot}82$ at $\alpha = 0{\cdot}99$
Sum total	$0{\cdot}808\times10^{5}$	45		

compliance with Himmelblau (1972) the absolute maximum for the GS was studied by means of a simplex method with imposed limitations in accordance with the intervals of change of the independent factors. The value of the absolute maximum GS = 243°TB was obtained at DE = 59·3%, $M_w = 73{\cdot}5 \times 10^3$D (D = Dalton), and $p = 91{\cdot}6\%$. This result indicates that the increase in the pectic preparations purity resulted in an increase in the GS which was to be expected, while with respect to the M_w the optimal value was obtained at a value different from the maximum of the M_w. Further investigation is necessary to clarify the size of the supramolecular formations on the GS. As for the optimum of the DE it was obtained at a value that corresponded to the relatively greatest conformation flexibility of the pectic macromolecule.

Studying the acid deesterification of apple pectins one of the authors (Kratchanov & Balakireva, 1972) has found that the maximum stability of 65% sugar jellies is obtained at DE = 57–63%. In the work of Duria and Vladimirov (1978) the maximum GS of different apple pectins was DE = 59%. The detailed studies on the conformation properties of pectic substances from the point of view of the theory of persistent polymer chains made by Plashchina *et al.* (1985) showed that in the 52–61% range of the degree of esterification a maximum flexibility of the pectin macromolecule was observed and this was also the range of the maximum stability of high-sugar jellies. Fishman *et al.* (1986) also consider that within the range of DE = 57% there is a maximum of the hydrophobic interaction and the formation of hydrogen bonds between the macromolecules.

Since in most practical applications of the pectic substances it is easier to characterize their molecular weight indirectly using the values of the intrinsic viscosity $[\eta]$, we tried to find the functional relationships of the gel strength on the DE, $[\eta]$ and the purity, similar to those reflected in eqn (10) (see Table 4).

The intervals of change of the DE and the purity remained the same because the same pectic preparations were used. The intrinsic viscosity changed within the following range:

$$0{\cdot}47\frac{\mathrm{dl}}{\mathrm{g}} \leqslant [\eta] \leqslant 3{\cdot}54\frac{\mathrm{dl}}{\mathrm{g}}$$

The results of the statistical analysis are given in Tables 6 and 7.

The experimental data are adequately described by the following equation:

$$Z(\mathrm{GS}) = f(\mathrm{DE}\%, [\eta], p\%)$$

TABLE 6
Statistical Data of the Model of Multiple Regression Dependence of the GS on the DE%, [η] and the Purity of Pectic Preparations of Various Origin

Variables	*Average values*	*Standard deviations*	*Partial correlation coefficients*	*Regression coefficients*	*Standard errors of regression coefficients*	*Calculated t values*
X_1	55·24	12·4	0·665	19·62	2·054	9·552
X_2	1·09	0·654	−0·656	29·48	2·294	1·285
X_3	76·62	13·79	0·992	5·895	0·7487	7·874
X_1^2	$3·202 \times 10^3$	$1·293 \times 10^3$	0.619	−0·1664	0·02302	−7·229
X_2^2	4·377	2·591	0·863	−6·897	0·8183	−0·8428
$X_1.X_2$	$1·1152 \times 10^2$	3·572	0·750	2·728	0·703	3·883
$X_1.X_2.X_3$	$0·837 \times 10^4$	$0·344 \times 10^4$	0·581	$3·134 \times 10^{-2}$	$0·571 \times 10^{-2}$	−5·485
Dependent values	180·1	40·91	—	—	—	—

$R_M = 0·9263$.

TABLE 7
Dispersion Analysis of Multiple Regression Dependence GS = *F*(DE%, [η], *p*%)

Source of dispersion	*Sum of squares*	*Degrees of freedom*	*Average squares*	*F-criterion*
Regression	$0·7037 \times 10^5$	7	$0·1005 \times 10^5$	Experimental 36·26
Deviations from regression	$0·1165 \times 10^5$	42	$0·2774 \times 10^3$	$F_{\text{theor.}}(7;24) = 2·24$ at $\alpha = 0·95$
Sum total	$0·8202 \times 10^5$	49		

$$Z = -0{\cdot}928 + 19{\cdot}62x_1 + 29{\cdot}48x_2 + 5{\cdot}895x_3 - 0{\cdot}1664x_1^2 - 6{\cdot}897x_2^2 + 2{\cdot}728x_1x_2 - 0{\cdot}031\,34x_1x_2x_3 \tag{11}$$

The multiple correlation coefficient is $R_M = 0{\cdot}9263$. The experimentally calculated value of Fisher's criterion is $F^{\circ}_{cr} = 36{\cdot}26$ at $F'_{cr} = (7{\cdot}38/\alpha = 0{\cdot}99) = 4{\cdot}82$. Therefore, 85·8% of the dispersions of experimental values can be explained by eqn (11). The tests for a maximum value of eqn (11) gave the following coordinates of the maximum gel strength:

$$x_1^{\max}(\mathrm{DE}) = 58{\cdot}3\%$$

$$x_2^{\max}([\eta]) = 1{\cdot}58\ \mathrm{d}l/g$$

$$x_3^{\max}(p) = 91{\cdot}6\%$$

$$\mathrm{GS} = 242\ {}^{\circ}\mathrm{TB}$$

Despite the good approximation of eqns (10) and (11) to the experimental data, they do not include additional factors which are directly related to the gel properties of the pectic substances, namely the cation composition of pectin, the acetyl content, the content of neutral sugars in the pectin macromolecule, etc. These additional data should be available for a more detailed simulation of the effect of various factors on the gel properties of pectic substances.

REFERENCES

Afifi, A. A. & Azen, S. P. (1979). *Statistical Analysis. A Computer Oriented Approach*, Academic Press Inc, New York.

Baker, G. L. (1926). *Ind. Eng. Chem.*, **18**, 89.

Berth, G., Anger, H. & Linow, F. (1977). *Die Nahrung*, **21** (10), 939.

Berth, G., Anger, H. & Lexow, D. (1980). *Die Nahrung*, **24** (6), 529.

Berth, G., Anger, H., Plaschchina, I. G., Braudo, E. E. & Tolstogusov, V. B. (1982). *Carbohydrate Polymers*, **2**, 1.

Bettelheim, F. A. (1970). *Biological Macromolecules Series*, **3**, 131.

BeMiller, J. M. (1986). *ACS Symposium Series*, **310**, 2.

Brandt, S. (1970) *Statistical and Computational Methods in Data Analysis*, Elsevier Science Publishing Co. Inc., New York.

Duria, M. & Vladimirov, G. (1978). *Food Industry (Bulgaria)*, No. 4, 33.

Eskin, V. E. (1986). Light dispersion by polymer solutions and properties of the macromolecules, Nauka, Leningrad, 53.

Fishman, M. S., Pepper, L. & Pfeffer, P. E. (1986). *Advances in Chemistry Series*, **213**, 57.

Glikman, S. A. & Orlov, S. A. (1951). Works of the all-union conference of colloidal chemistry, Moskwa, 296–304.

Himmelblau, D. (1972). *Applied Non-Linear Programming*, McGraw-Hill Book Company, New York.

IBM (1970). System/360 Scientific Subroutine Package (360 A-CM-03 x) version III, Technical Publication Department, New York.

Johnson, H. (1980). *Numerical Methods in Chemistry*, Marcel Dekker Inc., New York.

Jordan, R. C. & Brant, D. A. (1978). *Biopolymers*, **17**, 2885.

Kirthev, N., Panchev, I. & Kratchanov, Chr. (1988). *International Journal of Food Science & Technology* (in press).

Kratchanov, C. G. & Balakireva, B. N. (1972). *Travaux Scientifiques* (Inst. Technol., Plovid, Bulgaria), **XIX** (III) 81.

Kratochvil, P. (1982). *Pure & Applied Chemistry*, **54** (2), 379.

Nelson, D. B. (1977). *Proc. Int. Soc. Citriculture*, **3**, 739.

Owens, H. S., McCready, R. M., Shepherd, A. D., Schultz, T. H. & Pippen, E. L. (1952). *I. C. Report*, **340**, 7.

Pilnik, W. (1980). *European Symposium on Fiber in Human Nutrition*, Paris, 21–23 October, p. 91.

Plashchina, I. G., Semenova, M. G., Braudo, E. E. & Tolstoguzov, V. B. (1985). *Carbohydrate Polymers*, **5**, 159.

Prochazka, O., Tuzar, Z. & Kratochvil, P. (1983). *Macromolecular Chemistry*, **184**, 2097.

Rees, D. A. (1972). *Biochemistry Journal*, **126**, 257.

Robinson, G., Ross Murphy, S. B. & Morris, E. R. (1982). *Carbohydrate Research*, **107**, 17.

Senkievitch, S. I., Belavtzeva, E. N., Plashchina, I. G., Braudo, E. B., Kamenskaia, E. V. & Tolstogusov, V. B. (1979). *Biophysics*, **XXIV** (4), 637.

Smidsrod, O. & Haug, A. (1971). *Biopolymer*, **10**, 1213.

Smith, J. E. &. Stainsby, G. S. (1977). *British Polymer Journal*, **9**, 284.

Sorochan, V. D., Dzizenko, A. K., Bodin, N. S. & Ovodov, Yu. S. (1971). *Carbohydrate Research*, **20**, 243.

Taylor, A. J. (1982). *Carbohydrate Polymers*, **2**, 9.

Tverdohlebova, I. I. (1981). Macromolecules conformation. Viscosimetric evaluation method, Chimia, Moskwa.