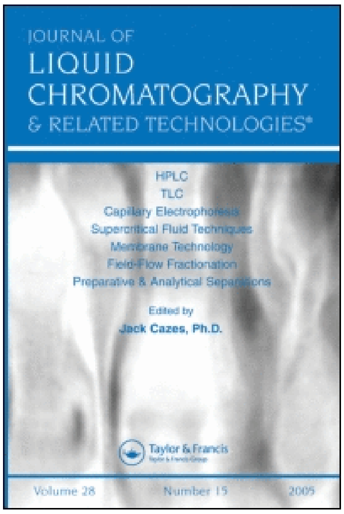

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Lambros Farmakis[a]; George Karaiskakis[a]; Athanasia Koliadima[a]
[a] Department of Chemistry, University of Patras, Patras, Greece

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INVESTIGATION OF THE VARIATION OF THE MASS RATIOS FOR LARGE AND SMALL STARCH GRANULES WITH THE pH AND IONIC STRENGTH OF THE DISPERSING MEDIUM BY SEDIMENTATION/STERIC FIELD-FLOW FRACTIONATION

Lambros Farmakis, George Karaiskakis, and Athanasia Koliadima*

Department of Chemistry, University of Patras,
26504 Patras, Greece

ABSTRACT

The relatively new technique of Sedimentation/Steric Field-Flow Fractionation (Sd/St FFF) is a simple, fast, and accurate method for the size separation and characterization of starch granules. In the present work, the Sd/St FFF technique was used for the calculation of the mass ratios of the A-large and B-small granules from barley and wheat starch samples. The mass ratios were obtained from the distribution curves of the starch samples at various pH and ionic strength of the suspending medium, in the presence or the absence of the surfactant FL-70. The influence of the suspension pH and ionic strength on the mass ratios of

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*Corresponding author. E-mail: akoliadima@chemistry.upatras.gr

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A- and B-granules is discussed in relation to the zeta potentials of the particles, which were measured by a microelectrophoresis apparatus.

Key Words: Sedimentation/steric FFF; Starch characterization; Starch mass ratios

INTRODUCTION

Starches are principal food-reserve polysaccharides in the plant kingdom. They form the major source of carbohydrates in the human diet and are of great industrial importance.[1] Starch from various sources have individual characteristic properties: shape, size, composition, and crystallinity of the granules.[2] In cereal, starch can be found in two types of granules, large and small and are made up of amylose and/or amylopectin molecules arranged radically.[1,3,4] The large granules are more susceptible to chemical and enzymatic hydrolysis than the small ones, so it is very important to know the particle size and the variation of the mass ratios (large and small granules) in the dispersing medium, in order to select the optimal conditions for further investigation.

For wheat and barley starches (that we are using in the present work) the granules' diameter lies in the range between 1 and 35 μm, while their shape is almost spherical. Both samples show a characteristic bimodal size distribution and the two size populations usually being termed A- and B-, respectively, for the large and small particles.

Several techniques are used for the size characterization of starch granules. Light scattering and scanning electron microscopy are the common methods to analyze and characterize the particles. Sedimentation/Steric field-flow fractionation (Sd/St FFF) is a simple and accurate technique for separation and characterization of colloidal materials and macromolecules.[5–10] It is an elution technique, and the retention volume under selected experimental conditions is immediately related to the number and weight average particle diameter, or to the particle mass ratio. The accurate determination of the above parameters is dependent on a number of experimental parameters, among which the surface potential of the particles, as well as the nature, pH, and ionic strength of the suspending medium.[11] In the present work, we used the Sd/St FFF technique for the study of the influence of the ionic strength and the pH of the suspending medium on the number average diameter and the mass ratios of the barley and wheat starch granules.

The suspension's ionic strength and pH influence the dispersion properties of starch, which are dependent on the forces between the surface of the starch and the molecules of the media, compared with forces preventing the adherence of granules to each other, which lead to starch's granule aggregation and the forces between the granules and the channel wall, which influence the retention time,

t_r.[12,13] While the retention volume in Sd/St FFF, Vr_i, is proportional to the cube of the particle diameter, d_i,[14] the Vr_i in Steric FFF (St FFF) is inversely proportional to the diameter d_i according to the equation:[7,15]

$$Vr_i = \frac{wV^0}{3\gamma}\frac{1}{d_i} \tag{1}$$

where V^0 is the column void volume and γ is the steric correction factor depending on lift forces and hydrodynamic effects. Since there are no general theoretical expressions to describe hydrodynamic lift forces, an experimental calibration curve is necessary. It has been mentioned previously,[9,11] that using well characterized standards under appropriate conditions, the plot of $\log t_r$ vs. $\log d$ normally yields a straight line.

EXPERIMENTAL

The experimental procedure has been described in detail elsewhere.[9] The Sd FFF system employed had a channel void volume of 1.57 cm^3.

Standard polystyrene latex spheres from Polysciences Inc. with nominal diameters of 5.725 ± 0.278, 10.568 ± 1.034, 14.571 ± 1.657, 22.000 ± 2.593, and 25.962 ± 2.718 μm were used for the calibration plot.

The electrolyte added to the carrier solution to adjust its ionic strength was potassium nitrate (KNO_3) in a range of 10^{-3} M to 10^{-1} M from Riedel-De Haen A. G, while the pH of starch dispersion was adjusted with HNO_3 (From Riedel-De Haen A. G.) and KOH (from Merck A. G.).

As carrier solvent we used either triple distilled water or triple distilled water containing 0.5% v/v FL-70 (Fisher Scientific Co.), a low alkalinity mix of anionic and nonionic surfactants, and 0.02% w/w NaN_3 (Fluka).

Two barley starch samples (labeled as N- and K-), which were produced by the same procedure but at different times (different preparation line), provided by Dr. Chmelik, Institute of Analytical Chemistry, Czech Academy of Science, Brno, Czech Republic and one wheat starch sample from Fluka AG (Catalog no. 85647) were employed. The starch granules were suspended in the carrier liquid and sonicated for 5 min as a further aid to particle dispersion. The concentration of the resulting starch granule suspension was kept constant (10 mg/mL) in all experiments. Injection of 100 μL volume of the starch suspension was made into the channel by a microsyringe. Following injection, the longitudinal flow ($= 195$ mL h^{-1}) was stopped for 10 min to allow for sample relaxation.

According to the principle of density compensation described earlier,[16] and taking into account that the densities of the starch and the polystyrene latexes are 1.51 g/mL and 1.05 g/mL, respectively, the field strength, G, for starch must be reduced by a factor of 10.3, compared to that used with polystyrene latex spheres for the calibration plot. Since G for latexes was $G = 169\,\mathrm{g} = 1000\,\mathrm{rpm}$, the appropriate field strength for starch used was $G = 16.4\,\mathrm{g} = 312\,\mathrm{rpm}$.

The electrophoretic mobilities and the zeta (ζ) potentials of dispersed starch samples were measured by using the Zetasizer 5000 equipment from Malvern, while the pH of starch dispersion, was measured by the pH-meter model 507 from CRISON (Spain).

RESULTS AND DISCUSSION

In the present work, the calibration plot is given by the equation:[7,9]

$$\log t_{ri} = -1.3397 \log d_i + 2.6196 \tag{2}$$

where d_i are the particle diameters of the starch granules, which were determined from the retention times t_{ri}. From all the d_i values of a fractogram obtained by Sd/St FFF, the number average particle diameter, d_N, can be calculated from the relation:[9]

$$d_N = \frac{\sum_i d_i n_i}{\sum_i n_i} = \frac{\sum_i (6w_i/\pi\rho_\varsigma d_i^3) d_i}{\sum_i (6w_i/\pi\rho_\varsigma d_i^3)} = \frac{\sum_i w_i/d_i^2}{\sum_i w_i/d_i^3} \tag{3}$$

where n_i is the number of the particles having constant diameter d_i and w_i is given by the relation:

$$w_i = n_i \frac{1}{6} \pi \rho_\varsigma d_i^3 \tag{4}$$

where ρ_s is the density of the particles.

The mass particle size distributions, $p(d)$, are obtained from the known equation:[7,16]

$$p(d) = c(t_R) d \dot{V} S_d t_{R1} \left(\frac{t_R}{t_{R1}}\right)^{(S_d+1)/S_d} \tag{5}$$

where $c(t_R)$ is the detector signal and $\dot{V}$ is the volumetric flow rate, while S_d ($=-1.3397$) and t_{R1} ($=10^{2.6196}$) are the negative slope and the constant of the calibration plot (Eq. 2).

Influence of the pH of the Suspending Medium on the Mass Ratios of Barley Starch Granules

Figure 1 shows four "raw" fractograms, which express the detector response profile over the separation retention volume span for the N- and

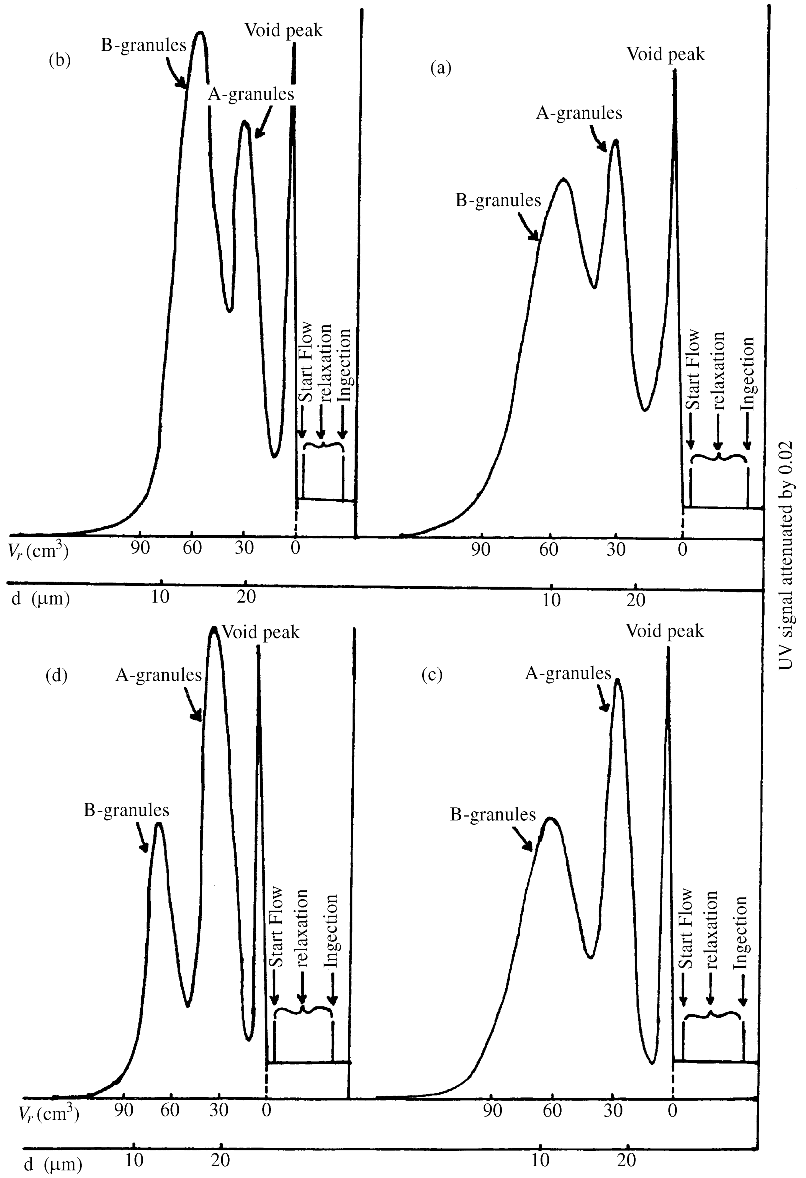

Figure 1. Fractograms and particle diameters scales of the barley N- and K-samples obtained by Sd/St FFF: (a) N-sample in the presence of 0.5% v/v FL-70; (b) N-sample in the absence of FL-70; (c) K-sample in the presence of surfactant; (d) K-sample in the absence of surfactant.

K-barley starch samples at pH = 7.0, in the presence (a and c) and the absence (b and d) of the surfactant FL-70. They show a bimodal size distribution for the populations of A-large and B-small starch granules. For comparison purposes, scanning electron micrographs of the N- and K-barley starch granules dispersed in different media were obtained by using a JEOL JSM-5200 scanning electron microscope (SEM) from JEOL (Tokyo, Japan) (cf. Fig. 2).

The fractograms indicate, also, that in both cases (N- and K-samples) the second peak corresponding to the small B-granules is broader in the presence of

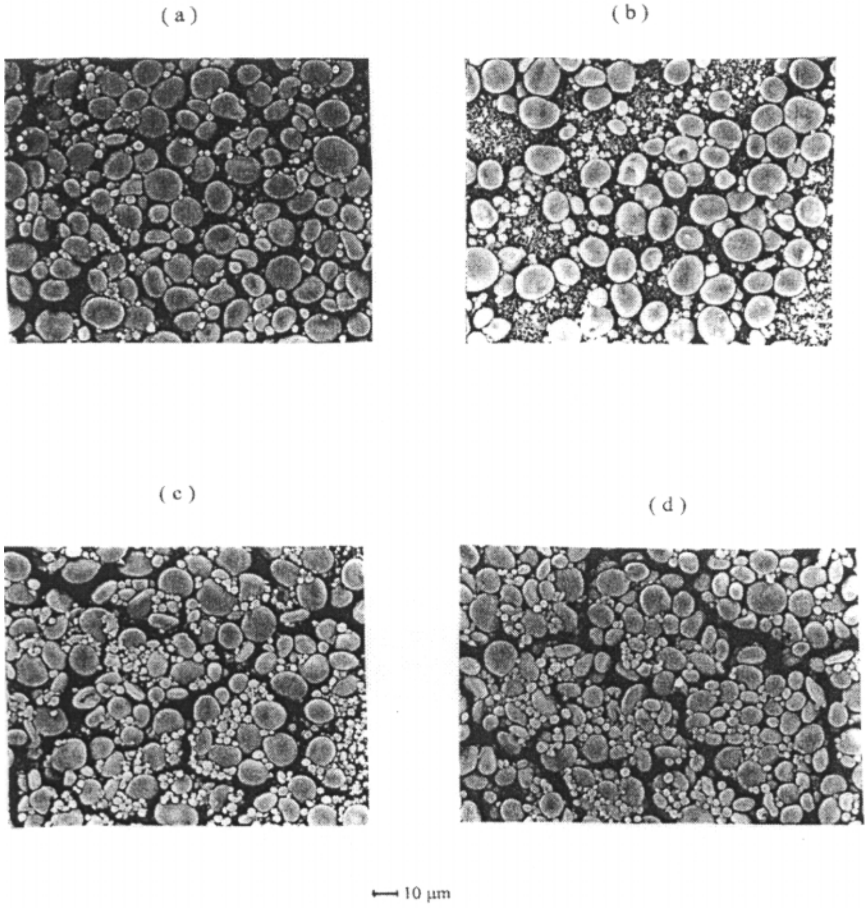

Figure 2. Scanning electron micrographs (SEM) of the dry suspensions of the barley N- and K-samples dispersed in various media. The (a), (b), (c) and (d) in this and the following figures correspond to the conditions described in Fig. 1.

the surfactant FL-70, indicating that the mass ratio of the B-granules is lower in the absence of FL-70, compared to that in the presence of the surfactant, due to possible aggregation of the B-granules in the absence of the detergent.

Figure 3 shows the mass distribution curves of the fractograms shown in Fig. 1. The mass percentages of A- and B-granules for the barley N-sample at various pH values of the suspending medium, when it contains 0.5% v/v FL-70, are compiled in Table 1. It can be seen, that in the pH range 7.5–11.5 the suspension pH does not influence the mass ratio of A- and B-granules, while at lower pH values, the mass percentage of A-granules increases and the mass percentage of B-granules decreases with the pH of the suspending medium.

The corresponding mass ratio values for the N-sample at various pH values of the suspending medium, when the suspension is clear triple distilled water, are given in Table 2.

The last table shows, that in the absence of surfactant, the suspension pH strongly influences the mass ratio of A- and B-granules for the barley N-sample.

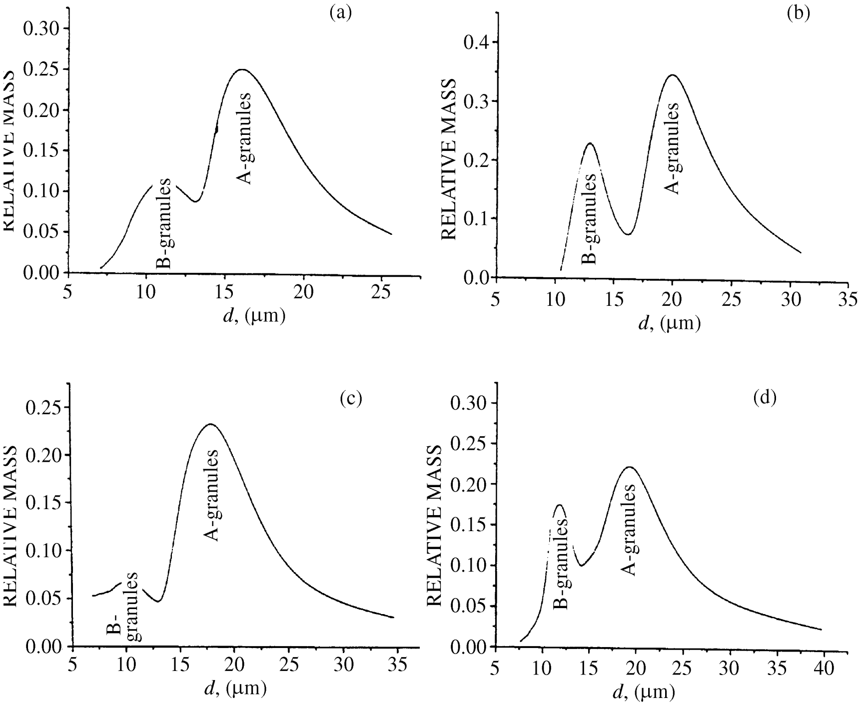

Figure 3. Mass distribution curves for the barley N- and K-starch samples obtained by Sd/St FFF.

Table 1. Mass Ratios of A-Large and B-Small Granules for the Barley N-Sample at Various pH Values of the Suspending Medium Which Contains 0.5% v/v FL-70

pH	A (%)	B (%)
6.5	77.9	22.1
7.0	82.8	17.2
7.5	90.4	9.6
8.5	90.5	9.5
9.5	92.9	7.1
10.5	89.1	10.9
11.5	89.0	11.0

With the only exception of $\text{pH} = 4$, all the remaining results show that the mass ratio of the large A-granules increases with the increasing pH until approximately $\text{pH} \approx 10.5$, at which value the mass ratio remains constant. On the other hand, the mass ratio of the small B-granules decreases with the increasing suspension pH.

By comparing the results of Tables 1 and 2, we can see that in the pH range 7.5–11.5 the mass ratio of A- and B-granules for the N-sample are higher in the presence of the surfactant FL-70, indicating that a possible aggregation of the small B-granules occurs in the absence of the detergent. In support of the above assumption, which was also mentioned previously, is the fact that the number average diameters of the B-granules measured by Sd/St FFF are higher in the

Table 2. Mass Ratios of A-Large and B-Small Granules for the Barley N-Sample at Various pH Values of the Suspending Medium in the Absence of the Surfactant FL-70

pH	A (%)	B (%)
4.0	81.9	18.1
6.0	65.8	34.2
6.5	70.6	29.4
7.0	75.3	24.7
7.5	76.7	23.3
8.5	79.0	21.0
9.5	79.9	20.1
10.5	88.0	12.0
11.5	85.3	14.7

absence of FL-70 (cf. Table 3). In the pH range 7.5–11.5, the mass ratio of A- and B-granules are constant and independent of the suspension pH, when the dispersing medium contains FL-70. With the exception of $\mathrm{pH} = 4.0$, all the remaining results of Table 2 show that the mass ratio of A-granules increases as the suspension pH increases. At the higher pH range ($\mathrm{pH} > 10.5$), the mass ratio of the large A-granules for the barley N-sample in the absence of surfactant, approaches the constant value of the same mass ratio when the dispersing medium contains FL-70.

The mass percentages of A- and B-granules for the barley K-sample at various pH values of the suspending medium, when it contains FL-70, are given in Table 4. It can be seen, that the suspending pH does not influence the mass ratio of A- and B-granules in the pH range 7.5–11.5, a behavior, which was also observed with the N-sample.

The mass percentages of A- and B-granules for the same K-sample, in the absence of the surfactant FL-70, are compiled in Table 5. It can be seen, that the mass percentage for the A-granules increases with the suspension pH in the pH range 6.3–7.5, and then remains constant up to $\mathrm{pH} = 9.5$. On the other hand, the mass percentage for the B-granules decreases with the pH of the suspending medium in the pH range 6.3–7.5, and then remains constant up to $\mathrm{pH} = 9.5$.

Table 3. Number Average Diameters for the Large, d_{N_1}, and Small, d_{N_2}, Starch Granules of the Barley N-Sample Determined by Sd/St FFF at Various pH Values of the Suspending Medium

Carrier Solution	pH	d_{N_1} (μm)	d_{N_2} (μm)
Triple distilled water	6.5	17.1	7.8
+ 0.5% v/v FL-70	7.0	16.9	9.8
	7.5	16.5	9.7
	8.5	15.6	9.5
	9.5	17.3	8.3
	10.5	16.9	9.2
	11.5	16.3	9.6
Triple distilled water	4.0	17.2	9.1
	6.0	20.3	13.7
	6.5	20.6	13.9
	7.0	19.5	12.7
	7.5	19.7	11.9
	8.5	19.5	11.9
	9.5	18.3	10.2
	10.5	19.8	10.1
	11.5	19.6	11.7

Table 4. Mass Percentages of A- and B-Granules for the K-Barley Sample at Various pH Values of the Suspending Medium in the Presence of FL-70 (0.5% v/v)

pH	A (%)	B (%)
6.5	94.0	6.0
7.0	96.5	3.5
7.5	88.4	11.6
8.5	84.7	15.3
9.5	87.1	12.9
10.5	87.6	12.4
11.5	87.3	12.7

Comparison of the results of Tables 4 and 5 leads to the conclusion that when the suspension pH is higher than 7.5, the mass percentages of the A- and B-granules for the barley K-sample are approximately the same in the presence and the absence of the surfactant FL-70, and independent of the suspension pH. When the suspension pH is lower than 7.5, the mass percentages of A- and B-granules for the K-sample in both cases (when the suspending medium contains or not FL-70) differ significantly from those found when the pH is higher than 7.5. At pH values higher than 7.5, the mass percentages of A- and B-granules for the K-sample are relatively higher in the presence of the detergent FL-70, showing that a possible aggregation of the B-small granules occurs in the absence of the surfactant. In support of the above assumption, is the fact that the number average diameters of the B-granules are higher in the absence of FL-70 (cf. Table 6).

In order to further investigate if the starch granules interact with themselves to form aggregates, or with the Hastelloy-C channel wall, the z potentials of the

Table 5. Mass Percentages of A- and B-Granules for the K-Barley Sample at Various pH Values of the Suspending Medium in the Absence of FL-70

pH	A (%)	B (%)
6.3	61.6	38.4
7.0	76.7	23.3
7.5	83.7	16.3
8.5	82.4	17.6
9.5	79.8	20.2

Table 6. Number Average Diameters for the Large, d_{N_1}, and Small, d_{N_2}, Granules of the Barley K-Sample at Various pH Values of the Suspending Medium

Carrier Solution	pH	d_{N_1} (μm)	d_{N_2} (μm)
Triple distilled water + 0.5% v/v FL-70	6.5	22.9	8.6
	7.0	18.4	8.7
	7.5	16.8	8.7
	8.5	17.7	9.2
	9.5	17.6	9.8
	10.5	17.2	9.4
	11.5	17.4	9.3
Triple distilled water	6.3	19.6	13.5
	7.0	18.7	11.1
	7.5	18.9	10.8
	8.5	18.0	10.3
	9.5	16.2	9.2

N- and K-barley starch granules were measured at various pH values of the suspension (cf. Fig. 4). From the last figure, it is shown that both N- and K-samples carry positive and negative charged groups at the surface. The fact that the N-sample in the absence of the surfactant FL-70, seems to have only negative charges in the whole working pH range ($2.0 < \text{pH} < 12.0$), can be attributed to the relatively large standard deviations of the measured z potentials. The isoelectric point for both N- and K-samples in the presence and the absence of FL-70, is almost identical and very close to pH = 2.0. The z potentials in the pH range 2.5–12.0 confirm that both N- and K-samples are “anionic starches”.

Generally speaking, the N- and K-barley starch granules, as far as their mass ratios for the A-large and B-small granules is concerned, behave similarly in the pH range 7.5–11.0, in which the interactions forces between particle-particle and particle-wall are almost negligible, when the suspension contains the surfactant FL-70. On the other hand, in the absence of the same surfactant, the mass ratios for the N- and K-samples deviate significantly. It can be attributed rather to the surfactant effect than to the different preparation line of the two samples.

Influence of the Ionic Strength of the Suspending Medium on the Mass Ratios of Wheat Starch Granules

Figure 5 shows the fractograms for the wheat starch granules obtained by Sd/St FFF at various concentrations of electrolyte(KNO_3) in the suspending

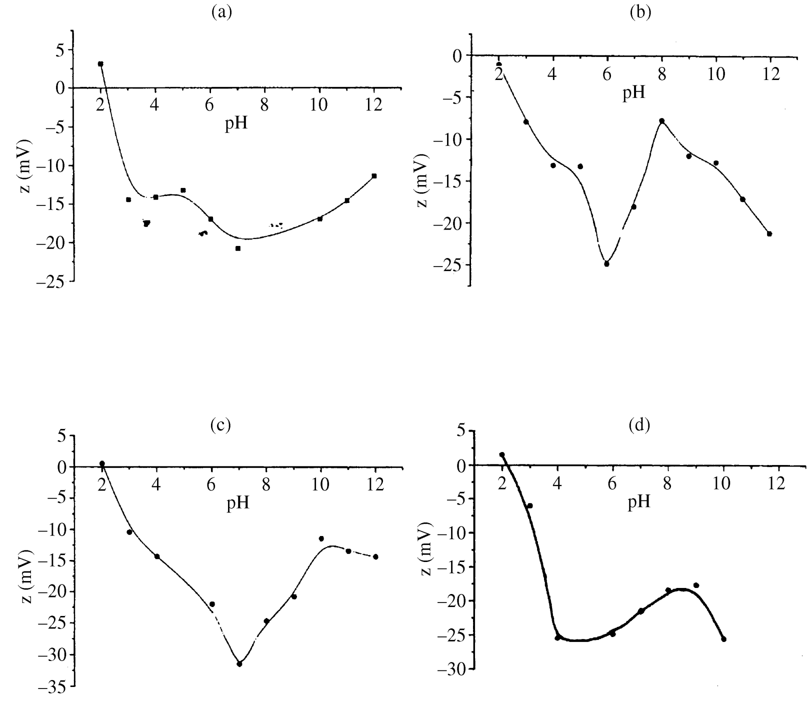

Figure 4. Zeta potential for the barley N- and K-starch granules as a function of the suspension pH.

medium. The mass distribution curves for A-large and B-small wheat starch granules calculated by the Eq. (5) are shown in Fig. 6, while the mass percentages for the two populations of the particles are given in Table 7. This table shows, that by increasing the concentration of the electrolyte, which entails the increase of the ionic strength of the suspending medium, the mass percentages of B- granules decrease. This happens due to the electrolyte influence on the interaction potential energy, $V(h)$, between the colloidal particles and the channel wall, which can be estimated by the sum of the Van der Waals, $V_6(h)$, and double-layer, $V_{DL}(h)$, contributions.[17,18]

$$V(h) = V_6(h) + V_{DL}(h) = \frac{A_{132}}{6}\left[\ln\left(\frac{h+2\alpha}{h}\right) - \frac{2\alpha(h+\alpha)}{h(h+2\alpha)}\right] + 16\varepsilon\alpha\left(\frac{kT}{e}\right)^2 \tanh\left(\frac{e\psi_1}{4kT}\right)\tanh\left(\frac{e\psi_2}{4kT}\right)e^{-\kappa h} \qquad (6)$$

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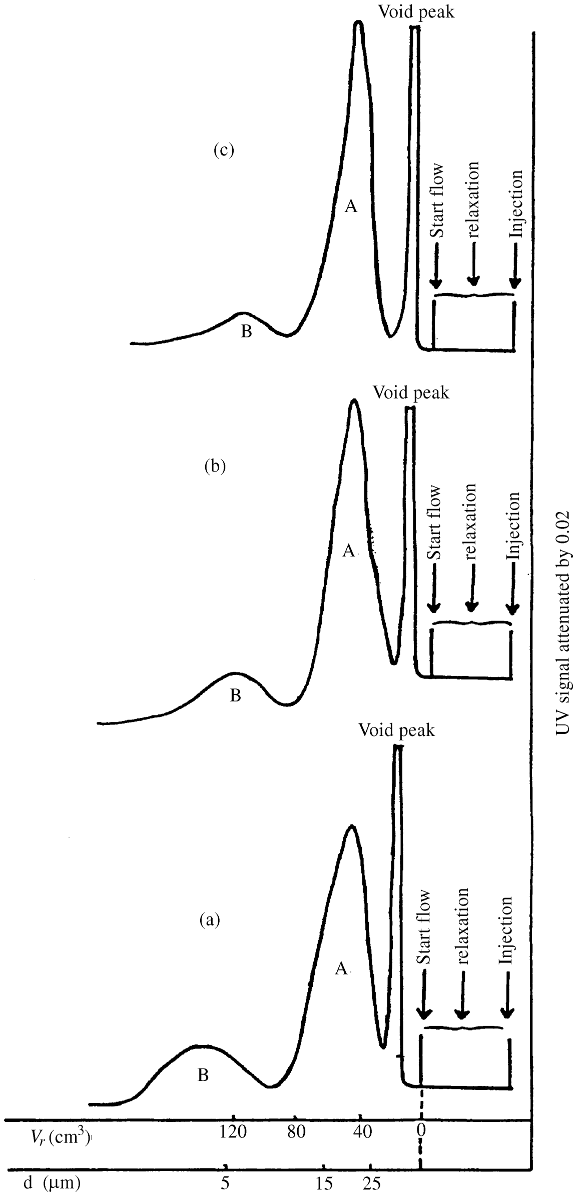

Figure 5. Fractograms and particle diameter scales of the wheat starch granules obtained by Sd/St FFF: (a) in the presence of 0.5% v/v FL-70; (b) in the presence of 0.5% v/v FL-70 + 10^{-2} M KNO_3; (c) in the presence of 0.5% v/v FL-70 + 10^{-1} M KNO_3.

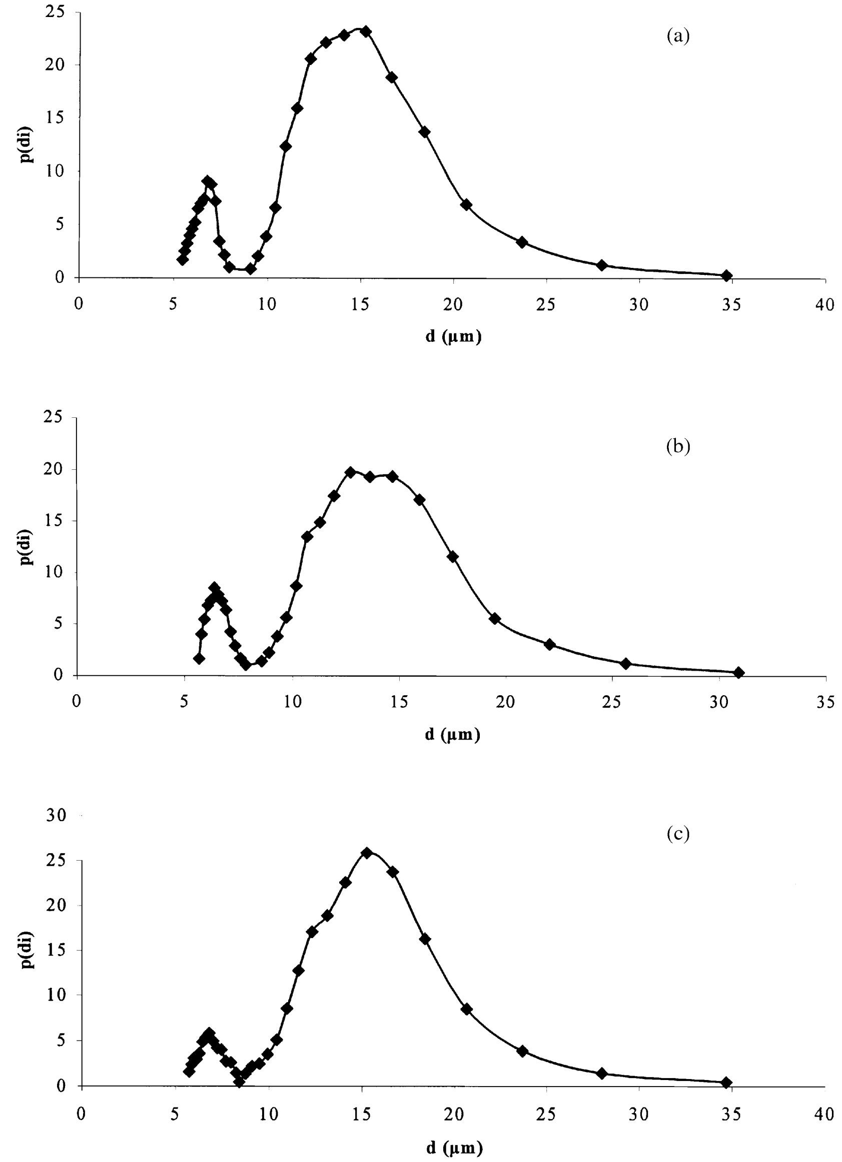

Figure 6. Mass distribution curves of wheat starch samples obtained by Sd/St FFF. The (a), (b) and (c) in this figure correspond to the conditions described in Fig. 5.

Table 7. Mass Percentages of Wheat Starch Sample at Various Potassium Nitrate Concentrations of the Suspending Medium

Carrier Solution	A (%)	B (%)
0.5% FL-70 + 0%KNO_3	90.3	9.7
0.5% FL-70 + 1×10^{-3} KNO_3	90.6	9.4
0.5% FL-70 + 3×10^{-3} KNO_3	90.8	9.2
0.5% FL-70 + 7×10^{-3} KNO_3	92.8	7.3
0.5% FL-70 + 1×10^{-2} KNO_3	93.9	6.1
0.5% FL-70 + 3×10^{-2} KNO_3	95.3	4.7
0.5% FL-70 + 7×10^{-2} KNO_3	95.7	4.3
0.5% FL-70 + 1×10^{-1} KNO_3	95.8	4.2

where h is the separation distance between the sphere and the channel wall, α is the particle radius and A_{132} is the effective Hamaker constant for media 1 and 2 interacting across medium 3, ε is the dielectric constant of the liquid phase, e is the electronic charge, ψ_1 and ψ_2 are the surface potentials of the solid surfaces and κ is the reciprocal Debye length. The reciprocal double-layer thickness is given by the expression

$$\kappa^{-1} = BI^{1/2} \tag{7}$$

where B is a constant and I is the ionic strength of the suspending medium. The Hamaker constant depends only on the molecular properties of the particles and the channel wall as well as on the suspending medium, so in the present work, it can be considered stable.

By increasing the ionic strength, the repulsive forces between the particles and the channel wall decrease. So, we should expect a higher retention time, which leads to lower values of particle diameters. Comparing the d_N values for wheat starch granules, as they are given in Table 8, we observe that the ionic strength's influence is negligible.

Although the starch granules have negative surface charges,[19] the particle–particle interactions are of importance in the steric range by changing the ionic strength. Table 7 shows, as mentioned above, that the mass percentage of small granules decreases by increasing the ionic strength of the suspending medium. According to this observation, we may assume that aggregation phenomena are present, even though the number average diameters for both populations remain constant. These phenomena are important when the electrolyte concentration increases from 10^{-3} M to 10^{-2} M KNO_3, while it remains stable when the electrolyte concentration ranges from 10^{-2} M to 10^{-1} M KNO_3. The above observations are in a good agreement with the zeta potentials of the wheat starch

Table 8. Number Average Diameters for the Large, d_{N_1}, and Small, d_{N_2}, Starch Granules of the Wheat Sample Determined by Sd/St FFF at Various Potassium Nitrate Concentrations of the Suspending Medium

Carrier Solution	d_{N_1}	d_{N_2}
0.5% FL-70 + 0%KNO_3	13.8	6.7
0.5% FL-70 + 1×10^{-3} KNO_3	13.7	6.4
0.5% FL-70 + 3×10^{-3} KNO_3	13.4	6.5
0.5% FL-70 + 7×10^{-3} KNO_3	13.9	6.4
0.5% FL-70 + 1×10^{-2} KNO_3	12.5	6.4
0.5% FL-70 + 3×10^{-2} KNO_3	13.8	6.5
0.5% FL-70 + 7×10^{-2} KNO_3	14.5	7.1
0.5% FL-70 + 1×10^{-1} KNO_3	13.6	6.7

granules as a function of the ionic strength of the suspending medium, as they are shown in Fig. 7.

As a general conclusion, the suspension pH in the range 7.5–11.5 does not influence the mass percentages of A- and B-starch granules. On the other hand, when the suspension pH is lower than 7.5, the mass ratios of A- and B-granules is

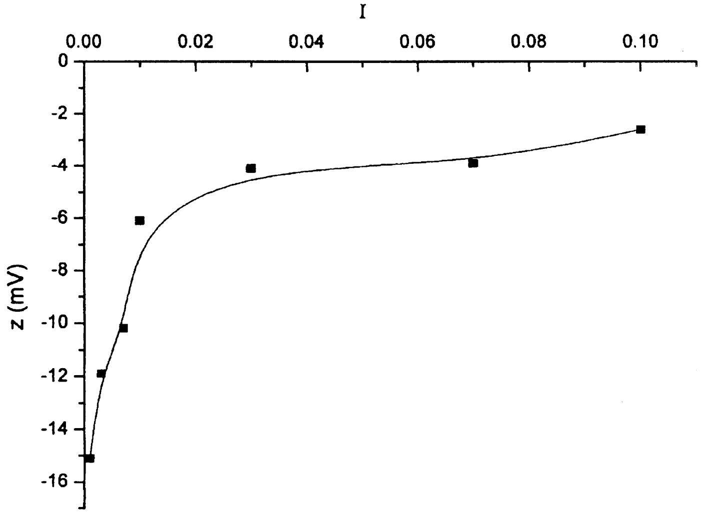

Figure 7. Zeta potential for the wheat starch sample as a function of the suspension ionic strength, I.

dependent on the nature of starch and the particular pH. The ionic strength of the suspension in the range of 10^{-3} to 10^{-2} influences the mass percentages of starch granules by increasing the particle-particle interactions, which lead to aggregation phenomena between the small granules, even though the number average diameters for the large and small starch granules remain approximately constant.

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REFERENCES

1. Jay-lin, J. Starch Functionality in Food Processing. In *Starch-Structure and Functionality*; The Royal Society of Chemistry: 1997; 27 pp.
2. Radley, J.A. *Industrial Uses of Starch and its Derivative*; Applied Science Publishers Ltd.: London, 1976; 87 pp.
3. Fredriksson, H.; Silverio, J.; Andersson, R.; Eliasson, A.-C.; Åman, P. Carbohydr. Polym. **1998**, *35*, 119–134.
4. Franco, C.M.L.; do Rio Petro, S.J.; Ciacco, C.F.; Geraldo, B. Starch **1992**, *44*, 422–426.
5. Giddings, J.C. Anal. Chem. **1981**, 1170A–1175A.
6. Giddings, J.C.; Karaiskakis, G.; Caldwell, K.D.; Myers, M.N.; J. Coll. Interface Sci. **1983**, *92*, 66–80.
7. Giddings, J.C.; Moon, M.H.; Williams, P.S.; Myers, M.N. Anal. Chem. **1991**, *63*, 1366–1372.
8. Koliadima, A.; Karaiskakis, G. J. Chromatogr. **1990**, *517*, 345–359.
9. Farmakis, L.; Sakellaraki, J.; Koliadima, A.; Gavril, D.; Karaiskakis, G. Starch **2000**, *52*, 275–282.
10. Contado, C.; Riello, F.; Blo, G.; Dondi, F. J. Chromatogr. A **1999**, *845*, 303–316.
11. Farmakis, L.; Koliadima, A.; Karaiskakis, G. J. Liq. Chromatogr. & Rel. Technol. **2002**, *25* (2), 167–183.
12. Hiemenz, P.C. *Principles of Colloid and Surface Chemistry*; Marcel Dekker, Inc.: New York, 1977; 457–467.
13. Marsh, R.A.; Waight, S.G.; Wycombe, H. Starch **1982**, *34*, 149.
14. Karaiskakis, G.; Myers, M.; Caldwell, K.D.; Giddings, J.C. Anal. Chem. **1981**, *53*, 1314–1317.
15. Dalas, E.; Karaiskakis, G. Coll. Surf. **1987**, *28*, 169–183.

16. Moon, M.H.; Giddings, J.C. J. Food Sci. **1993**, *58*, 1166–1171.
17. Ruckenstein, E.; Marmur, A.; Gill, W.N. J. Coll. Interface Sci. **1977**, *61*, 183.
18. Israclachvili, J.N. *Intermolecular and Surface Forces*; Academic Press: London, 1987; 144 pp.
19. Hansen, M.E.; Giddings, J.C. Anal. Chem. **1989**, *61*, 811–819.

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