J. Agric. Sci. Mansoura Univ., 28 (2): 1203 - 1212, 2003

RHEOLOGICAL BEHAVIOUR OF FABA BEAN PROTEIN CONCENTRATES

Khalil, H.I. and E.I. Yousif
Food Sci. Dept., Fac. Agric. Ain Shams Univ., Shoubra El-Kheima, Cairo, Egypt.

ABSTRACT

Flow properties of faba bean protein concentrates were studied using Coaxial rotational viscometer to measure the effect of concentrations (9%, 12%, 15% and 18%) and temperatures (30°, 40°, 50°, 60° and 70°C) on their rheological parameters. The protein concentrate samples were prepared from raw seeds or from seeds subjected to soaking-germination, autoclaving and microwaving. Results showed that the protein concentrates followed a non-Newtonian behaviour with a pseudoplastic nature. Heating treatments (autoclaving and microwaving) of germinated faba bean seeds resulted in protein concentrates with high viscosity values. The rheological parameters (K and τ_o) increased exponentialy with increasing concentrations and showed reduction with increasing temperature up to 60°C. At 70°C a reversible effect has been observed, where the viscosity and constant values has been increased consequently the change in the structure of protein molecules. Calculated activation energy values using the Arrhenius approach were in the range of 5.96 to 18.65 kJ/mol. Different rheological models were employed and the model of Herschel-Bulkley was found to be the most suitable formulation representing the rheological behaviour of faba bean protein concentrates. Fitted equations developed to predict the combined effect of concentration and temperature on viscosity of the tested samples were found to be adequate predictions, that may be used to estimate viscosity values during processing.

Keywords: Faba bean, Protein concentrate, Rheology, Flow models.

INTRODUCTION

The formation of protein networks is an important function of proteins in food system. Protein network formation normally requires at least some protein denaturation and is therefore, often associated with thermel processing (Schneider *et al.*, 1986 and Schwenke *et al.*, 1990).

Aqueous protein dispersions and their characteristics are of particular interest. One reason is that the behaviour of protein dispersions, specially the viscosity behaviour, gives some information concerning stability or changes of aggregates or molecules. Another reason is the importance of viscosity behaviour for technological purposes, e.g., mixing, pumping, piping, heating, spray drying and others, for quality control prior to and during the manufacturing process, as well as for the final product (Rha and Pradipasena, 1986). In addition, rheological parameters can be useful indices of structural changes in proteins (Paulson and Tung, 1988).

Influence of protein concentration and temperature on viscosity behaviour of faba bean protein isolate were examined (Schmidt and Schmandke, 1987).

Schmidt *et al.*, (1986) found that the initial measurements of apparent viscosity of vicia faba protein isolate suspensions showed that increases in viscosity with increasing protein concentration were non-linear. In general, faba bean protein isolate exhibited plastic flow, with pseudoplastic flow detectable only in suspensions of low viscosity. Percent of plastic flow increased with protein concentration, temperature rise, or prolonged heating time.

However, few data were recorded for the rheological behaviour of faba bean protein concentrate, therefore, the aim of the present research is to determine the rheological parameters (e.g. yield stress, flow behaviour index and consistency coefficient) of treated and untreated faba bean protein concentrate suspensions. The suitability of the common time-independent, rheological models, employed to fit the shear rate/shear stress data, has also been examined.

MATERIALS AND METHODS

Faba bean protein concentrates were prepared according to Baker *et al.* (1979) from faba bean powder suspension as described by Khalil and Yousif (2002). Samples of protein concentrates were dissolved in 0.1N NaoH solution to obtain a homogenous solutions as suggested by Muschiolik and Schmandke (2000).

Rheological properties of faba bean protein concentrates were determined using a coaxial rotational viscometer (Rheotest 2, MLW pruefgeratewerk Medingen, Germany) equipped with a temperature controlled circulating water bath. Shear rate and shear stress data were measured for each sample at concentrations, of 9, 12, 15 and 18% and at temperatures ranging from 30°C to 70°C.

The apparent viscosity of the concentrates at shear rates of 81 s^{-1} was calculated from the experimental values of shear stress at different concentrations and temperatures by dividing the shear stress by shear rate. Sometimes, specially when a broad range of shear rates is encountered, it becomes necessary to use more than one model to fit data and to know which models the samples fit (Ofoli, 1990). Thus, there are different models which describe the non-Newtonian behaviour of fluids (e.g. Power-law, Casson, and Herschel-Bulkley (HB) equations: 1, 2 and 3 respectively) as outlined:

$$\tau = K.\gamma^{n} \qquad (1)$$

$$\tau^{0.5} = \tau^{0.5} + K_{c}.\gamma^{0.5} \qquad (2)$$

$$\tau = \tau_{o} + K_{HB}.\gamma^{n} \qquad (3)$$

Where:-

τ = shear stress (dyne/cm^2); τ_o = yield stress (dyne/cm^2); γ = shear rate (s^{-1}); K = Coefficient of consistency (dyne. s^n/cm^2); K_c = coefficient of Casson viscosity (dyne. s/cm^2); K_{HB} = consistency coefficient of Herschel-Bulkley equation (dyne. s^n/cm^2) and n = flow behaviour index (dimensionless).

Equations 1 and 2 were employed to calculate the rheological parameters by using the linear regression according to SAS (1996), while for equation (3) a non-linear regression procedure was employed to estimate it constants as described by Rao *et al.* (1975).

The effect of temperature on the viscosities of the faba bean protein concentrates was described by the Arrhenius relationship (Tang *et al.*, 1993).

$$\eta = \eta_{o} \exp (Ea/RT) \qquad (4)$$

Where:

η is the viscosity (Pa. s); η_o (Pa. s) is the viscosity at infinite temperature; Ea is the activation energy of the flow (kJ/mol); R is the gas constant (kcal/mol. K) and T is the absolute temperature (K).

Hysteresis (Thixotropic) behaviour was calculated as mentioned by Charm (1978).

RESULTS AND DISCUSSION

Dynamic viscosity

Figs. 1 and 2 show typical examples for the relationship between dynamic (apparent) viscosity and shear rate of protein concentrate samples prepared from treated and untreated faba bean. The dynamic viscosity decreased with increase in shear rate and temperature. The dynamic viscosity of the protein concentrate showed a shear thining behaviour, as could be seen from the sample plot (Figs. 1 and 2). It is obviously that the dynamic viscosity of the tested samples was affected by both of shear rate and protein concentration. A decrease in apparent viscosity values was observed by change in the applied shear rates, particularly at low range (Figs. 1 and 2). With increasing of concentrattion, the increase in dynamic viscosity was observed for both treated and untreated protein concentrates.

The apparent viscosity was higher in autoclaved samples than the rest of other treatments including the untreated samples. However,at elevated temperature (70°C) an increase in apparent viscosity of protein concentrates has been observed (Fig. 2), which agree with the results found by Schwenke *et al.* (1990) as well as Liu and Hung (1998).

Rheological model

The shear rate/shear stress data were analysed to examine the extent of fitting by common rheological models such as Power law model, Casson model, and Herschel-Bulkley (HB) model. The results of such examination are included in Table (1) and could be summarized as follows:

Flow behaviour index (n) obtained by using the Power law model was low, whereas the HB model results in higher and more accurate values at all shear rates (Table 1). On the other hand, the HB model fits the data satisfactorily over the whole experimental range. The coefficient of determination (R^2) between the shear rate and shear stress ranged from 0.8986 to 0.9981; 0.7980 to 0.9992 and 0.9420 to 0.9997 for the Power law model, Casson model and HB model respectively. The suitability of the HB model, in comparison to other models, in representing shear rate / shear stress data of the protein concentrates, could be refered to the deduction of a definite values from the shear stress data, making the rest values be more accurate to match the applied shear rates. The deducted values represent the initial yield stress. The accuracy of the HB model for representing shear data of food suspensions has been reported by Bhattacharya and Bhat (1997).

Table (1): Rheological parameters of faba bean concentrate suspensions obtaind by application of different flow models.

Temp. (°C)	Raw faba bean protein concentrate																							
	Suspensions concentration (%)																							
	9						12						15						18					
	k	n	k_{HB}	n_{HB}	τ_{oHB}	τ_{oC}	k	n	k_{HB}	n_{HB}	τ_{oHB}	τ_{oC}	k	n	k_{HB}	n_{HB}	τ_{oHB}	τ_{oC}	k	n	k_{HB}	n_{HB}	τ_{oHB}	τ_{oC}
30°C	1.73	0.46	2.20	0.76	3.00	2.94	2.05	0.53	3.33	0.81	4.12	3.11	3.19	0.51	4.58	0.81	6.51	4.88	4.95	0.54	8.92	0.81	10.00	8.11
40°C	1.61	0.46	2.50	0.68	2.45	2.81	1.85	0.52	3.05	0.80	3.55	2.85	2.38	0.51	3.06	0.86	5.41	3.44	4.48	0.52	8.27	0.75	8.00	7.54
50°C	1.55	0.44	1.93	0.71	2.40	2.54	1.67	0.53	2.94	0.78	3.14	2.68	2.04	0.52	2.85	0.85	4.50	2.97	4.43	0.46	6.56	0.70	7.20	7.64
60°C	1.27	0.49	2.22	0.71	2.10	2.22	1.51	0.55	2.63	0.84	3.00	2.46	1.66	0.55	3.02	0.81	3.42	2.57	3.81	0.45	5.22	0.70	6.00	6.44
70°C	1.06	0.52	1.82	0.79	2.00	1.82	1.67	0.53	3.09	0.78	3.10	2.73	1.80	0.57	4.18	0.77	3.30	3.02	4.04	0.45	5.23	0.71	6.60	6.71
Soaked-germinated faba bean protein concentrate																								
30°C	9.44	0.44	11.05	0.72	17.00	15.94	19.65	0.44	19.94	0.62	16.50	23.08	144.15	0.28	95.92	0.37	53.00	156.59	341.57	0.35	341.57	0.35	0.00	450.65
40°C	8.24	0.42	8.14	0.72	15.00	13.61	18.96	0.41	16.64	0.60	16.50	22.51	113.62	0.31	102.67	0.33	13.30	136.66	297.98	0.36	297.98	0.36	0.00	400.85
50°C	7.44	0.40	6.76	0.71	13.22	12.04	18.61	0.38	14.99	0.57	16.00	22.53	99.81	0.33	99.81	0.33	0.00	121.62	226.63	0.41	226.63	0.41	0.00	291.06
60°C	6.85	0.37	5.67	0.68	11.20	11.06	17.47	0.37	13.89	0,57	15.00	21.08	108.68	0.34	108.68	0.34	0.00	134.49	236.80	0.41	236.80	0.41	0.00	303.10
70°C	6.65	0.36	6.01	0.64	10.00	11.00	18.50	0.35	14.67	0.53	15.00	22.76	115.36	0.34	115.36	0.34	0.00	136.09	253.94	0.40	253.94	0.40	0.00	360.81

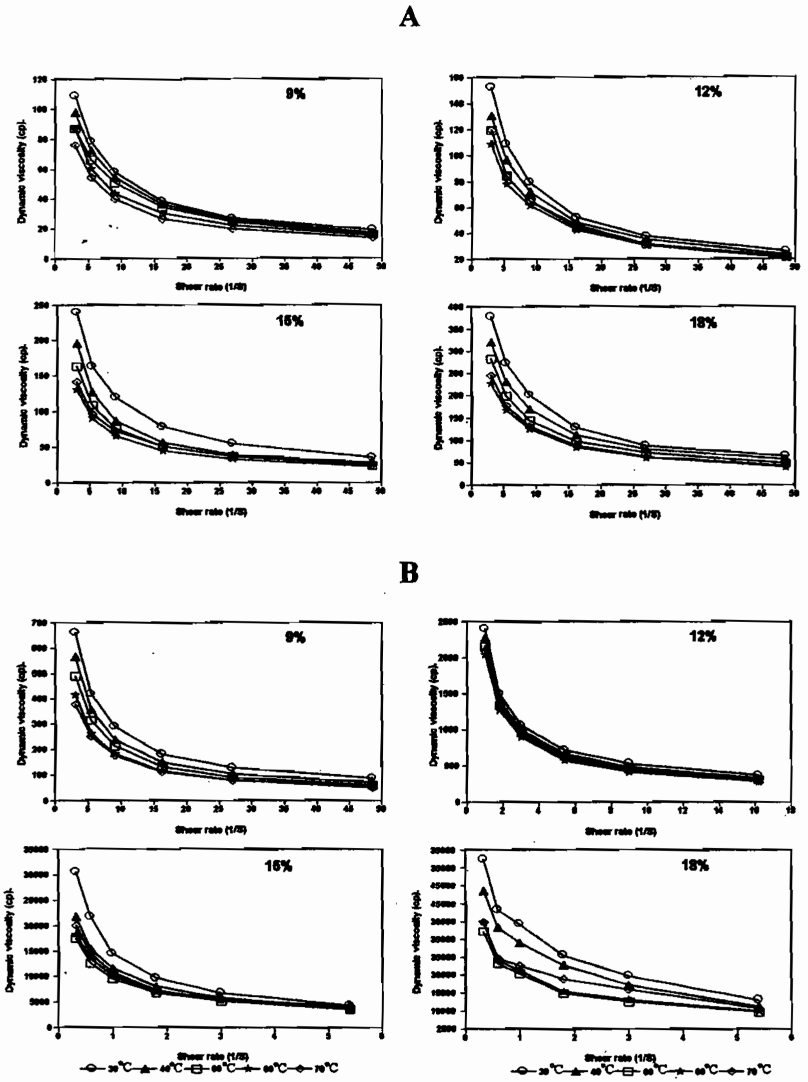

Fig.(1): Dynamic viscosity at different shear rates of faba bean protein concentrate suspensions prepared from: raw faba bean (A) and soaked and germinated faba bean (B).

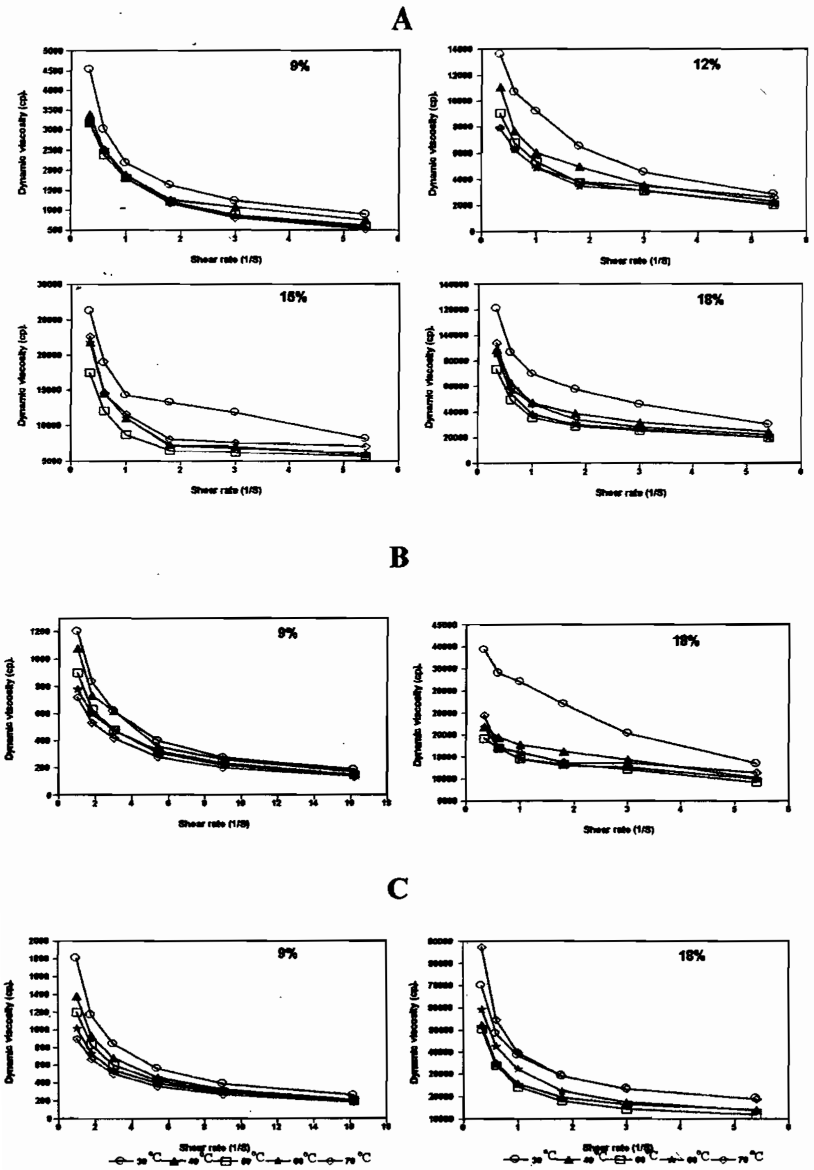

Fig.(2): Dynamic viscosity at different shear rates of protein concentrate suspensions prepared from autoclaved faba bean (A), microwaved faba bean for 3 min.(B) and 6 min. (C).

Yield stress (τ_o)

With increase in concentration, the yield stress of protein concentrates was markedly higher (Table 1), suggesting that the concentrated samples offer more resistance when the flow is initiated. The yield stress values of the specimens calculated by using a Casson model (equ. 2) ranged between 1.82 and 513.16 dyne/cm^2 for 9% and 18% concentrations, respectively indicating that the calculated values are much higher than the ones obtained from HB model (0 to 341.57 dyne/cm^2). It's recommended, therefore that the Casson model should not be used to calculate the yield stress of protein concentrates. For autoclaved faba bean protein concentrates, there were no yield stress values observed by using HB model and the same trend was noticed for microwaved (3 and 6 min.) samples specially at 15 and 18% concentrations.

Flow behaviour and consistency index

The untreated and treated faba bean protein concentrates exhibit a distinctly pseudoplastic behaviour, as reflected by the flow behaviour index (Table 1) which has values lower than 0.57 and for those calculated according to the Power law model the n-values ranged between 0.31 and 0.57. According to the HB model, the n-values layed between 0.32 and 0.84 which were higher than those calculated from Power law model.

It is worth mentioning that the magnitude of the flow behaviour index depends on the model employed; e.g., the HB model yields higher values than the Power law model. This is due to the existence of a yield stress term in the HB model, so that the HB model predicts a lesser pseudoplastic nature of the suspensions.

The consistency coefficient (k) obtained according to Power law model was in the range of 1.06 to 780.37 dyne.s^n/cm^2 for faba bean protein concentrate samples (Table 1). The same observation was notified for HB model. The k-values were more sensitive to solid concentration, and an increase in solid level markedly increases the consistency values. The k-values were the highest in autoclaved faba bean protein concentrates of 18% which recorded 780.37 dyne. s^n/cm^2 compared with other treated or untreated samples.

Activation energy:

Table (2) represents the values of activation energy (Ea) calculated according to Arrhenius equation (equ. 4). Results showed that the effect of temperature on the viscosity data of faba bean protein concentrates could be divided into two different phenomena according to the concentrations. At medium concentration (9% and 12%) the Ea-values of the concentrate samples prepared from treated faba beans were higher than those of raw untreated beans, which reflect the effect of the treatments on the conformation and structure of protein molecules.

Table (2): Arrhenius-type parameters relating the effect of temperature on apparent viscosity of faba bean protein concentrates.

Treatment	Raw (control)	Soaking-	Autoclaving	Microwaving	
Parameters		Germination		3 min.	6 min.
	Concentration of faba bean protein concentrate				
		9%			
η_o	1.52×10^{-2}	1.07×10^{-3}	6.0×10^{-3}	6.63×10^{-3}	5.51×10^{-3}
Ea	5.96	16.65	14.07	12.14	13.39
R^2	0.9998	0.9965	0.9981	0.9979	0.9182
		12%			
η_o	9.17×10^{-3}	6.58×10^{-3}	2.55×10^{-2}	5.86×10^{-3}	6.17×10^{-3}
Ea	8.36	13.98	12.77	15.45	16.14
R^2	0.9937	0.9958	0.9769	0.9144	0.9405
		15%			
η_o	6.79×10^{-4}	4.05×10^{-1}	2.19×10^{-1}	1.45×10^{-1}	1.95×10^{-1}
Ea	15.77	6.78	10.35	11.52	10.90
R^2	0.9626	0.9839	0.8325	0.9868	0.8437
		18%			
η_o	4.05×10^{-4}	9.57×10^{-1}	2.70×10^{-1}	4.87×10^{-1}	4.80×10^{-1}
Ea	18.65	7.46	12.81	9.20	11.07
R^2	0.9941	0.9995	0.9976	0.9576	0.9013

On other side, an opposite behaviour has been observed with samples containing higher protein concentration (15% and 18%), where the Ea-values of the concentrates prepared from raw untreated faba beans were higher than those prepared from the treated beans. The reason for such change in behaviour could be refered, as described by Tang *et al.* (1993), to the interference between the protein molecules at such high concentration, so that extension and mobility of the molecules becomes more restricted than in the suspensions with moderate concentrations.

Values of the activation energy (Ea) ranged between 5.96 and 18.65 KJ/mol for the different tested samples of protein concentrates. The Ea-values obtained in the present work agree with those of Ibarz and Sintes (1989), as well as Tang *et al.* (1993).

η_o-values in equation (4) are constants expressing the rate of collosion between the molecules and, in turn, the apparent viscosity (η_o) at an infinite high temperature. η_o increases with increasing concentration, e.g., being 5.5×10^{-3} and 4.8×10^{-1} Pa.s for 9% and 18% microwaved (6 min) faba bean protein concentrates respectively. As seen from Table (2), the higher the η_o-values, the lower are the corresponding values of Ea, which reflect the dependence of the activation energy needed to reduce the viscosity of a specimen on the intensity of collosion between the molecules.

Combined effect of concentration and temperature

Calculated parameters for the combined effect of concentration and temperature on viscosity of faba bean protein concentrates were as follows:

Raw protein concentrate: $\eta = -0.0378 + 0.0417\,C - 0.0055\,T$

Soaked-germinated protein concentrate: $\eta = -15.2846 + 1.7650\,C - 0.0599\,T$

Soaked-germinated and autoclaved protein concentrate: $\eta = -30.9809 + 3.9142\,C - 0.2060\,T$

Soaked-germinated and microwaved (3min.) protein concentrate: $\eta = -14.1285 + 1.9556\,C - 0.1052\,T$

Soaked-germinated and microwaved (6 min.) protein concentrate: $\eta = -29.3151 + 3.6698\,C - 0.1836\,T$

The coefficient of determination for this combined relationship was adequate, since the R^2-values were in the range of 0.8132 to 0.9264. These results agree with those reported by Ibarz and Sintes (1989) where R^2- values of the determination were in the range of 0.70.

Hysteresis phenomenon

Hysteresis expressed the difference in the shear stress values between the ascending and descending shear data of the samples of faba bean protein concentrates. Hysteresis values of faba bean protein concentrates were found to increase by increasing concentration and to decrease by increased temperature. For example, a 9% concentration of autoclaved faba bean protein concentrate showed a hysteresis value of 26.39 dyne/cm^2 at 30°C compared with 710.04 dyne/cm^2 for the 18% of corresponding sample. On other side, a 15% concentration pretreated by microwaving (6 min.) showed hysteresis values of 759.51 and 139.68 dyne/cm^2 at 30° and 70°C respectively, which agree with the results presented by Puppo and Anon (1999).

REFERENCES

Baker, E.C.; G.C. Mustakas and K.A. Warner (1979). Extraction of defatted soybean flours and flakes with aqueous alcohols: Evaluation of flavour and selected properties. J. Agric. Food Chem., 27:969-973.

Bhattacharya, S. and K.K. Bhat (1997). Steady shear rheology of rice-blackgram suspensions and suitability of rheological models. J. Food Engineering, 32:241-250.

Charm, S.E. (1978).The fundamentals of food engineering (3rd), AVI Publishing Co. Westport, Connecticut pp. 171-176.

Ibarz, A. and J. Sintes (1989). Rheology of egg yolk. J. Texture Studies, 20: 161-167.

Khalil, H.I. and E.I. Yousif (2002). Applicability of rheological models to estimate the flow behaviour of faba bean flour suspensions. Misr J. Agric. Engineering, 19: 799-811.

Liu, L..H. and T.V. Hung (1998). Flow properties of chickpea proteins. J. Food Science, 63: 229-233.

Muschiolik, G. and H. Schmandke (2000). Functional properties of faba bean products. p. 144. Schaker Publishing, Aachen, Germany.

Ofoli, R.Y. (1990). Interrelations of rheology, kinetics and transport phenomena in food processing. In "Dough Rheology and Baked Product Texture" eds. Faridi H. and J.M. Faubion, pp. 497-512. Van Nostrand Reinhold, New York.

Paulson, A.T. and M.A. Tung (1988). Rheology and microstructure of succinylated canola protein isolate. J. Food Science, 53:821-825.

Puppo, M.C. and M.C. Anon (1999). Soybean protein dispersions at acid pH. Thermal and rheological properties. J. Food Science, 64:50-56.

Rao, V.N.M.; D.D. Hamann and E.G. Humphries (1975). Flow behaviour of sweet potatoes puree and its relation to mouthfeel quality. J. Texture Studies, 6:197-209.

Rha, C.K. and P.Pradipasena (1986). Functional properties of food macromolecules. eds. Mitchell J.R. and D.A. Lederward, p. 79 Elsevier Applied Science Publishers, London.

SAS (1996). Statistical Analysis System. SAS user's guide: Statistics. SAS institute inc. editors, Cary, NC, USA.

Schmidt, G. and H. Schmandke (1987). On the viscosity behaviour of field bean protein isolates in dependence on their degree of acetylation. Die Nahrung, 31:809-815.

Schmidt, G.; H. Schmandke and R. Schoettel (1986). Viscosity behaviour of Vicia faba protein isolates and their acetylated derivatives. Acta Alimentaria, 15:175-186.

Schneider, CH; G. Muschiolik; M. Schultz and H. Schmandke (1986). The infleuence of process conditions and acetylation on functional properties of protein isolates from broad beans. Die Nahrung, 30:429-431.

Schwenke, K.D.; L. Prahl; A.N. Danilenko; V.J. Grinberg and V.B. Tolstoguzov (1990). Continuous conformational change in succinylated faba bean protein isolates. Die Nahrung, 34: 399-401.

Tang, Q.; P.A. Munro and O.J. McCarthy (1993). Rheology of whey protein concentrate solutions as a function of concentration, temperature, pH and salt concentration. J. Dairy Research, 60:349-361.

السلوك الريولوجى لمركزات بروتين الفول البلدى

هانى ادريس خليل – السيد ابراهيم يوسف

قسم علوم الاغذية – كلية الزراعة – جامعة عين شمس – شبرا الخيمة – القاهرة

استهدف البحث دراسة خصائص السريان لمركزات بروتين الفول البلدى باستخدام جهاز اللزوجة الاسطوانى الدورانى اللامركزى باجراء بعض المعاملات المبدئية على الفول البلدى (النقع – الانبات) وكذلك بعض المعاملات الحرارية المختلفة (التعقيم والمعاملة بالموجات القصيرة جدا) ومدى تأثر خواص القوام بكل من التركيزات (٩، ١٢، ١٥، ١٨%) ودرجات الحرارة (٣٠°، ٤٠°، ٥٠°، ٦٠°، ٧٠°م). واوضحت النتائج المتحصل عليها ان مركزات البروتين سلكت سلوكا لانيوتونيا من نوع شبيهات البلاستيك وكانت قيم اللزوجة اعلى فى العينات المعاملة حراريا مقارنة بمركزات الفول البلدى غير المعاملة وكذلك المعاملة بالنقع والانبات.

وحدث زيادة لا اسية لكل من اللزوجة ومعامل القوام والجهد الابتدائى للسريان بزيادة التركيز وانخفاض القيم المتحصل عليها مع زيادة درجة الحرارة حتى ٦٠°م، وعند ٧٠°م حدث تأثير عكسى حيث ازدادت القيم نتيجة للتغير الحادث فى تركيب جزئ البروتين. وكانت قيم الطاقة التنشيطية المحسوبة من معادلة ارهينيوس فى المدى من ٥,٩٦ الى ١٨,٦٥ كيلو جول/مول. وتم استخدام العديد من النماذج الريولوجية المختلفة للتعرف على مدى ملاءمتها لمركزات بروتين الفول البلدى، ووجد ان انسب نموذج هو نموذج هيرشل بلكلى لوصف سلوك السريان. وتم استنباط معادلة للتنبؤ بالتأثير المشترك لكل من التركيز ودرجة الحرارة وعلاقته باللزوجة للعينات المختبرة واوضحت معامل ارتباط جيد ويمكن اخذها فى الاعتبار فى عمليات التصنيع المختلفة لمركزات بروتين الفول البلدى.