Nauka Przyroda Technologie

2012
Tom 6
Zeszyt 4

ISSN 1897-7820 http://www.npt.up-poznan.net
Dział: Nauki o Żywności i Żywieniu

JOLANTA GAWAŁEK[1], PIOTR WESOŁOWSKI[2]

[1]Institute of Food Technology of Plant Origin
Poznań University of Life Sciences
[2]Institute of Chemical Technology and Engineering
Poznań University of Technology

EXAMINATION OF RHEOLOGICAL PROPERTIES OF AQUEOUS SOLUTIONS OF SODIUM CASEINATE

BADANIE WŁAŚCIWOŚCI REOLOGICZNYCH WODNYCH ROZTWORÓW KAZEINIANU SODU

Summary. Application of sodium caseinate as a functional additive in manufacturing processes requires production of its concentrated aqueous solutions which, in industrial conditions, presents a number of difficulties. In order to develop an effective and optimal industrial process of mixing – manufacturing a concentrated solution of sodium caseinate, it is essential to know rheological properties in a definite range of concentrations changing in the course of the dissolving process. The material for investigations was typical commercial sodium caseinate in the form of dry powder manufactured in Poland from acid casein using the method of extrusion. The objective of the undertaken empirical studies was the assessment of the impact of the concentration on rheological properties of sodium caseinate concentrates. Investigations were carried out for five concentrates manufactured in a mixer equipped in a mechanical agitator at concentrations ranging X (%) $\in$ (2.5÷12.5) and changing mass proportions of sodium caseinate in the aqueous solution as follows: G_S/G ($kg_S \cdot kg^{-1}$) = 0.025. On the basis of the obtained research results, classical flow curves were plotted for individual concentrates. The determined values of viscosity and density of the examined solutions were correlated in the form of $\eta = f(G_S/G)$ and $\rho = f(G_S/G)$ dependencies which were used during the determination of classical characteristics of mixing forces essential for the assessment of energetic expenditures required to manufacture concentrates in a mixer equipped in a mechanical agitator. The density of the examined concentrates increased in a way directly proportional, while the dynamic viscosity coefficient increased exponentially together with the increase of sodium caseinate concentration. Sodium caseinate concentrates exhibited Newtonian character in the examined range of concentrations.

Key words: sodium caseinate concentrates, rheology, density, viscosity

Introduction

Due to its specific properties (emulsification capability, emulsion stabilisation, foam producing capability and water absorption), sodium caseinate finds frequent application in meat-delicatessen, baking and confectionary industries in production of food and pharmaceutical articles, beverages, as well as various dietary products (VEGA and ROOS 2006, SZPENDOWSKI et AL. 2010). The application of sodium caseinate as a functional additive in production processes most frequently requires preparation of its concentrated aqueous solutions which presents certain difficulties in industrial practice. In order to design an effective and optimal industrial process of mixing – manufacturing a concentrated solution of sodium caseinate, it is indispensible to know rheological properties in a definite range of concentrations changing in the course of the dissolving process. LOVEDAY et AL. (2010) described colloidal glass behaviour sodium ceseinate dispersions with concentration > 23%. Area of interest in this paper was rheological behaviour of sodium caseinate solutions of the concentrate range < 15%.

Materials and methods

The material for investigations was typical commercial sodium caseinate in the form of dry powder manufactured in Poland from acid casein with the assistance of the extrusion method.

The objective of the undertaken empirical studies was the assessment of the impact of the concentration on rheological properties of sodium caseinate concentrates. Investigations were carried out for five concentrates manufactured in a mixer equipped in a mechanical agitator at concentrations ranging X (%) $\in$ (2.5÷12.5), changing mass proportions of sodium caseinate in the aqueous solution as follows: G_S/G ($kg_S \cdot kg^{-1}$) = 0.025.

Sodium caseinate concentrates were manufactured at the Institute of Chemical Technology and Engineering of Poznań University of Technology on a general purpose stand for investigations of mixing processes in multiphase systems.

During the first stage of experimental investigations on the physical properties of sodium caseinate concentrates density ρ ($kg \cdot m^{-3}$) measurements were carried out using for this purpose an aerometer.

In the second stage of studies, runs of classical flow curves were determined linking the recorded shear stress τ ($N \cdot m^{-2}$) with the applied rate of shear γ (s^{-1}) at definite concentrations of sodium caseinate concentrates X (%).

The described experiments were performed at the Institute of Food Technology of Plant Origin of Poznań University of Life Sciences using a rotational-oscillating rheometre DSR 500 (*Dynamic Stress Rheometer*) of Rheometric Company with controlled stress and rate of shear. The basic parts of the rheometre (Fig. 1) included: power transmission system, optical sensor, air bearing and measuring system. The head of the rotational-oscillating rheometre with controlled stress (Fig. 1) transfers the regulated rotational moment, consequently – the controlled stress, on to the torsion bar of the rheometre and measures the induced deformation (PRUSKA-KĘDZIOR et AL. 2003).

Gawałek J., Wesołowski P., 2012. Examination of rheological properties of aqueous solutions of sodium caseinate. Nauka Przyr. Technol. 6, 4, #80.

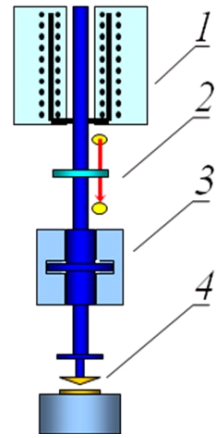

Fig. 1. Diagram of a rotational--oscillating rheometre: 1 – power transmission system, 2 – optical sensor, 3 – air bearing, 4 – measuring system
Rys. 1. Schemat reometru rotacyjno-oscylacyjnego: 1 – układ napędowy, 2 – czujnik optyczny, 3 – łożysko powietrzne, 4 – układ pomiarowy

The rotational moment is induced by an electronically controlled induction motor. The appropriate internal control and temperature compensation of the motor guarantee accuracy of the transferred tangential strain. The optical sensor which consists of a light source and a photocell divided by two diffraction partitions is situated below the drive system. The diffraction partitions produce two independently running light beams: internal which determines the absolute position of the torsion bar of the rheometre and external which determines its relative position (torsion angle of the bar).

The head of the rheometre is supported by the air bearing which minimises mechanical resistance and ensures the transfer of the induced rotational moment almost without loss. Residual resistance and inertia effects are corrected by internal software. The measuring system is made up of two parts. The upper part is combined with the torsional bar, whereas the bottom, stationary part of the measuring system is built into the base of the rheometre.

Prior to each measurement, the inertia of the measuring system was determined. Rheometre calibration took place automatically on the basis of the measurement of absolute forces. The measuring system was thermostated with the accuracy of ±0.1°C using the Peltier effect. The setting of the measuring gap took place automatically. Calculations of individual parameters were carried out with the assistance of internal algorithms constituting part of the software of the rheometre.

A cone-plate type measuring system was employed in which the cone diameter was 40 mm, the angle of the element of the cone – 0.4 rad and the size of the measuring gap between the cone and plate – 0.0559 mm.

Equilibrium flow curves were determined for all the examined samples. In the course of measurements, samples were sheared in conditions of controlled shearing rate performing the SRS test (*Steady Rate Sweep*). Sampling conditions of measuring points were determined in the course of preliminary investigations. The rest time between consecutive measurements was established at 10 s, whereas the measuring time amounted to 30 s. If the equilibrium time in the examined sample at the set shearing rate was reached at the time interval shorter than the assumed one, the measured values were

recorded automatically and the consecutive shearing rate was measured. Values of the shearing rate were changed in a logarithmic mode measuring 20 points per decade.

Measurement data acquisition took place in real time which allowed current control of the course of individual flow curves plotted in the form of $\tau = f(\log \dot{\gamma})$ (Fig. 3 a) as well as $\tau = f(X)$ dependence (Fig. 3 b) on the screen of the auxiliary computer.

The applied rheometre made it possible, for all concentrates (X = const) at the step change of shear at the range of $\dot{\gamma} \in (10 \div 501)$, to record shear stress within $\tau \in (0 \div 60)$ limits.

Results and discussion

The obtained density measurement results presented in Figure 2 were described by the following dependence:

$$\rho = 1158.4 \cdot X + 917.4 \tag{1}$$

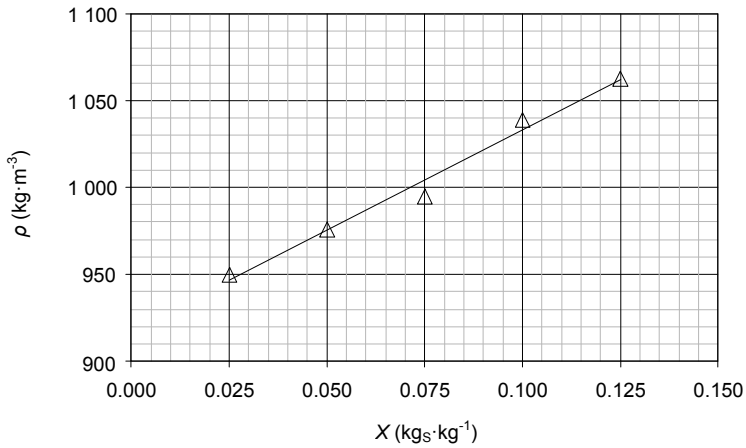

Fig. 2. Diagram of the dependence of density on the concentration of sodium caseinate concentrates
Rys. 2. Wykres zależności gęstości od stężenia koncentratów kazeinianu sodu

Equation (1) describes experimentally obtained measurement points characterised by scatter smaller than ±2%.

Flow curves determined for individual sodium caseinate concentrates were presented in Figure 3 a in the form of $\tau = f(\log \dot{\gamma})$ dependence and in Figure 3 b – in the form of $\tau = f(X)$ dependence.

The obtained empirical results are illustrated in Figure 4 in the form of the following dependence:

$$\tau = f(\dot{\gamma}, X) \tag{2}$$

Gawałek J., Wesołowski P., 2012. Examination of rheological properties of aqueous solutions of sodium caseinate. Nauka Przyr. Technol. 6, 4, #80.

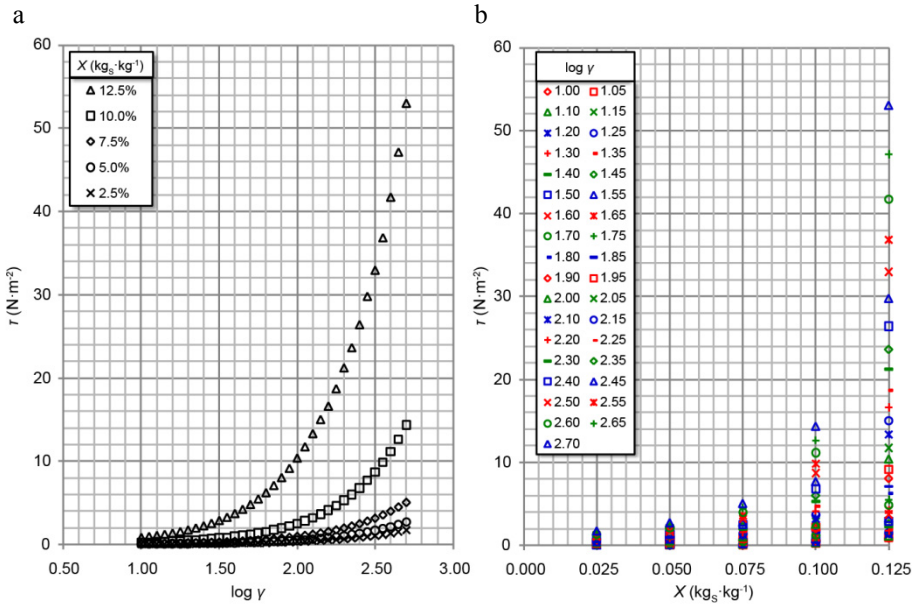

Fig. 3. Comparison of the run of the experimental dependences: a – $\tau = f(\log \gamma)$ for X = const, b – $\tau = f(X)$ for $\log \gamma$ = const

Rys. 3. Porównanie przebiegu zależności doświadczalnych: a – $\tau = f(\log \gamma)$ dla X = const, b – $\tau = f(X)$ dla $\log \gamma$ = const

The presented experimental results (Fig. 4) show unequivocally that the recorded tangential strains τ increased both with the increase of the shearing rate γ, as well as with the increase in the mass proportion of sodium caseinate X in the examined concentrates.

On the basis of the presented research results, an attempt was made to determine the rheological nature of the examined sodium caseinate concentrates. For this purpose, rheological parameters occurring in the Ostwald – de Waele equation (KEMBŁOWSKI 1973) were determined for all measurement series obtained experimentally:

$$\tau = K \cdot \gamma^n \tag{3}$$

Values of consistence coefficient K ($N \cdot s^n \cdot m^{-2}$) determined using the regression method and the characteristic flow index n, found in equation (3) were illustrated in Figure 5 depending on concentrations of the examined sodium caseinate concentrates.

The results obtained in the experiment (Fig. 5) confirmed clearly the increase of the consistence coefficient K occurring in equation (3) together with the increase in concentrations of the examined sodium caseinate concentrates. However, first and foremost, the discussed results show that the characteristic flow index was constant and very close to the value of n = 1 for all the examined concentrates which makes it possible to put forward a thesis that, within the examined range of concentrations, the sodium caseinate

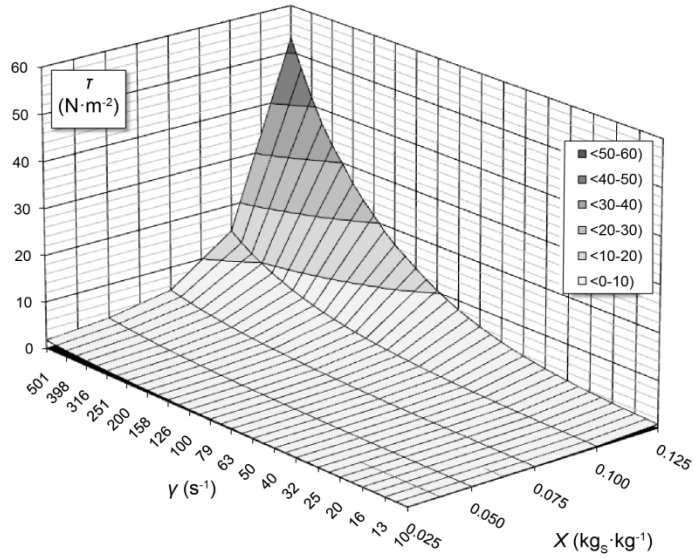

Fig. 4. Diagram of the dependence of tangential strains on the shearing rate at definite concentrations of sodium caseinate concentrates
Rys. 4. Wykres zależności naprężeń stycznych od prędkości ścinania przy określonych stężeniach koncentratów kazeinianu sodu

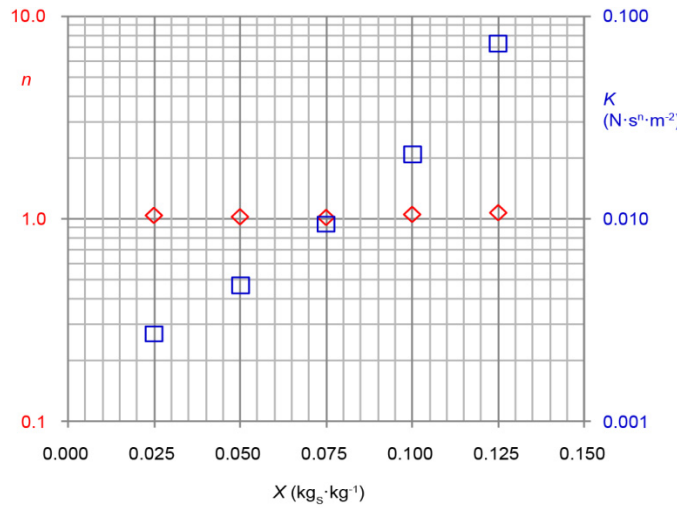

Fig. 5. Diagram of the dependence of consistence coefficient K and the characteristic flow index n, found in equation (3), at definite concentrations of sodium caseinate concentrates
Rys. 5. Wykres zależności współczynnika konsystencji K i wskaźnika płynięcia n, wyznaczonych z równania (3), przy określonych stężeniach koncentratów kazeinianu sodu

concentrates exhibited a character complying with the classical Newton model equation (FERGUSON and KEMBŁOWSKI 1995):

$$\tau = \eta \cdot \gamma \tag{4}$$

In order to corroborate the thesis about the Newtonian nature of the examined sodium caseinate solutions, the dynamic viscosity coefficient η occurring in equation (4) was calculated which – for concentrates of a definite concentration – should be constant in the entire range of the shearing rate γ.

Figure 6 presents the dependence of dynamic viscosity coefficients calculated on the basis of equation (4) for all the examined sodium caseinate concentrates. The obtained results confirmed a relative stability of this parameter in the entire examined range of shearing range variability for the concentrates of a defined concentration which corroborates the possibility of adopting Newtonian nature.

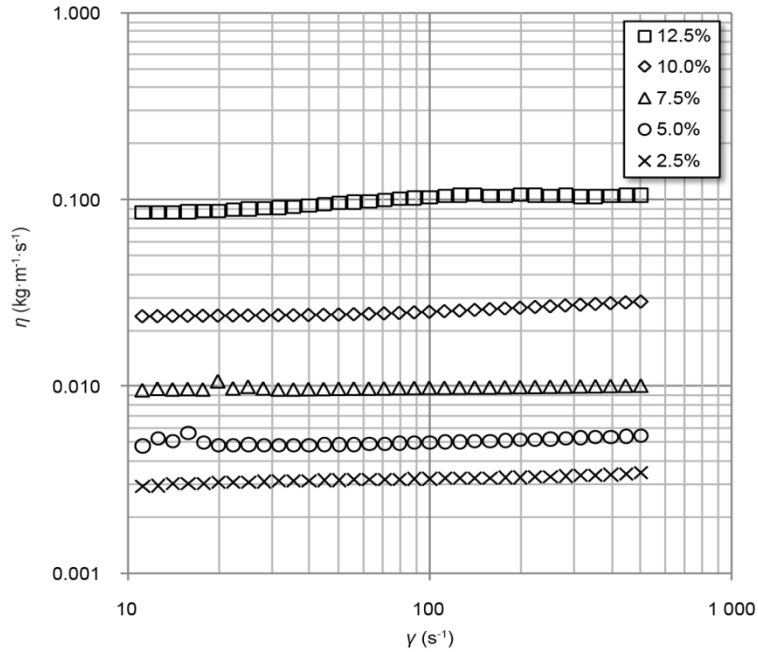

Fig. 6. Diagram of the dependence of the dynamic viscosity coefficient on the shearing rate at definite concentrations of sodium caseinate concentrates
Rys. 6. Wykres zależności dynamicznego współczynnika lepkości od prędkości ścinania przy określonych stężeniach koncentratów kazeinianu sodu

The dependence of the calculated mean values of dynamic viscosity coefficients on the concentration of all the examined sodium caseinate concentrates is shown in Figure 7. Following the performed regression calculus, the dependence presented in Figure 7 was described by the regression:

$$\eta = 1.3 \cdot 10^{-3} \cdot e^{33.9X} \tag{5}$$

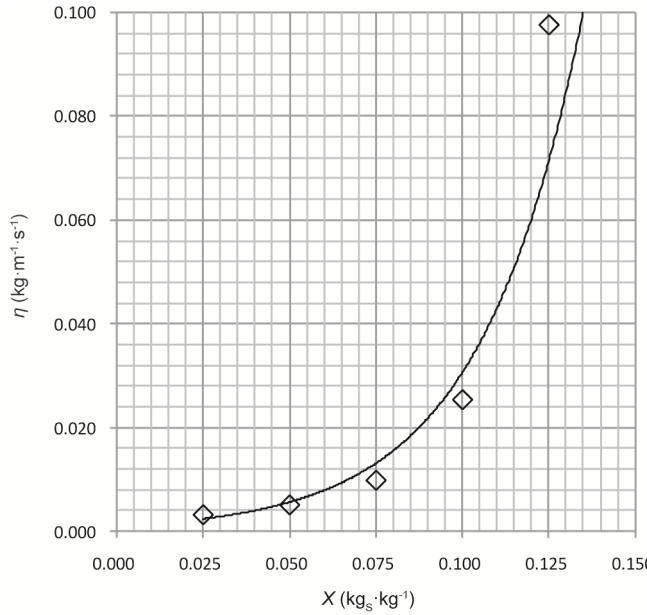

Fig. 7. Diagram of the dependence of the dynamic viscosity coefficient on the concentration of sodium caseinate concentrates
Rys. 7. Wykres zależności dynamicznego współczynnika lepkości od stężenia koncentratów kazeinianu sodu

Equation (5) describes correlated experimental points with a scatter not exceeding ±15%.

Conclusions

1. Density of the examined concentrates increased in direct proportion to the concentration increase of sodium caseinate (equation (1), Fig. 2).

2. Sodium caseinate concentrates exhibited a Newtonian nature within the examined range of concentrations (equation (4), Fig. 5).

3. Dynamic viscosity coefficient increased exponentially with the increase of sodium caseinate concentration (equation (5), Fig. 7).

4. The obtained regression dependences describing the density and dynamic viscosity coefficient of the examined sodium caseinate concentrates were utilized to verify classical strength characteristics of the applied mixers. The thesis that the application of an agitator pumping the mixed system up reduces energy expenditure required to carry out the process of solubilizing sodium caseinate in water in comparison with the agitator pumping it down put forward on the basis of observations made in the course of the performed experiments was corroborated.

Gawałek J., Wesołowski P., 2012. Examination of rheological properties of aqueous solutions of sodium caseinate. Nauka Przyr. Technol. 6, 4, #80.

References

FERGUSON J., KEMBŁOWSKI Z., 1995. Reologia stosowana. Marcus, Łódź.

KEMBŁOWSKI Z., 1973. Reometria płynów nienewtonowskich. WNT, Warszawa.

LOVEDAY S.M., RAO M.A., CREAMER L.K., SINGH H., 2010. Rheological behavior of high-concentration sodium caseinate dispersions. J. Food Sci. 75, 2: N30-N35.

PRUSKA-KĘDZIOR A., LEFEBVRE J., KĘDZIOR Z., 2003. Zastosowanie metod reologicznych w technologii żywności i biotechnologii. In: Metody pomiarów i kontroli jakości w przemyśle spożywczym i biotechnologii. Eds. M. Jankiewicz, Z. Kędzior. Wyd. AR, Poznań: 433-499.

SZPENDOWSKI J., SZYMAŃSKI E., STANIEWSKI B., BOHDZIEWICZ K., 2010. Właściwości ekstruzji. Żywn. Nauka Technol. Jakość 69, 2: 62-75.

VEGA C., ROOS Y.H., 2006. Invited review: spray-dried dairy and dairy-like emulsions-compositional considerations. J. Dairy Sci. 89, 2: 383-401.

BADANIE WŁAŚCIWOŚCI REOLOGICZNYCH WODNYCH ROZTWORÓW KAZEINIANU SODU

Streszczenie. Zastosowanie kazeinianu sodu jako dodatku funkcjonalnego w procesach produkcyjnych najczęściej wymaga wytworzenia jego skoncentrowanych wodnych roztworów, co w praktyce przemysłowej nastręcza pewne trudności. W celu zaprojektowania skutecznego i optymalnego przemysłowego procesu mieszania – wytwarzania skoncentrowanego roztworu kazeinianu sodu konieczna jest znajomość właściwości reologicznych w określonym zakresie stężeń, zmieniających się w procesie rozpuszczania. Materiał do badań stanowił typowy, handlowy kazeinian sodowy w postaci suchego proszku, produkowany w Polsce z kazeiny kwasowej metodą ekstruzji. Celem podjętych badań doświadczalnych była ocena wpływu stężenia na właściwości reologiczne koncentratów kazeinianu sodu. Badania wykonano dla pięciu koncentratów, wytworzonych w mieszalniku z mechanicznym mieszadłem, w zakresie stężeń X (%) $\in$ (2,5÷12,5), zmieniając udział masowy kazeinianu sodu w wodnym roztworze z krokiem G_S/G ($kg_S \cdot kg^{-1}$) = 0,025. Na podstawie wyników badań wykreślono klasyczne krzywe płynięcia dla poszczególnych koncentratów. Wyznaczone wartości lepkości i gęstości badanych roztworów skorelowano w formie zależności $\eta = f(G_S/G)$ i $\rho = f(G_S/G)$, które wykorzystano podczas wyznaczania klasycznych charakterystyk mocy mieszania niezbędnych do oceny nakładów energetycznych ponoszonych na wytwarzanie koncentratów w mieszalniku z mechanicznym mieszadłem. Gęstość badanych koncentratów wzrasta wprost proporcjonalnie, natomiast wartość dynamicznego współczynnika lepkości wzrasta wykładniczo wraz ze wzrostem stężenia kazeinianu sodu. Koncentraty kazeinianu sodu w badanym zakresie stężeń wykazują charakter newtonowski.

Słowa kluczowe: koncentraty kazeinianu sodu, reologia, gęstość, lepkość

Corresponding address – Adres do korespondencji:
Jolanta Gawałek, Instytut Technologii Żywności Pochodzenia Roślinnego, Uniwersytet Przyrodniczy w Poznaniu, ul. Wojska Polskiego 31/33, 60-624 Poznań, Poland, e-mail: jolgaw@up.poznan.pl

Accepted for print – Zaakceptowano do druku:
5.09.2012

For citation – Do cytowania:
Gawałek J., Wesołowski P., 2012. Examination of rheological properties of aqueous solutions of sodium caseinate. Nauka Przyr. Technol. 6, 4, #80.