

STEADY-STATE VISCOSITY OF THE LIQUID TWO-PHASE DISPERSE SYSTEM WATER-CASEIN-SODIUM ALGINATE

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ABSTRACT

The steady-state viscosity (η^) of the liquid two-phase disperse system water-casein-sodium alginate of varying composition, with a disperse particle diameter of about $30\text{ }\mu\text{m}$, has been investigated in the shear rate range $\dot{\gamma} = 10^{-2}$ – 10^7 s^{-1} . The flow curves obtained are similar in shape. They are invariant in composition and can be fitted to the flow curve equation ($\eta^*/\eta_0^* = f(k\dot{\gamma})$) where η_0^* is the Newtonian viscosity obtained from data at low shear stresses and k is an empirical parameter. Both η_0^* and k depend on the composition of the two-phase system.*

The experimental dependence of the viscosity on the composition follows a logarithmic additivity law at high shear stresses, but at low shear stresses the observed viscosities are lower than would be predicted by this law. The experimental dependence of the ratio k/η_0^ (the mean activation volume) on the composition is also not in agreement with the additivity law. These special features of the steady-state flow of the investigated disperse system are explained by the presence of a low-concentration interphase layer having a lower viscosity and less pronounced non-Newtonian behaviour than the disperse and continuous phases. This interphase layer exists in other two-phase systems which consist of a solvent and two incompatible polymers. For this reason, the rheological behaviour of the system investigated may be expected to be common for two-phase systems of this type, particularly protein-polysaccharide mixtures in water.*

NOMENCLATURE

- 1 protein phase
- 2 polysaccharide phase

3	interphase layer
a	parameter characterising the interphase layer thickness
A	sodium alginate
A'	pre-exponential factor in the Frenkel-Eyring equation
$[A]_2$	sodium alginate weight concentration in the polysaccharide phase
$[A]_3$	mean sodium alginate weight concentration in the interphase layer
B	parameter taking into account the effect of the interphase layer on the disperse system viscosity
C	casein
$[C]_1$	casein weight concentration in the protein phase
$[C]_3$	casein weight concentration in the interphase layer
D	parameter taking into account the effect of the interphase layer on the mean activation volume of the disperse system
E^*	activation energy for viscous flow of the disperse system
E_i	activation energy for viscous flow of the i -phase
k	shear rate reduction parameter
W	water
y_i	effective volume fraction of the i -phase in the equivalent three-phase system 1-2-3
β	RT (gas constant \times temperature)
$\dot{\gamma}$	shear rate
$\tilde{\gamma}$	disperse rate reduction parameter
η^*	steady-state disperse system viscosity
$\tilde{\eta}^*$	reduced viscosity of the disperse system
η_i	viscosity of the i -phase
$\eta_{i,0}$	initial viscosity of the i -phase
η_0^*	initial viscosity of the disperse system
θ	characteristic relaxation time
θ^*	characteristic relaxation time of the disperse system
θ_i	characteristic relaxation time of the i -phase
τ	shear stress
τ'	shear stress satisfying the condition $B = 0$
ϕ_i	volume fraction of the i -phase in the disperse system 1-2
ω	activation volume
ω^*	mean activation volume of the disperse system

1. INTRODUCTION

Spinneretteless (matrix) spinning is a new approach to the problem of food protein texturisation. This method of spinning is based on the development of an anisotropic structure from a flowing two-phase disperse system consisting of protein, poly-

saccharide and water. As a result of the rapid gelation of one or both phases the emulsion is converted into a two-phase anisotropic gel. The gel is a system of anisodiametrical, gel-shaped, disperse particles (microfibrils) located parallel to one another in the gelatinous disperse phase. The texture of these anisotropic gels resembles muscle tissue and, thus, they can form the basis of meat analogues (Tolstogusov, 1978; Antonov *et al.*, 1980). The two-phase disperse system, water (W)-casein (C)-sodium alginate (A), is one of those capable of anisotropic gel formation. Ionotropic gelation by the action of Ca^{2+} and H^+ ions is used in this case. The anisotropic gels produced using this system, have a number of good functional properties (Antonov *et al.*, 1981) which makes them of interest in simulated meat technology. Because of the technological value of this system a detailed investigation of its rheological properties was undertaken. This paper reports the results of investigations of variations in the steady-state viscosity of this system over wide ranges of shear rates and protein phase volume fractions. The dependence of the steady-state viscosity on these two parameters has been represented by a master curve using the reduced variables method. The results have been discussed in terms of theories which have been developed for systems consisting of a solvent and two thermodynamically incompatible polymers.

2. EXPERIMENTAL

2.1. Materials

2.1.1. *Casein*: Whole casein prepared by the method of Hammersten was obtained from Biochemreactive (USSR). It was dissolved in 0.1 M NaOH to give a solution of concentration 8% w/v and pH 7.2 and then centrifuged to separate insoluble impurities, concentrated by ultrafiltration up to 17% w/v and lyophilised.

2.1.2. *Alginate*: Sodium alginate (batch N30105) was obtained from BDH (UK). It was dissolved in water and centrifuged to separate insoluble impurities prior to lyophilisation. The mannuronic and guluronic acid compositions were determined using the method reported by Penman & Sanderson (1972). This involves splitting the alginate into alternating and homopolymeric fractions by partial acid hydrolysis, and determining the relative proportions of mannuronic acid blocks and guluronic acid blocks in the homopolymeric fraction by pmr spectroscopy in D_2O . The contents of MM and GG blocks and the MG alternating region was 30, 20 and 50%, respectively.

The intrinsic viscosity measured at 20°C in 0.19 M NaCl + 0.01 M NaF with an Ubbelohde capillary viscometer was determined as 9.70 dl g^{-1} . The sedimentation and diffusion coefficients measured in a pH 7.0 phosphate buffer ($\mu = 0.05$) using an ultracentrifuge (3170B (MOM, Hungary)) and a diffusometer (HTB-1a (Hitachi, Japan)) were $S_{20}^0 = 3.54 \pm 0.05$ and $D_{20}^0 = 1.76 \pm 0.15 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$. From these values a molecular weight of 124 000 was calculated.

2.2. Methods

2.2.1. *Preparation of disperse systems*: The phase diagram for the water-casein-alginate system, determined as described by Antonov *et al.* (1977), is shown in Fig. 1. If an attempt is made to prepare a homogeneous solution of alginate and casein where the concentration of the two components is in a region above the binodal line, then separation into two phases will occur. The composition of these phases is found by extrapolating the tie lines to the binodal. Extrapolation to the right yields the composition of the protein phase (phase 1) and extrapolation to the left yields the composition of the polysaccharide phase (phase 2). The ratio of the volume fraction of the protein phase to the polysaccharide phase is determined by the relative lengths of the tie line to the left and to the right of the point determined by the initial composition. The composition of the two phases on which the experiments described in this work were performed is defined by the two solid points in Fig. 1, i.e. protein phase (phase 1): 13.4% w/v casein, 0.3% w/v alginate; polysaccharide phase (phase 2): 0.6% w/v casein, 2.3% w/v alginate.

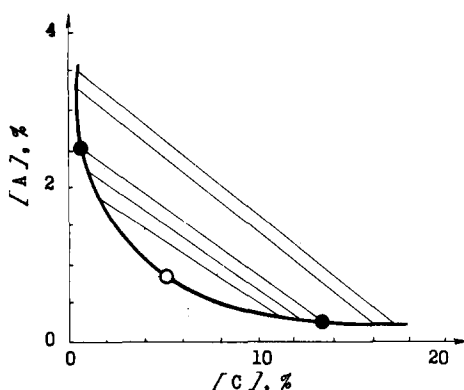


Fig. 1. Phase diagram of the system water (W)-casein (C)-sodium alginate (A) at pH=7.2 and 25°C. The thick line is a binodal, the thin lines are tie lines; —○— is the critical point; —●— represents the composition of the protein and polysaccharide phases in the disperse system. For a discussion of the diagram see text.

The ratio of the volume fractions of the two phases was varied by altering the initial composition along the tie line joining the two solid points and the emulsion composition was characterised by the value of the protein phase volume fraction (ϕ_1). The protein and polysaccharide were dissolved in water and the pH of the two phase systems was 7.2. According to the optical microscopy data, the mean diameter of the emulsion disperse particles was about 30 μm independent of the composition.

2.3. Measurement of the Steady-state Viscosity

The steady-state viscosity (η^*) of the single-phase and biphasic systems was determined at 25°C using three viscometers:

1. A precision rotational viscometer (VMV-03n (Topchiev Institute for Petrochemical Synthesis, Academy of Sciences of the USSR)) for the shear rate range $\dot{\gamma} = 10^{-2}$ – 10 s^{-1} .
2. A second rotational viscometer (Rheotest 2, (MLW, East Germany)) for the shear rate range $\dot{\gamma} = 1$ – 10^3 s^{-1} .
3. A scanning capillary viscometer (SCV 06 (Topchiev Institute for Petrochemical Synthesis, Academy of Sciences of the USSR)) for the shear rate range $\dot{\gamma} = 10^3$ – 10^7 s^{-1} .

The viscometers were calibrated using standard oils obtained from The Centre of Metrology and Standardisation, Moscow, USSR and it is estimated that the error in viscosity measurement did not exceed $\pm 5\%$. The initial viscosity (η_0^*) is determined as the mean value of the viscosity in the interval $\dot{\gamma} = 10^{-2}$ – 1 s^{-1} or alternatively by extrapolation of a linear plot of the logarithm of the viscosity against shear stress (τ) to $\tau = 0$ in the shear stress range $\tau = 15$ – 50 Pa .

3. RESULTS AND DISCUSSION

Figure 2 presents the flow curves of pure phases (curve a = phase 1, curve c = phase 2), as well as those of the two-phase system (emulsion) with $\phi_1 = 0.5$. As can be seen from this figure, the results of the measurements carried out using different viscometers

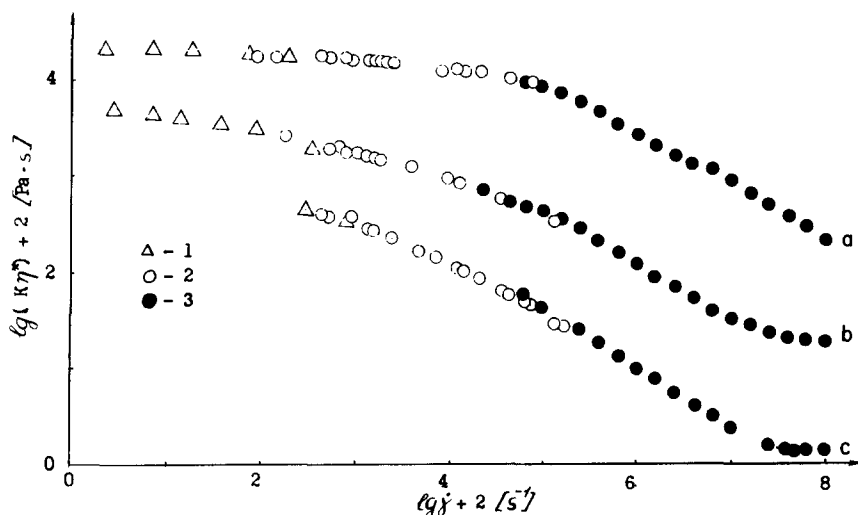


Fig. 2. Flow curves of the investigated liquid two-phase disperse system water-casein-sodium alginate with the protein phase volume fraction $\phi_1 = 0.5$ (curve b, $K = 10$), as well as the curves of their phases (curve a is the protein phase, $K = 100$; curve c is the polysaccharide phase, $K = 1$) measurements carried out using the viscosimeters (1) VMV-03n, (2) Rheotest 2, and (3) SCV 06 at 25°C .

are in a good agreement. The flow curves for the two-phase system with other values of the phase 1 volume fraction, lie between the pure phase curves and are similar in shape.

The data obtained can be presented in the form of a master curve which is independent of the composition of the emulsion (Vinogradov & Malkin, 1977). If the initial viscosity (η_0^*) is used as a viscosity reduction parameter, and the empirical parameter k is used to reduce the shear rate, the reduced viscosity is determined by

$$\tilde{\eta}^* = \eta^* / \eta_0^*$$

and the reduced shear rate by

$$\tilde{\dot{\gamma}} = k \dot{\gamma}$$

Figure 3 presents the master flow curve $\log_{10} \tilde{\eta}^*$ versus $\log_{10} \tilde{\dot{\gamma}}$ and Figs 4 and 5 show the dependence of the reduction parameters η_0^* and k on the emulsion composition. The results displayed in Figs 3-5 permit the viscosity of the disperse system to be obtained for any composition over a wide range of shear rates.

Attempts to fit the master curve by the Ree-Eyring equation,

$$\eta^* / \eta_0^* = \eta_\infty^* / \eta_0^* + (\text{arc sinh } \theta^* \dot{\gamma}) / \theta^* \dot{\gamma}$$

where θ^* is a characteristic relaxation time and η_∞^* is the limiting Newtonian viscosity obtained at high shear rates, have not been successful. The best fit is obtained with $\theta^* = k = 2.9 \times 10^{-3}$ s and $\eta_\infty^* / \eta_0^* = 7 \times 10^{-3}$ when the standard deviation of experimental values of the viscosity from the theoretical curve is equal to $\pm 29\%$. The equation predicts a more abrupt transition into the non-Newtonian region and a stronger dependence of the viscosity on the shear rate in this region than is observed.

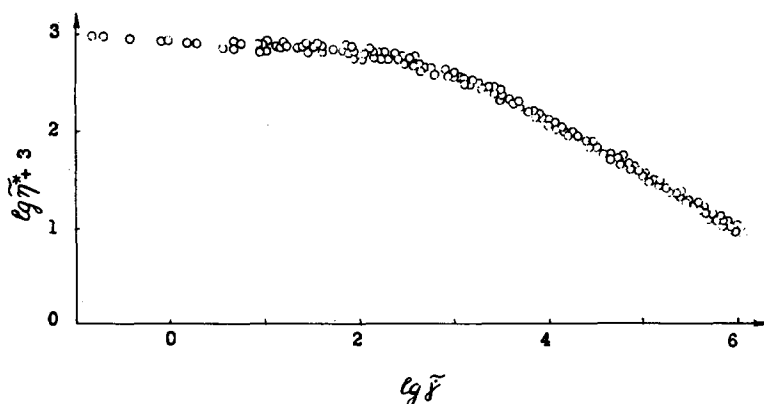


Fig. 3. Master flow curve of the investigated two-phase disperse system water-casein-sodium alginate at 25°C.

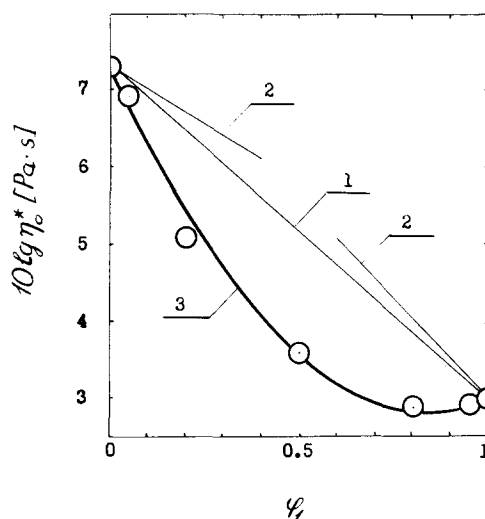


Fig. 4. Dependence of the initial viscosity for the investigated liquid two-phase disperse system water-casein-sodium alginate on the protein phase volume fraction at 25°C (the points are the experimental data). Curve 1 is calculated from eqns (1), (2a) and (2b); curve 2 is calculated from eqn (3); curve 3 is calculated from eqn (12) at $B = -0.623$.

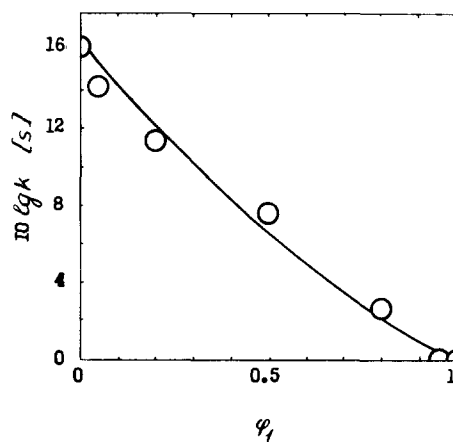


Fig. 5. Dependence of the shear rate reduction parameter on the protein phase volume fraction for the investigated liquid two-phase disperse system water-casein-sodium alginate.

η_0^* can be considered as the most important rheological characteristic of these systems. As can be seen from Fig. 4, η_0^* for the two-phase systems is lower than would be predicted from the viscosities of the separate phases using the logarithmic additivity law:

$$\log_{10} \eta^*(\tau) = \sum_{i=1}^2 \phi_i \log_{10} \eta_i(\tau) \quad (1)$$

where ϕ_i , η_i ($i = 1, 2$) are the volume fractions and the viscosities of the separate phases respectively. Such a dependence of viscosity on composition is typical of polymeric emulsions (Van Oene, 1978). The viscosity of emulsions with an infinitesimal interfacial tension was considered in the most general form in Hashin's rigorous phenomenological theory (Hashin, 1964) and in Brennen's statistical theory (Brennen, 1975).

Hashin (1964) gives the following expressions for the lower and upper limits of η_0^* , respectively:

$$\eta_0^* = \eta_{1,0} + \phi_2 [(\eta_{2,0} - \eta_{1,0})^{-1} + 2\phi/5\eta_{1,0}]^{-1} \quad (2a)$$

$$\eta_0^* = \eta_{2,0} + \phi_1 [(\eta_{1,0} - \eta_{2,0})^{-1} + 2\phi_2/5\eta_{2,0}]^{-1} \quad (2b)$$

where $\eta_{i,0}$ ($i = 1, 2$) are the separate phase initial viscosities. It is easy to show that these expressions almost coincide with the logarithmic additivity law (eqn 1).

According to Brennan (1975), the dependence of the initial viscosity on the emulsion composition takes the form

$$\eta_0^*/\eta_i = 1 + 10(\lambda - 1)(16 + 19x^7 + 19\lambda(1 - x^7)) x^3/F \quad (3)$$

where

$$F = 96 + 400x^3 - 672x^5 + 450x^7 + 76x^{10} + \lambda(178 + 75x^3 - 126x^5 + 25x^7 - 152x^{10}) \\ + \lambda^2(76 - 475x^3 + 798x^5 - 475x^7 + 76x^{10})$$

$$i = 2, \lambda = \eta_{1,0}/\eta_{2,0}, x^3 = \phi_1 \text{ at } \phi_1 < 0.5$$

and

$$i = 1, \lambda = \eta_{2,0}/\eta_{1,0}, x^3 = \phi_2 \text{ at } \phi_1 > 0.5$$

This dependence is presented in Fig. 4 (curve 2). It can be seen that it predicts somewhat higher viscosities for the two-phase system than the logarithmic additivity law.

Thus, the experimental data are not in agreement with Hashin's or Brennen's theories. A possible reason for this discrepancy is due to the effects related to the presence of the interphase boundary.

We suggest that the emulsion may be regarded, to a first approximation, as a three-phase system consisting of the protein phase (1), the polysaccharide phase (2) and an

interphase layer (3). The composition of phases 1 and 2 is known. As to the composition of phase 3, it may be assumed that the mean concentrations of each of the polymers in it are lower than those in the phases where these polymers are dominant. If this were not true phase 3 would be unstable with respect to concentration fluctuations. This assumption is illustrated in Fig. 6.

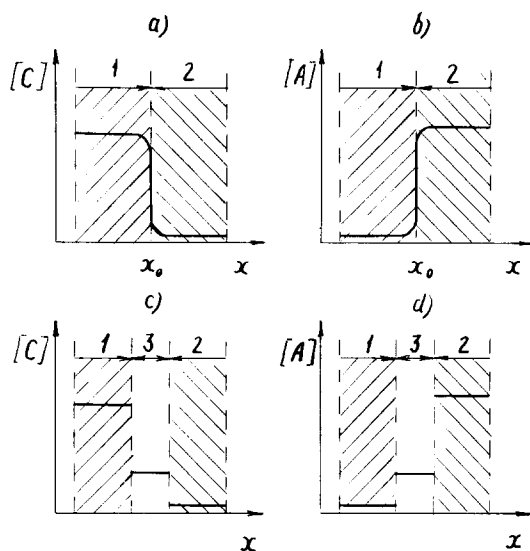


Fig. 6. Schematic profiles of casein [C] and sodium alginate [A] concentrations along the axis perpendicular to the interphase (a and b are the liquid two-phase disperse system water-casein-sodium alginate; c and d are the equivalent three-phase system. 1, 2, 3 are the protein, polysaccharide and interphase layer phases, respectively).

While investigating the two-phase disperse system water-gelatin-dextran, we have ascertained that there is a lower polymer concentration in the interphase layer, i.e. 'negative' absorption (Belkina *et al.*, 1974), which manifested itself as a preferential orientation of gelatin fibrils perpendicular to the boundary of the gelatin gel-dextran phase.

It is difficult to determine directly the rheological properties of the interphase layer. However, if it contains a relatively low polymer concentration it may be assumed that its viscosity at low shear stresses is small compared with the other two phases and that its non-Newtonian behaviour is less pronounced. Thus at low shear stress

$$\eta_3 \ll \eta_i \quad (i = 1, 2)$$

and at high ones

$$\eta_3 \sim \eta_i \quad (i = 1, 2)$$

Using the framework of the Frenkel-Eyring viscosity theory (Frenkel, 1975; Glasstone *et al.*, 1948) we suggest a general approach to the description of rheological properties of emulsions formed by two incompatible polymers and a solvent.

Assuming that the viscous flow activation energy of the equivalent three-phase system (E^*) is a simple volume average of the activation energies of each phase, then

$$E^*(\tau) = \sum_{i=1}^3 y_i E_i(\tau) \quad (4)$$

where y_i ($i = 1, 2, 3$) is the effective volume fraction of the phases and E_i is the corresponding activation energies.

It is reasonable to assume that the effective volume fraction of the interphase layer (y_3) is proportional to the volume fraction of the disperse (particulate) phase, if the disperse particle dimensions are constant. If one also assumes that $\phi_1 = 0.5$ corresponds to the phase inversion point, then

$$y_3 = a\phi_1 \quad \text{at } \phi_1 < 0.5 \quad (5a)$$

and

$$y_3 = a\phi_2 \quad \text{at } \phi_1 > 0.5 \quad (5b)$$

where a is a constant. These may be approximated by a continuous function of the form

$$y_3 = a\phi_1\phi_2 \quad (6)$$

It is now necessary to express the effective volume fractions in terms of the real volume fraction of phases 1 and 2 in the emulsion. Taking into account the normalisation condition

$$y_1 + y_2 + y_3 = 1 \quad (7)$$

and

$$\phi_1 + \phi_2 = 1 \quad (8)$$

then, in conjunction with eqn (6) it may be assumed, for the sake of simplicity, that

$$y_i = \phi_i - 0.5a\phi_1\phi_2 \quad (i = 1, 2) \quad (9)$$

Thus the dependence of the activation energy on the emulsion composition may be expressed as:

$$E^*(\tau) = \sum_{i=1}^2 (\phi_i - 0.5a\phi_1\phi_2) E_i(\tau) + a\phi_1\phi_2 E_3(\tau) \quad (10)$$

Assuming that

$$\eta^*(\tau) = A' \exp \left[\frac{E^*(\tau)}{\beta} \right] \quad (11a)$$

and

$$\eta_i(\tau) = A' \exp \left[\frac{E_i(\tau)}{\beta} \right] \quad (i = 1, 2, 3) \quad (11b)$$

where A' is the universal constant, and $\beta = RT$. The dependence of the viscosity on the emulsion composition is obtained from eqns. (10), (11a) and (11b), giving

$$\log_{10} \eta^*(\tau) = \sum_{i=1}^2 \phi_i \log_{10} \eta_i(\tau) + B(\tau) \phi_1 \phi_2 \quad (12)$$

where

$$B(\tau) = a[(\log_{10} \eta_3(\tau)) - 0.5(\log_{10} \eta_1(\tau) + \log_{10} \eta_2(\tau))] \quad (13)$$

The experimental data are well described by eqn (12). Curve 3 in Fig. 4 is obtained from this equation with the best fit value for $B(\tau = 0)$ of -0.623 . It is not sensible to discuss in detail the value of B obtained, since the latter involves two unknown values: the interphase layer viscosity $\eta_3(\tau)$ and the parameter a related to the interphase layer effective thickness. On the other hand, a qualitative analysis of the shear stress dependence on the value of B is possible.

As mentioned above, the interphase layer viscosity shows less pronounced non-Newtonian behaviour than phases 1 and 2. In such a case one may assume that the value of parameter B should decrease, as the stress increases, and it becomes equal to zero at a certain stress τ' (this is illustrated in Fig. 7). Equation (13) shows that

$$B(\tau_1) = 0 \quad (14)$$

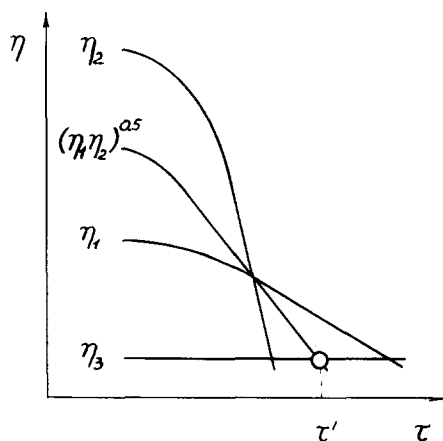


Fig. 7. The scheme illustrating the dependence of parameter B in eqn (12) on the shear stress (η_1 , η_2 , η_3 are the protein, polysaccharide and interphase layer phase viscosities, respectively; τ' corresponds to the condition $B(\tau) = 0$, eqn (14)).

if

$$\eta_3(\tau') = [\eta_1(\tau') \eta_2(\tau_1)]^{0.5} \quad (15)$$

When this condition holds the viscosity of the emulsion measured at the stress $\tau = \tau'$ will obey the logarithmic additivity law (compare eqns (1) and (12)) and there will be a linear relationship between the protein phase volume fraction ϕ_1 and $\log_{10} \eta^*$. As shown in Fig. 8 this condition holds when $\tau = 10^3$ Pa.

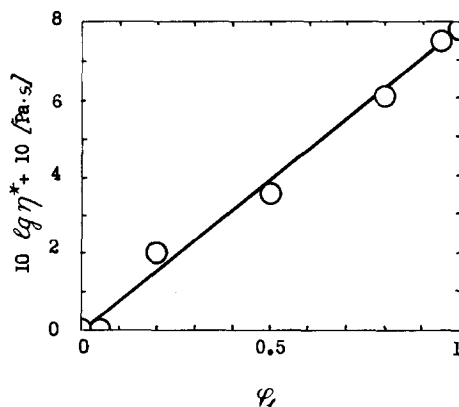


Fig. 8. Dependence of viscosity of the investigated liquid two-phase disperse system water-casein-sodium alginate on the protein phase volume fraction at 25°C and $\tau = 10^3$ Pa (the points are the experimental data, the line is calculated from eqn (1)).

Using the three-phase model the dependence of the reduction parameter (k) on the emulsion composition can also be analysed. By definition (Vinogradov & Malkin, 1977)

$$k(\phi_1) = \theta^*(\phi_1)/\theta_1 \quad (16)$$

where $\theta^*(\phi_1)$ and θ_1 are the characteristic relaxation times of the emulsion and reference phase 1, respectively. According to the activation theory of viscosity (Ree & Eyring, 1955),

$$\theta = \beta\omega\eta_0 \quad (17)$$

where ω is the activation volume. Thus

$$k(\phi_1) = \omega^*(\phi_1) \eta_0^*(\phi_1) / \omega_1 \eta_{1,0} \quad (18)$$

where $\omega^*(\phi_1)$ and ω_1 are the activation volumes of the emulsion and reference phase 1, respectively. From the observed dependence of k and η_0^* on ϕ_1 (Figs 4 and 5), the relationship between activation volume and emulsion composition is found to be

$$\omega^*(\phi_1) \propto k(\phi_1) / \eta_0^*(\omega_1) \quad (19)$$

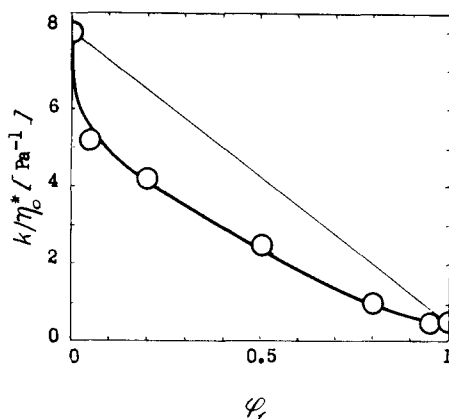


Fig. 9. Dependence of k/η_0^* (proportional to the mean activation volume), on the protein phase volume fraction for the investigated liquid two-phase disperse system water-casein-sodium alginate (the thin line represents the additivity law).

A plot of k/η_0^* against ϕ_1 is shown in Fig. 9. It is significant that the plot is convex downwards. To interpret this, we assume that

$$\omega^* = \sum_{i=1}^3 y_i \omega_i \quad (20)$$

From eqns (6), (9) and (20)

$$\omega^*(\phi_1) = \sum_{i=1}^2 \phi_i \omega_i + D \phi_1 \phi_2 \quad (21)$$

where $D = a(\omega_3 - 0.5(\omega_1 + \omega_2))$. According to eqn (21) the dependence of k/η_0^* or ω^* on ϕ_1 should be of the form shown in Fig. 9 provided $D < 0$, or

$$\omega_3 < 0.5(\omega_1 + \omega_2) \quad (22)$$

In accordance with the activation theory of viscosity (Ree & Eyring, 1955) the larger the activation volume, the more pronounced the non-Newtonian character of the flow. Therefore, eqn (22) is in principle, equivalent to the assumption that the non-Newtonian character of the flow is more pronounced for phases 1 and 2 than for the interphase layer. Thus, the experimental dependence of the shear rate reduction parameter on the emulsion composition qualitatively agrees with the concepts developed to explain the nature of the steady-state flow behaviour of these systems.

4. CONCLUSION

Steady-state flow of the liquid two-phase disperse system water-casein-sodium alginate has a number of special features:

1. At low shear stresses the observed viscosities are lower than would be predicted by the logarithmic additivity law.
2. At high shear stresses the dependence of viscosity on the disperse system composition follows the logarithmic additivity law.
3. The dependence of the mean activation volume on the disperse system composition is not in agreement with the additivity law.

This behaviour can be understood if the active role of the interphase layer on the flow process is taken into account. In this respect, this layer may be regarded as a rheological subsystem. Mean concentrations of each of the polymers in the interphase layer are lower than the concentrations in the phases where they dominate. For this reason the interphase layer has a relatively low viscosity, and shows less pronounced non-Newtonian behaviour than the other two phases.

At low stresses where the interphase layer viscosity is considerably lower than the viscosities of the phases, the interphase layer plays the role of a lubricant between the phases. This lubricant effect results in the experimental dependence of viscosity on the disperse system composition that lies below the plot corresponding to the logarithmic additivity law. One may expect that the lubricant effect of the interphase layer should diminish with the increasing stress, as the viscosities of the phases approach the interphase layer viscosity. As a consequence, the experimental dependence of viscosity on the disperse system composition approaches the logarithmic additivity law at high stresses.

Interpretation of the experimental results in terms of the logarithmic additivity law support the view that the activation energy for the viscous flow of the disperse system is determined by a simple volume averaging of the activation energies of the two-phase and interphase layers.

The presence of an interphase layer with a low viscosity and containing relatively low concentration of polymer is apparently typical of two-phase systems of the type 'solvent—two incompatible polymers'.

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