

Integral equation for calculation of distribution function of activation energy of shear viscosity

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Abstract

A new technique of calculation of a distribution function of activation energy ($f(E)$) of shear viscosity based on a regularization procedure applied to the Fredholm integral equation of the first kind has been developed using the Baxter-Drayton and Brady model for concentrated and flocculated suspensions. This technique has been applied to the rheological data obtained at different shear rates for aqueous suspensions with fumed silica A-300 and low-molecular (3,4,5-trihydroxybenzoic acid and 1,5-dioxynaphthalene) or high-molecular (poly(vinyl pyrrolidone) of 12.7 kDa and ossein of 20–29 kDa) compounds over a wide concentration range (up to 25 wt% of both components) and at different temperatures. Monomodal $f(E)$ distributions are observed for the suspensions with individual A-300 or A-300 with a low amount of adsorbed organics. In the case of larger amounts of nanosilica and organics the $f(E)$ distributions are multimodal because of stronger structurization and coagulation of the systems that require a high energy to break the coagulation structures resisting to the shear flow.

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1. Introduction

Concentrated colloidal suspensions are widely used as paints, foods, etc., in which solid particles and organic molecules, especially macromolecules, can strongly interact [1–4]. Complex systems including polymers, low-molecular organics, solid nanoparticles, and water or other solvents are of importance for many practical applications [5–9]. Therefore appropriate estimations of the energetic characteristics of viscous flows in similar complex systems are of interest not only from theoretical point of view but also from practical one [10]. If the attractive forces (electrostatic, dispersive, and hydrogen binding) are stronger than repulsion ones and Brownian forces, particles and organics can form aggregates (clusters) up to a continuous coagulation structure. This structure can be destroyed under flow which can also change the dispersion mi-

crostructure. The rheological characteristics of these colloidal systems depend on the rates of break and renewal of the bonds between particles and macromolecules, i.e., on the thixotropy effects. A lot of different models was developed to describe the rheological properties of the colloidal systems [2,10–20]. The Ree and Eyring model [11–13] was used to explain shear viscosity of concentrated suspensions. It gives the dependence of the viscosity η on a shear rate assuming that the motion of particles can be described as activated jumps from the cage formed by the nearest neighbors to holes into the adjoining cages. The frequency of these jumps can be written in the form of Arrhenius equation

$$v = v_0 \exp\left(-\frac{E}{k_B T}\right), \quad (1)$$

where $v_0 \sim D_0/a^2$, a is the particle radius, D_0 is translational diffusion coefficient, k_B is the Boltzmann constant, T is the temperature, and E is the activation energy of the jumps. This frequency changes due to the shear effect $E^* = E \pm \xi \sigma$, where

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σ is the shear stress, and ξ is the structural factor depending on the cage size [10]. The sign “–” corresponds to the jumps in the flow direction and the sign “+” accounts for the opposite direction. The shear rate is proportional to the difference between the frequencies of these opposite jumps that results in [10]

$$\dot{\gamma} = \frac{1}{\beta} \sinh\left(\frac{\xi\sigma}{k_B T}\right), \quad (2)$$

where

$$\beta = v_0^{-1} \exp\left(\frac{E}{k_B T}\right). \quad (3)$$

The non-Newtonian viscosity of monomolecular liquids can be written as [10]

$$\eta = \frac{A \sinh^{-1}(\beta\dot{\gamma})}{\beta\dot{\gamma}}, \quad (4)$$

where

$$A = \frac{\beta k_B T}{\xi}. \quad (5)$$

For multicomponent systems the viscosity represents a sum

$$\eta = \sum_{i=1}^n \frac{A_i \sinh^{-1}(\beta_i \dot{\gamma})}{\beta_i \dot{\gamma}}, \quad (6)$$

where i denotes the number of flow units in the system with n components. In the case of colloidal particles ($i = 1$) and solvent molecules ($i = 2$) Eq. (6) results in

$$\eta = \frac{A_1 \sinh^{-1}(\beta_1 \dot{\gamma})}{\beta_1 \dot{\gamma}} + A_2, \quad (7)$$

because of condition $\beta_2 \dot{\gamma} \ll 1$ [10].

Baxter-Drayton and Brady [14] modified this theory to model the viscosity of flocculated colloidal dispersions when the Brownian motion is not predominant. Similar arguments on the stress-induced variation of the activation energy barrier lead to [10]

$$\eta = (\eta_0 - \eta_\infty) \frac{\sinh^{-1}(\beta' \dot{\gamma})}{\beta' \dot{\gamma}} + \eta_\infty, \quad (8)$$

where

$$\beta' = c \frac{a^2 k_B T}{D_0 E} \exp\left(\frac{E}{k_B T}\right), \quad (9)$$

where η_0 and η_∞ are the viscosity at the shear rate $\dot{\gamma} \rightarrow 0$ and $\dot{\gamma} \rightarrow \infty$, respectively, and c is a proportionality constant related to the network structure [10,14].

Yziquel et al. [20] proposed a structural network model based on a modified upper convected Jeffreys model with a single relaxation time and a kinetic equation to describe the flow-induced microstructure evolution. The authors applied this model to concentrated suspensions of fumed silica A-200 ($C_{SiO_2} = 7\text{--}14.5$ wt%) and showed that the energy-dependent model provides good agreement with the experimental data.

Water-soluble polymers such as poly(ethylene glycol), PEG, poly(propylene glycol), PPG, poly(ethylene oxide), PEO, poly(vinyl pyrrolidone), PVP, etc., which are characterized by relatively weak intermolecular interactions between the molecules

in aqueous solutions (because of the absence of the hydrogen bonds between them) but by strong hydrogen bonds with water molecules, are widely used to vary the rheological properties of solutions of organics or suspensions with solid particles [1–4]. The aqueous systems, including macromolecules of another kind (e.g., proteins, starch, cellulose, polysaccharides, etc.) which can form the hydrogen bonds one with another, as well as with water molecules and solid particles, are of interest for food, pharmaceutical and other industries. PEG (which can be considered as a representative of the first kind macromolecules) possessing an extremely high affinity for water has been widely used as an agent to induce cell aggregation and fusion, and the physicochemical principles of its function are only becoming understood recently [3]. If PEG is adsorbed or covalently link to the cell or vesicle surface, the surface force profile becomes entirely repulsive, and aggregation and fusion is inhibited [3]. Monkos [4] studied the viscosity of ovalbumin (which can be considered as a representative of the second kind macromolecules) aqueous solutions as a function of temperature and of protein concentration (C_p). The viscosity–temperature dependence was used with a modified Arrhenius equation to estimate the activation energy of viscous flow for hydrated and unhydrated ovalbumin which changes between 30 and 100 kJ/mol at $C_p = 0.6\text{--}43$ wt%. Raghavan and Khan [8] studied suspensions of fumed silica (3–10 wt%) in polypropylene glycol (PPG, molecular weight 725, viscosity $\eta_{PPG} \approx 1.2$ poise at ambient conditions) which exhibit shear-thickening under steady shear and “strain-thickening” under oscillatory shear. The combination of shear- and strain-thickening behavior was explained using a clustering mechanism, which attributes the various phenomena to the formation of temporary, flow-induced clusters. The authors assumed that two regimes of strain-thickening are a result of differences in the relative ease of cluster formation. On the analysis of the above results one can observe two opposite effects in the suspensions with a mixture of organics and solid nanoparticles. The first one is the clustering of the system when the immobilized molecules (such as PEO, PEG, PPG, PVP, etc.) tend to weak interaction with already covered surface of particles and this particular case corresponds to relatively low viscosity, i.e., small activation energy of the shear viscosity. In the case of strong interaction between molecules (e.g., proteins) and both covered and noncovered particles, the structurization leads to formation of a continuous network or very large clusters (large coagulation structures) in the dispersion. Clearly this results in a high viscosity of the systems at high activation energy of the break of the coagulation structures enhancing the viscosity. Adequate energetic characterization of non-Newtonian flows with the suspensions of both types, which include colloidal particles and adsorbed and dissolved organics, is of interest. However, in the case of transition of the system from the first type to the second one it is difficult to determine adequate average energetic characteristics by the methods described elsewhere [4,10–14] because the system can be heterogeneous and clustered (i.e., there are very different cages). Transferring of particles or molecules between cages is activated process, which can be modeled as activated jumps. The presence of different cages (hierarchy of clusters) can affect

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