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The Dilatancy of Colloidal Structures and Polymer Solutions

I.F.Efremov

The dilatant regime in the flow of dispersions under the constrained conditions of the interaction of colloidal particles resistant to aggregation is discussed. In this case the system behaves as a dilatant periodic colloidal structure of the second type with a limited volume of the medium (PCS_2) in which a positive disjoining pressure $\pi_2 > 0$ operates. The similarity in the dilatant behaviour of dispersed systems and structured solutions of surfactants and polymers is demonstrated. With increased concentration of ions (and also of particle size), the dilatant regime passes into an anomalously viscous (thixotropic regime), i.e. under these conditions the dilatant PCS_2 is converted into a thixotropic PCS_1 (of the first type) in which $\pi_1 < 0$.
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I. INTRODUCTION

The unusual rheological properties of colloidal structures, which usually exhibit a non-Newtonian viscosity, have already been investigated for a long time. However, until recently most interest was shown in the behaviour of dispersions, whose shear deformation is accompanied by an appreciable decrease of the effective viscosity as a consequence of the breakdown of the colloidal structure under the influence of gradient fluxes in the liquid medium†.

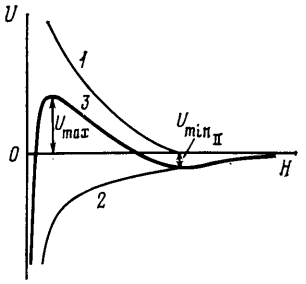


Figure 1. Potential curves for the interaction of two disperse particles: 1) repulsive curve; 2) attractive curve; 3) resultant curve in the presence of a repulsion barrier U_{max} and a secondary minimum with a depth $U_{min\,II}$ (U is the potential energy of the interaction of the particles and H the distance between them).

†A change in viscosity is also possible as a consequence of the orientation of the anisometric micro-objects in the stream, but these effects are comparatively small and will not be considered here[1-4].

The magnitude of the anomaly in the viscosity is determined by the change in the stability of the structure in the deformation process. The stability of a thixotropic system depends in its turn on the binding energy between its constituent elements and correspondingly on the depth of the secondary minimum on the potential interaction curves (Figs.1 and 2).[5]

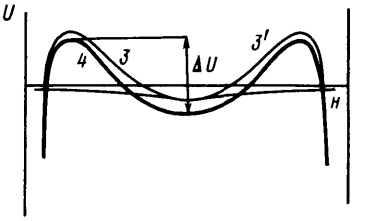


Figure 2. Potential curve for the interaction of a single test particle with two neighbouring particles (curve 4) in the presence of an energy minimum ΔU. Curves 3 and 3' are the resultant pair interaction curves.

The systems arising as a result of the fixation of micro-objects at the secondary minimum constitute periodic colloidal structures of the first type (PCS_1) with thixotropic properties. As a rule the PCS_1 are of a local character, i.e. they are not formed throughout the bulk of the system (under certain conditions and at a sufficiently high concentration in the solid phase, complete immobilisation of the dispersion is possible) and consist of ordered micro-regions (tactoids) alternating with individual "amorphous" sections with a lower density[6]. Such a tactoid structure, which is known for dispersions of many substances, particularly argillaceous minerals[7-10], is responsible for the possibility of the appearance of anomalies in viscosity, whose magnitude $\eta_0 - \eta_m$

(η_0 and η_m are the viscosities of the virtually undisrupted structure and the structure disrupted to the maximum extent) naturally depends on the depth of the potential minimum $U_{min\ II}$ (Fig.3)[1,11,12].

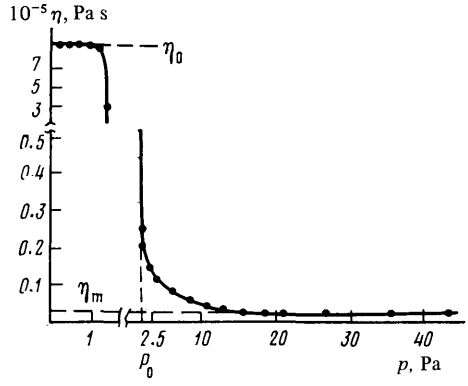


Figure 3. Dependence of the viscosity on the shear stress in a 10% aqueous (wt.%) dispersion of bentonite[11].

At the same time the authors of a number of studies[13-15] drew attention to the fact that the magnitude of the anomaly in viscosity does not determine the capacity of the system for thixotropic recovery and is not an unambiguous characteristic of thixotropic properties: thixotropy is defined as the isothermal and reversible sol ⇌ gel transformation[16,17]. One should bear in mind that many colloidal structures decompose irreversibly (partially or completely); complete reversibility is a rare case arising as a consequence of syneresis and other possible processes#. Fully irreversible PCS are not strictly speaking thixotropic systems. However, the origin, structure, and many properties, for example peptisability, are similar for reversible and irreversible PCS. Furthermore, both types of PCS undergo syneresis, which can be sharply accelerated due to external influences leading to the breakdown of the structure and can occur with partial or complete precipitation of the phase. However, there is a possibility of a microrecovery to some extent, which can be inferred solely on the basis of special studies.

Despite the large number of studies on thixotropy[1,5,6,11-27], little is known about the mechanism of the recovery processes, their energetics, and kinetics. Thus it is not clear which dispersions can recover their structure, to what extent, and over what period. One of the causes of this situation is apparently insufficient investigation of the structural transformations at the microlevel with determination of quantitative rules governing the interaction of micro-objects in external force fields. In a number of studies an attempt has been made at a quantitative interpretation of the thixotropic recovery on the basis of general equations, which are usually empirical (or semiempirical) (see, for example, Refs.23, 24, and 28-31). The results of the analysis of thixotropic multicomponent mixtures with allowance for the kinetics of the breakdown and recovery of the structural elements have been published[12,26]. A model of a thixotropic system, developed using the methods of hydrodynamics, rheology, and information theory as well as the mathematical apparatus of Markovian processes has been proposed[32]. The phenomenon of thixotropy has also been considered on the basis of the thermodynamics of irreversible processes[33,34].

It has been noted[14,35] that thixotropy can be of two kinds: based on stability and characterising the breakdown and recovery of the structural network, and based on viscosity and reflecting the breakdown and recovery of individual aggregates of colloidal particles.

Dilatancy, usually expressed by an increase of viscosity over a certain medium range of deformations, is, in addition to thixotropy, also a characteristic rheological property of colloidal dispersions (Fig.4). Dilatancy frequently plays an important role in industrial and natural processes. Dilatant effects frequently hinder the technology and transport of dispersions and limit the intensification of deformation processes[6,36-41]. Dilatant rocks (various types of earth, soil, etc.), whose rheology is of interest to many specialists, are widely distributed in nature; dilatancy has a major influence on the behaviour of these rocks (for example, in different instances of "stabilisation" of clay ground[42], in the treatment of soils[43], in different rheological processes, etc.). At the same time the causes of the onset of the dilatant flow regime have been inadequately determined and the existing explanations are not unique[5,6,15,36,44-46].

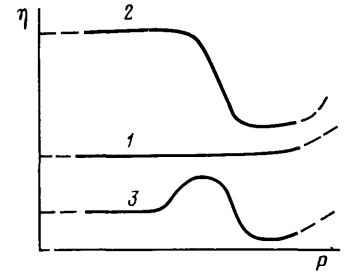


Figure 4. Dependence of the viscosity on the shear stress for different systems: 1) pseudoplastic (Bingham); 2) structural-viscous (thixotropic); 3) dilatant.

II. THE PROBLEM OF THE DILATANCY OF DISPERSIONS WITH MODERATE AND LOW CONCENTRATIONS OF THE SOLID PHASE

According to the literature[47-49], dilatancy (dilatation) is defined as a homogeneous deformation involving the volume expansion of highly concentrated dispersed systems. The expansion of such dispersions is caused by the fact that, with increase in the rate of shear, the particles pass into a less close-packed state generating pores which suck in the liquid: the volume of the system then increases and the dissipation of energy is enhanced. This is observed particularly clearly in pastes where the dispersed particles are almost close-packed. On deformation, the particles move away from one another (some approach one another), which

#Various binding mixtures, in which solidification processes take place, increasing the stability and the possibility of its restoration after the breakdown of the structure of the mixture, are frequently classified as reversible systems. In this case the term "reversibility" naturally has a limited significance.

leads to an increase of volume[6,21,50-52]. The volume of many disperse systems with close-packed particles changes on deformation regardless of whether the gaps between the particles are filled with water or air[51]. The viscosity and volume of certain concentrated dispersions increase as the rate of shear is altered, although there is in all probability no direct contact between their colloidal particles[53,54].

However, dilatant phenomena are more varied than would follow from the concept of dilatancy as deformation of volume expansion[48-50]. From the standpoint of these ideas, it is difficult to explain rheological data such as the absence of expansion in the dilatant deformation regime, for example, in starch pastes[52]; some workers believe that an increase of volume in dilatancy is altogether non-obligatory[21]. Furthermore, dilatancy has been observed in many dispersions containing the solid phase in an amount much smaller than would correspond to close-packing.

The range of compositions of dilatant dispersions is very wide. Thus, starting from systems concentrated to the limiting extent, for example, hydro-dispersions of silica or quartz glass (with a volume fraction of the solid phase $\phi = 0.85-0.87$),[55,56] the following systems are dilatant: dispersions of alumina in water (0.60) [56] and of iron in carbon tetrachloride (0.46),[57] aqueous clay strata (0.40–0.47),[58] quartz (0.41–0.45),[59] and starch (0.38–0.48),[56,59] dispersions in liquids of different kinds, latices (0.30–0.50),[44,45,60-62] titanium dioxide (0.30–0.43),[63,64] barium sulphate and carbonate (0.30),[65] latex PCS (0.12–0.40),[66-68] etc.

The above features—dilatancy of colloidal structures with a low content of the disperse phase and the absence of expansion on shear—led to the postulation of various mechanisms of dilatancy (more precisely of the increase of viscosity on shear) in dispersions with high and low concentrations[15,44,45,51,53,61,69-71]. Different terms have been proposed for the deformation of the latter systems: "quasi-dilatancy"[44,61], "pseudo-dilatancy"[72], "antithixotropy"[73], "negative thixotropy"[74,75], etc., the term "dilatancy" being retained for processes consistent with the definition given above[47-50]. However, this terminology has not gained wide currency.

The complexity of the problem under discussion arises from the fact that the increase of viscosity on shear or, in other words, the increase of the resistance offered by the system to external influences may be a consequence of the occurrence of different (one or several simultaneous) comparatively little investigated processes (many of which are reversible), rather than of the absence of a unified terminology; this greatly hinders the determination of the real mechanism responsible for the behaviour of the system under deformation conditions. We may note the following processes.

1. Reversible deformation of a highly concentrated dispersion accompanied by an increase of the viscosity and volume of the system (the Reynolds and Reiner dilatation[47-49]).

2. Reversible deformation of dispersions at moderate and low concentrations accompanied by an increase in viscosity at constant volume (quasi-dilatancy as defined by Krasheninnikov and coworkers[44,61]).

3. Rheopey—acceleration of the restoration of the thixotropic structure disrupted beforehand (as defined by Freundlich and Yuliusburger[76]).

4. Long-range aggregation (long-range coagulation) with fixation of micro-objects at the secondary potential minimum as well as short-range coagulation (fixation at the primary minimum) induced by the flow (Fig.5).[5,77-85] The statistical theory of aggregation under the conditions of steady-state flow has been developed[86].

5. Stabilisation of the dispersion as a result of unidirectional and periodic deformations and their superposition[14,87-89] as well as vibro-treatment[90-92]. It has been noted[89] that, depending on the rate of shear or the frequency of sinusoidal vibrations of a kaolin hydrodispersion, either thixotropic or dilatant effects arise in the latter. An increase of the rate of shear with the same stress under the conditions of the superposition of two types of deformation can arise in flow through tubes as a consequence of the appearance of random sources of vibrations. It has been concluded[92] that the capacity for thixotropic transformations of a dispersion compacted by vibro-treatment increases with increasing density of the medium. However, the increase of viscosity with increasing density of the medium greatly exceeds its decrease due to the thixotropic breakdown. The characteristics of the formation and breakdown of dispersed structures under the conditions of the joint action of vibration and surfactant additives have been discussed[93].

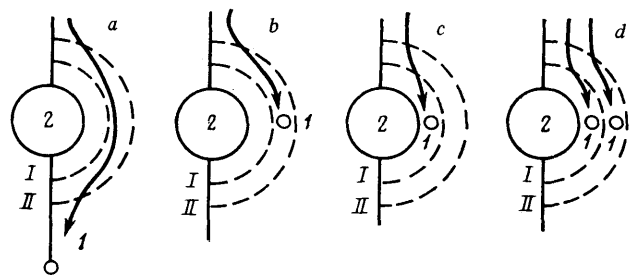


Figure 5. Schematic illustration of the interaction of micro-objects in a flow: *a*) no bond formed between particles *1* and *2*; *b*) particle *1* fixed at the secondary (II) minimum; *c*) particle *1* fixed at the primary (I) minimum; *d*) particles *1* fixed at the primary and secondary minima[80].



Figure 6. Electron micrograph of the aggregation of rod-shaped sepiolite particles having electrical dipole moments[94].

6. Stabilisation of the colloidal structure as a result of its rearrangement under the influence of the flow. For example, the structure comprising non-uniformly arranged particles can become stabilised after the particles have been more uniformly distributed, or the strength of the bonds between anisometric particles—rods and plates with permanent electric dipole moments—can increase under the influence

of hydrodynamic forces which is apparently characteristic of dispersions of argillaceous minerals (Fig.6).[5,81,94-99]

7. The fluidity of a dispersion can diminish following the onset of turbulence, which can be interpreted as an increase of viscosity[100-103]; this is by no means always easy to observe, particularly for an anomalously microturbulent regime and also in the presence of aggregation processes[104].

Furthermore, considerations have been put forward concerning the possibility of other processes leading to the stabilisation of the system. It has been suggested[105] that the elasticity of dispersions of gas carbon black in a mineral oil is determined by the breakdown of the network of carbon black particles with formation of chain fragments; the formation of the coagulation network and the rearrangement of its structure in dilatancy has been indicated in a number of studies. Many investigators have noted the need to take account of the interaction forces, the solvation effects, and other factors which can influence the flow regime. Despite the importance of such explanations, they are nevertheless largely hypothetical and are usually one-sided.

The determination of the mechanisms of processes occurring in disperse systems subjected to external force fields is an extremely complex problem whose solution solely with the aid of rheological methods, without a detailed description of the system, as a rule involves considerable difficulties. As a result of failure to take into account this factor adequately, a heterogeneous rheological terminology has arisen[14,15,70,88,90]; there have been frequent instances of the incorrect employment of different terms, which has been discussed in a number of studies[13-15,70,99,106], as well as others. Thus the term "rheopexy"[107,108] has apparently been used (in conflict with the definition of Freundlich and Yuliusburger[76]) to denote a dilatant increase in the viscosity of the dispersion§; the increase of the viscosity of a surfactant solution with a simultaneous alteration of pH has been called a rheopectic increase[109]. The changes in the viscosity of a polymer solution under the influence of shear deformation are frequently referred to as thixotropic (Refs.110, 111, etc.), which cannot be regarded as correct.

Processes in which the stability or viscosity of the system decreases are frequently classified as thixotropic, although in terms of their mechanisms they can be very remote from thixotropy[106]. As an example, one may quote the decrease of the elastic properties of a polymer solution following the rupture of the three-dimensional network arising as a consequence of the chemical "cross-linking" of the chain, as well as the disruption of gel monolith (swollen fibre, hydrated sorbent, etc.). A different significance is frequently imparted to the concept of colloidal structures in rheological studies; attention has been drawn[71,81] to the insufficiently clear-cut nature of the term "coagulation structures", which does not reflect the entire wide variety of different types of dispersions[5,81,99,112,113].

The inadequate investigation of dilatancy phenomena precludes a sufficiently complete explanation of the fundamental experimental data. For example, it is not clear what determines the difference between the volume of a close-packed disperse phase and its volume under conditions where dilatant flow begins; this difference can be small in some cases[56,114], while in others it can be very significant[57,65-68,115]. Furthermore, the question arises why dilatancy is manifested in poly(vinyl chloride) plastisols ($\phi = 0.5$) for particles of one size, while in the presence of particles of two sizes there is no dilatancy[116]; the dilatancy of paint and varnish systems based on TiO_2 disappears at 50 °C,[64] while in the case of quartz glass dispersions it disappears at 80 °C.[117]

Studies have been published recently on the rheological properties of PCS. It was found that PCS_2 (with a limited volume of the medium) at moderate and low concentrations are of the dilatant type under certain conditions in contrast to PCS_1 which are pseudoplastics. A detailed quantitative characterisation of these dispersions permitted an interpretation, somewhat different to the previous one, of the deformation processes and the establishment of the overall factors which determine the onset of a dilatant regime in various systems.

III. DILATANT-THIXOTROPIC TRANSFORMATIONS OF PERIODIC COLLOIDAL STRUCTURES

The differences between the PCS of different types are determined by the nature and forces of the interaction between micro-objects[5,81]. The PCS_1, which have arisen as a consequence of the predominance of attraction forces over long distances, are thixotropic systems which are both reversible and partly or completely irreversible. A second type of periodic colloidal structures (PCS_2), with a limited volume of the dispersion medium, is characterised by the predominance of repulsion forces over attraction forces, i.e. in the PCS_2 the dispersed particles interact under "constrained" conditions, which determines the large-scale nature of the order. Therefore, the PCS_2 fill almost the entire volume and their quasi-crystallinity is frequently readily indicated by their rainbow colour[118]. The constrained conditions play an important role in the behaviour of dispersions: ease of peptisation, liquefaction following the addition of a small amount of electrolyte, and conversion into thixotropic PCS_1 on addition of a further amount of the electrolyte (Fig.7) are characteristic of PCS_2.[5] The PCS_2—dispersions stabilised by the presence of double ionic layers (DIL) or adsorption-solvate layers (ASL)—have dilatant properties [this has been established in a study of aqueous dispersions of polyacrylonitrile (PAN) [66-68,119] and Al_2O_3 (Refs.120–123 and others)].

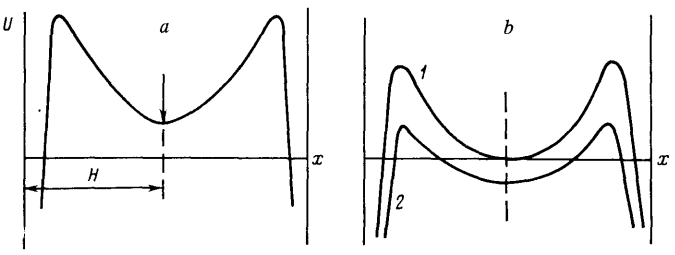


Figure 7, Potential curves for the interaction of particles: *a*) in the presence of a low content of electrolyte—in PCS_2; *b*) with increase of the content of electrolyte—in PCS of an intermediate type (curve *1*) and in PCS_1 (curve *2*).

§ It has been suggested[15,70] that the anomalous increase of viscosity on shear deformation without an increase in the volume of the system be called kinepexy (instead of quasi- or pseudo-dilatancy, antithixotropy, etc.).

PAN dispersions ($a \approx 150$ nm; ξ-potential of 40–52 mV), which are dilatant at low NaCl concentrations (0.004–0.024 M) and thixotropic at moderate concentrations (0.024–0.035 M), belong to stable ion-stabilised systems in terms of the nature

of the sedimentation and the magnitude of the charge (Fig.8). Figs.9 and 10 present plots of the function $I/\tau = f(P)$, where τ is the time of the movement of the sphere in the cylinder of the viscometer and P is the applied load. Evidently, with decrease of the NaCl content or with increase of the PAN concentration, the dilatant section begins at lower flow rates and for higher loads. This is due to the increase of the specific effective volume (fraction) of the disperse phase ϕ_e, which includes its real volume ϕ and the volume of the surface layers ϕ_S (immobilised as a consequence of the formation of DIL or ASL on the surface of the particles). An increase of ϕ_e leads to a decrease of the effective free or vacant volume ϕ_V:

$$\varphi_v = 1 - \varphi_e = 1 - (\varphi + \varphi_s) \quad (1)$$

or

$$\varphi_v = \varphi_0 - \varphi_s , \quad (2)$$

where $\phi_0 = 1 - \phi = \phi_V + \phi_S$ is the volume fraction of the liquid medium including the volume of the surface layers (DIL or ASL). The decrease of ϕ_V (as a consequence of the increase of ϕ_S due to the decrease of c_{NaCl} and the expansion of the DIL or the increase of ϕ with increase of the PAN content) leads to a greater constraint on the movement of the particles, which hinders the relaxation of the stresses arising in the system. Therefore the smaller the value of ϕ_V, the lower the rates at which dilatancy begins and at the same time a greater force is required for deformation (other conditions being equal).

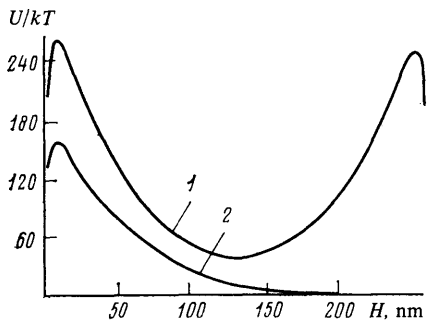


Figure 8. Potential curves for the interaction of PAN particles (for a volume concentration of the disperse phase $\phi = 0.25$) involving three particles with $\zeta = 52$ mV (curve *1*); for two particles with $\zeta = 41$ mV (curve *2*).

The fraction of "free" critical volume corresponding to the onset of the dilatant regime can be designated by $\phi_{V,cr}$. Then

$$\varphi_{v,cr} = 1 - \varphi_{e,cr} = 1 - (\varphi_{cr} + \varphi_{s,cr}) \quad (3)$$

or

$$\varphi_{v,cr} = \varphi_{0,cr} - \varphi_{s,cr} , \quad (4)$$

The above components of the volume fractions are illustrated in the schemes for model PCS_2 (Fig.11). Evidently the quantity $\phi_{e,cr} = 1 - \phi_{V,cr}$ should be approximately equal to the degree of saturation of the volume of the system by the solid phase for close-packed disperse particles in the absence of ionic and solvation layers, i.e. when $\phi_S = 0$ and

$$\varphi_{v,cr} = \varphi_{0,cr} = 1 - \varphi_{cr} . \quad (5)$$

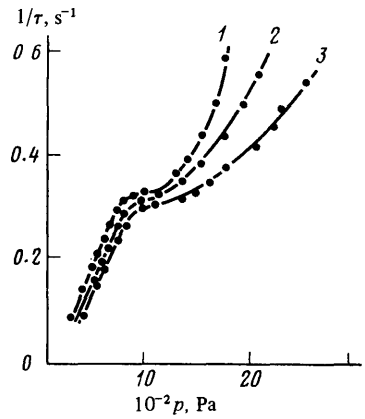


Figure 9. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions ($\phi = 0.165$) at 18 °C and different NaCl concentrations (M): 1) 0.020; 2) 0.014; 3) 0.004.

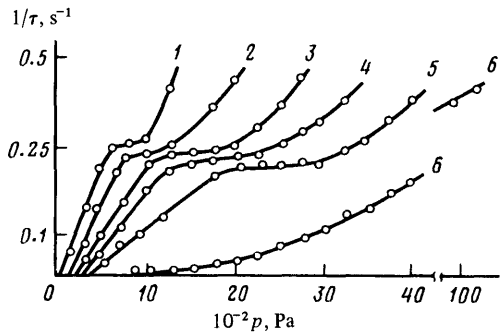


Figure 10. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions at 18 °C and different NaCl concentrations [1)–3) 0.024 M; 4) and 5) 0.005 M] and for different PAN volume fractions [1) 0.127; 2) 0.196; 3) 0.224; 4) 0.351; 5) 0.387; 6) 0.455].

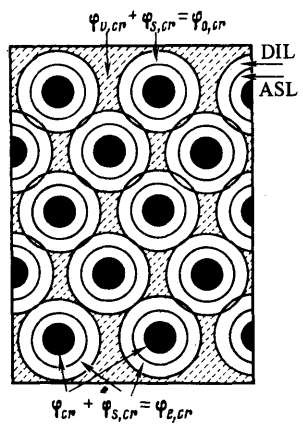


Figure 11. The periodic colloidal structure (PCS_2) stabilised by a double ionic layer. The effective volume (fraction) of the disperse phase and the "free" volume have critical values.

It follows from the above relations between the volume fractions [Eqns.(1)–(5)] that the differences between the critical concentrations of the disperse phase in different instances of deformation are caused mainly by the influence of the DIL and ASL, whose volume fraction $\phi_{s,cr}$ increases the volume fraction of the solid phase ϕ_{cr} to $\phi_{e,cr}$—the effective degree of volume saturation in "close" packing. In this case

$$\varphi_{e,cr} \simeq \varphi_{cr} + \varphi_{s,cr} \,. \qquad (6)$$

Thus the critical effective volume $\phi_{e,cr}$ is equivalent to the volume of the close-packed solid phase corresponding to the appearance of dilatancy; the quantity $\phi_{e,cr}$ then represents the sum of the critical volumes of the solid phase (ϕ_{cr}) and the protective layers ($\phi_{s,cr}$)(ASL and DIL) or, in other words, $\phi_{e,cr}$ is the effective hydrodynamic volume of the disperse phase.

The value of $\phi_{e,cr}$ for an ion-stabilised dispersion (Fig.11) can be determined with some approximation by plotting potential curves by the method of Efremov and coworkers[5,124] or analytically[125,126]. However, in order to obtain the true value of $\phi_{e,cr}$ for which the dilatant regime is established, it is necessary to take into account the relaxation times of the DIL and the entire disperse system, which is difficult. The DIL relaxation is known to be comparatively rapid[127]¶, but this applies also to DIL in the absence of structured boundary liquid layers, which can determine to a large extent the characteristic features of the rheological behaviour of concentrated dispersions—their structural-viscous properties.

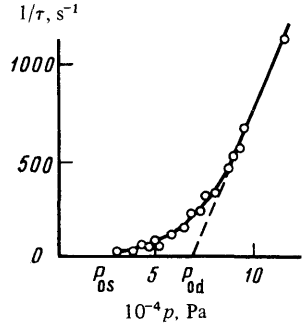


Figure 12. Dependence of the rate of deformation on the shear stress in an aqueous PAN dispersion (ϕ = 0.485) at an NaCl concentration of 0.005 M; P_{0S} = static limiting shear stress; P_{0d} = dynamic limiting shear stress.

The upper concentration limit, corresponding to the disappearance of dilatancy and the onset of structural-viscous flow (Fig.12), is therefore apparently determined by the long relaxation times of the system as a consequence of the decrease in the thickness of the liquid layers ($\phi_v \to$ min when $\phi \to$ max), the overlap of the compressed DIL, and the decrease of the depth of the energy well (Fig.13), which intensifies the aggregation and coagulation processes. The rupture of the bonds between particles undergoing rearrangement on deformation requires the application of appreciable loads. The system then behaves like thixotropic highly viscous PCS_1, which corresponds to the curve in Fig.12.

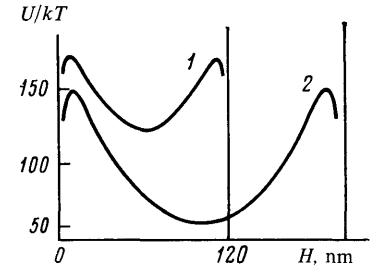


Figure 13. Potential curves for the interaction of the particles of aqueous PAN dispersions: 1) ϕ = 0.415 (distance between the surfaces $H_1 \cong$ 60 nm); 2) ϕ = 0.30 ($H_2 \cong$ 100 nm).[119]

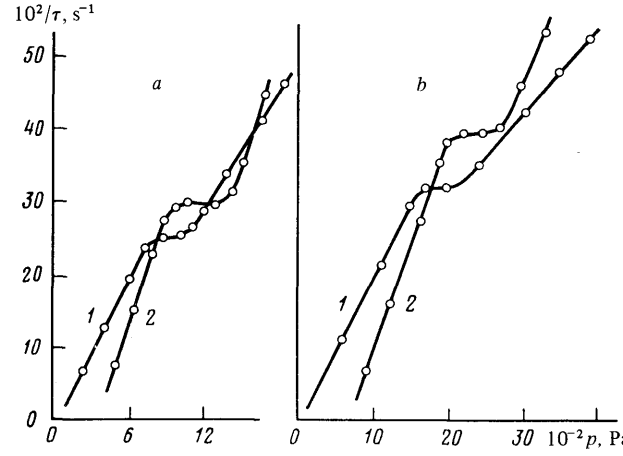


Figure 14. Dependence of the rate of deformation on the shear stress in aqueous PAN dispersions for c_{NaCl} = 0.22 M: *a*) ϕ_1 = 0.15 at 20 °C (curve *1*) and 68 °C (curve *2*); *b*) ϕ_2 = 0.25 at 10 °C (curve *1*) and 50 °C (curve *2*).[46]

With increase of temperature, the dilatant sections of the rheological curves for PAN dispersions shift to the region of higher rates of shear and a greater applied load (Fig.14). It is evident that (a), at a comparatively high temperature (68 °C) and a low PAN concentration (ϕ_1 = 0.15), the dilatant regime is shown fairly clearly as a consequence of the characteristics of the ionic stabilisation (a greater DIL thickness in the presence of a low content of ions and the retention of ionic stabilisation at elevated temperatures) and that (b) an increase of the PAN content shifts the dilatant section (like an increase of temperature) to the region of high rates of shear and a greater applied load.

¶ The DIL relaxation time θ is a function of the system parameters. Under the usual conditions, θ for a given solvent and electrolyte depends only on the concentration c_{el}. Thus, for an aqueous solution at the usual temperature $\theta \cong 10^{-10}/c_{el}$; when $c_{el} = 10^{-3}$ *N*, we have $\theta \cong 10^{-7}$ s.[127]

Interesting results have been obtained[120–123] in the study of aqueous dispersions of two fractions, I and II, of Al_2O_3 (with effective particle diameters of 4 and 40 μm and a nearly ellipsodal particle shape with an axial ratio of 1 : 3). The dispersion medium was a solution of sodium carboxymethylcellulose (0.1 wt.%); at pH 9.5 the particles had a ξ-potential of approximately −140 mV. Plots of potential curves for the interaction of the particles of the highly disperse Al_2O_3 system with $\phi \cong 0.50$ showed that it is a PCS_2 system in which repulsive forces predominate between the particles (separated by an average distance of 35 nm). The dispersion of large Al_2O_3 particles, fixed at the secondary potential minimum, is a thixotropic PCS_1. The study of the rheological properties of these systems reveals the following features.

1. The highly disperse PCS_2 (fraction I) has dilatant properties (Fig.15, curve *1*) due to the constrained conditions in the interaction of the particles.

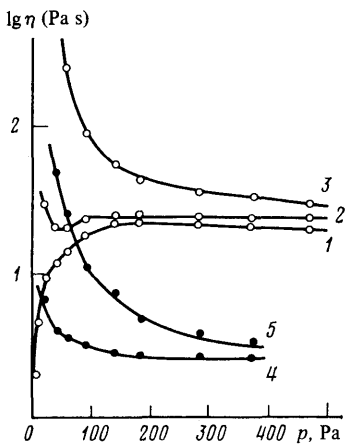


Figure 15. Rheological curves for Al_2O_3 dispersions characterising the change in the type of PCS as a function of the degree of dispersion of the solid phase and the KCl concentration (M): 1) 0; 2) 0.08; 3) 0.25 (fraction I); 4) 0; 5) 0.25 (fraction II).[122]

2. When small amounts of KCl are introduced into the PCS_2, the dilatant properties degenerate and the deformation regime becomes close to a Newtonian regime. A further addition of the electrolyte causes (in conformity with Fig.7) the conversion of the PCS_2 into the thixotropic PCS_1 (Fig.15, curves *2* and *3*).

3. When an electrolyte is introduced into the thixotropic PCS_1, formed by fraction II, with a low degree of dispersion, the latter is stabilised as a consequence of the increase in the depth of the minimum (Fig.15, curves *4* and *5*).

4. The dilatant regime in the deformation of the PCS_2 passes to a structural-viscous (thixotropic) regime when the disperse composition of the system is altered by adding to the latter fraction II, with a low degree of dispersion, instead of the same mass of fraction I (Fig.16). The transition $PCS_2 \rightarrow PCS_1$ then takes place and complex higher-order structures are formed (Fig.17);[99,128] in the latter the interaction of the large central particle with small particles can be illustrated by the periodic potential curve (Fig.18).[129] The breakdown of these complex aggregates under an external influence determines the structural-viscous deformation regime.

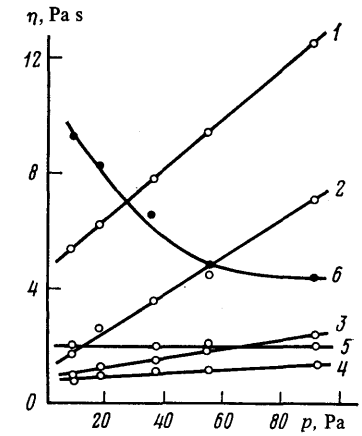


Figure 16. Flow curves for Al_2O_3 dispersions ($\phi \cong 0.50$) corresponding to different weight ratios of the fractions (I/II): 1) 80/20; 2) 70/30; 3) 50/50; 4) 40/60; 5) 20/80; 6) 10/90.[121]

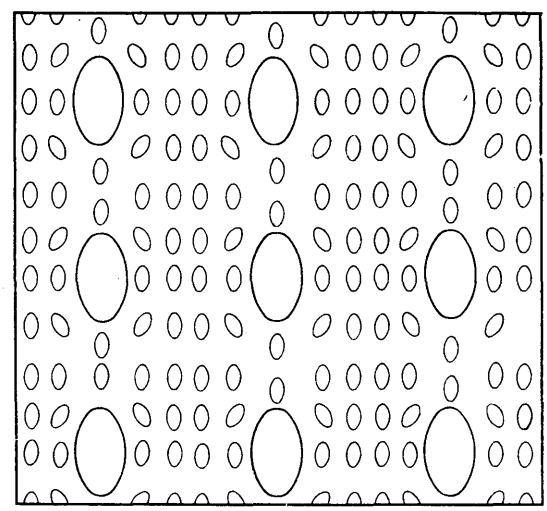


Figure 17. An element of a complex periodic colloidal structure consisting of large and small particles.

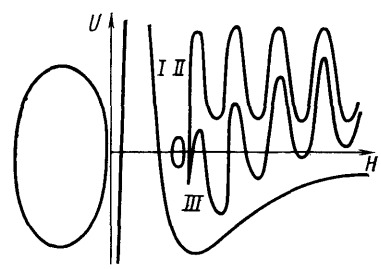


Figure 18. Potential curves characterising the interaction of small ellipsoidal particles with a large ellipsoidal particle: I) curve for the pair interaction of the particles; II) periodic curve for the interaction of several small particles in the absence of a large particle; III) overall curve for the interaction of heterogeneous particles.

5. The dilatant deformation regime in PCS_2 also passes to the structural-viscous regime after the introduction into the system of 1–2 wt.% of Latnensk clay (or a modified aerosil) instead of the corresponding amount of Al_2O_3 (Fig.19).[121] The considerable stabilisation of the dispersion after the introduction of the clay may be a consequence of the aggregation of heterogeneous particles, particularly when account is taken of the possibility that the clay particles have a permanent electric dipole moment[5,99]. The breakdown of these aggregates can lead to the structural-viscous deformation regime.

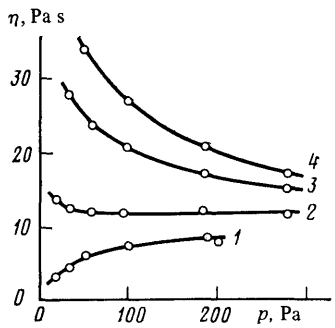


Figure 19. The influence of added Latnensk clay (instead of the corresponding amount of Al_2O_3) on the flow of Al_2O_3 dispersions (fraction I); percentage of clay (%): 1) 0; 2) 1.0; 3) 1.5; 4) 2.0.[121]

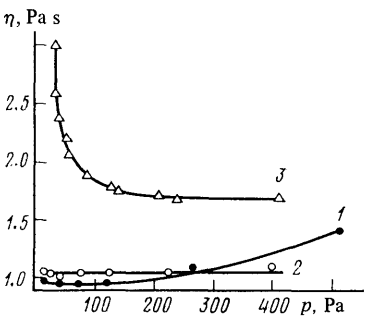


Figure 20. Dependence of the viscosity of aluminium hydroxide dispersions on the shear stress at different aluminium oxide nitrate concentrations (g litre^{-1}): 1) 16; 2) 60; 3) 100.[130]

Tikhonov and coworkers[121–123] showed for the first time that the rheology of dispersions is determined by their stability and hence by the conditions and the nature of the interaction forces between micro-objects: dilatant properties are manifested primarily in systems resistant to aggregation, under constrained conditions, while structural-viscous plastic properties are characteristic of less stable thixotropic dispersions.

The results of the study of dispersions of aluminium hydroxide in aqueous solutions of aluminium oxide nitrate have been published[130]. The content of the solid phase was 64% (ϕ = 0.64) in dispersions (1) and (3) and 62% (ϕ = 0.62) in dispersion (2). The shape of the colloidal particles (average diameter ~1 μm) was nearly spherical. In the presence of a low content of aluminium oxynitrate, the $Al(OH)_3$ dispersions are resistant to aggregation and exhibit dilatancy (Fig.20, curve *1*); with increase of the content of ions, there is a transition from the dilatant flow regime to the Newtonian regime and further to the structural-viscous regime, i.e. the $PCS_2 \rightarrow PCS_1$ transformation takes place (Fig.20, curves *2* and *3*). An increase of temperature causes the liquefaction of the system (as for PAN dispersions).

A transition of dilatant dispersions (ϕ = 0.48) of poly(methyl methacrylate) (PMMA) in dibutyl phthalate (DBP) to thixotropic structural-viscous systems on successive replacement of DBP by dioctyl sebacate (DOS) has been demonstrated[131] (Fig.21). The authors[131] explained this by the difference between the solvating properties of DBP and DOS, with which one can in the main agree, although the question of the role of the double ionic layers (DIL), which can significantly affect (together with solvation) the behaviour of dispersions, particularly in the region of high DOS concentrations, remains open. However, there can be hardly any doubt that the $PCS_2 \rightarrow PCS_1$ transition occurs in this instance.

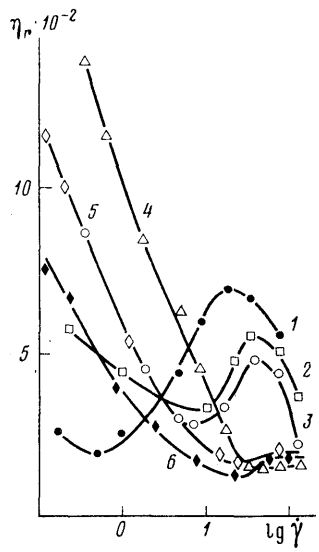


Figure 21. Dependence of the relative viscosity of a PMMA dispersion in DBP, DOS, and their mixtures on the rate of shear. DOS content (vol.%): 1) 0; 2) 10; 3) 20; 4) 40; 5) 70; 6) 100.[131]

IV. FACTORS DETERMINING THE DILATANT DEFORMATION REGIME

In the introduction it was noted that many investigators have pointed out various factors which in their view are responsible for the appearance of dilatancy on deformation of various dispersions. Consideration of these factors leads to the conclusion, that despite the significant differences in the nature and type of their influence, their action reduces ultimately to a decrease of the "free" volume ϕ_v of the system and to a greater retardation of the relaxation processes. It is then found that the results obtained in

the study of PCS, which were described in the preceding section, are of general significance and their use in rheological research is of definite interest. We shall consider the principal factors to which the majority of investigators refer when they explain the mechanism of the appearance of dilatant flow conditions.

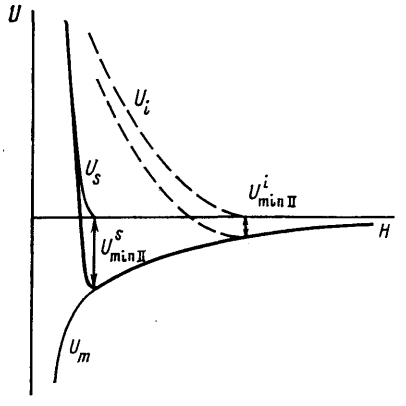


Figure 22. Potential pair interaction curves; $U^S_{min\,II}$—secondary minimum due to the presence of solvate layers on the surface; $U_S(H)$—repulsion energy curve for these layers; $U^i_{min\,II}$—secondary minimum due to the predominance of the attraction energy over long distances [$U_m(H)$ curve] over the double ionic layer repulsion energy [the $U_i(H)$ curve][99].

1. Adsorption-solvate Layers

It has been established[69] that dispersions (ϕ = 0.48) of the acrylonitrile–methacrylate copolymer in 1-propanol, 2-nitro-1-propyl acetate, and 2-nitro-1-butyl acetate are viscoplastic, while dispersions of the same copolymer in 2-nitro-1-propanol and 2-nitro-1-butanol are dilatant. The authors[69] explain the dilatancy by solvation and by the unusual behaviour of hydrogen bonds; at the same time they also postulate that the breakdown of the aggregates of the disperse particles formed at rest and the formation of coagulation structures should likewise give rise to dilatancy. Naturally, in viscoplastic dispersions the lower degree of solvation may be responsible for their structure being analogous to that of PCS_1. On the other hand, the more stable solvate layers, which might have been influenced by hydrogen bonds, can (when their thickness h is sufficiently great) lead to constrained conditions—a decrease of ϕ_V and the formation of dilatant PCS_2. This agrees with the fact that boundary liquid layers with retarded relaxation can impart a high viscosity to a system under constrained conditions. However, a final conclusion requires the experimental detection of these layers and the determination of the role of DIL, which should exist on the surface of the polymer particles and should also exert a stabilising effect and correspondingly diminish ϕ_V.

The rheology of PMMA dispersions in dilute poly(vinyl chloride) solutions and in dialkyl phthalates has been investigated[132,133]. It was shown that thixotropic behaviour is characteristic of dispersions with weak solvation and adsorption effects; on the other hand, the onset of dilatancy is associated with a fairly pronounced manifestation of these effects and also depends to some extent on the viscosity of the dispersion medium. A dilatant latex dispersion at rest has been considered[45] as a system of non-interacting swollen micro-objects separated by a structural-mechanical barrier. For fairly large shear stresses, capable of deforming layers of the swollen polymer and of overcoming the repulsion forces, a structural network arises, being deformed after the cessation of external influences. It has been concluded that, with increasing degree of lyophilicity, polymer dispersions pass from the thixotropic to the dilatant state (in other words, the $PCS_1 \rightarrow PCS_2$ transformation takes place). Thus, by altering the interaction at the polymer–plasticiser interface and by creating the optimum structure of the swollen layer on the surface of the polymer particles, it is possible to impart dilatant properties to the system. The decisive importance of solvation and adsorption in the dilatancy of dispersions has also been discussed in a number of other studies[63,64,134–137].

It has been established[63,64] that TiO_2 dispersions (ϕ = 30–42%) in white spirit possess thixotropic or dilatant properties depending on the content of alkyd resins: the dispersions are thixotropic for c_{SA} = 2–5% and dilatant for c_{SA} = 7.5%, where c_{SA} is the concentration of the surfactant. Thus the comparatively thin adsorption layer of the surfactant apparently determines the interaction of the TiO_2 particles over a long distance with formation of PCS_1 (Fig. 22);[99] thicker and highly viscous layers lead to constrained conditions and PCS_2, whose electrical conductivity is smaller by several orders of magnitude than that of PCS_1. The fact that dilatancy disappears at temperature up to 50 °C or with increase in the solvent power of the solvent constitutes an important confirmation of the validity of the postulate that the ASL play a decisive role in imparting dilatant properties to TiO_2 dispersions; ion-stabilised PCS_2 retain dilatancy at relatively higher temperatures[138]. A sharp decrease of the dilatancy of starch dispersions (ϕ = 0.48) with increase of temperature has been observed[117,139], while the dilatancy of an aqueous dispersion of quartz glass (ϕ = 0.77) disappears only at 80 °C. The ζ-potential is ~|30| mV for quartz particles in an aqueous medium at pH 5.0;[134] consequently the dispersion was in all probability an ion-stabilised PCS_2.

The influence of the adsorption layer of the surfactant on the effective volume fraction of the disperse phase for a small thickness of the layer h, i.e. $h/a \ll 1$,[140,141] has been taken into account with the aid of the following expression:

$$\varphi_e \approx \varphi(1+3\,h/a)\,, \qquad (7)$$

where ϕ is the volume fraction of the solid phase, h the thickness of the surfactant layer, and a the radius of the particles.

2. Double Ionic Layers

In view of their wide occurrence, DIL frequency exert a decisive influence on the onset of the dilatant deformation regime. This has been confirmed in the studies quoted in the previous section as well as a number of others. Thus the influence of the concentration of the dilute electrolyte, the nature and pH of the liquid medium, and the size and concentration of the disperse SiO_2 particles on the nature of the deformation of the system, has been studied in detail[134]. The determination of the sedimentation volumes and of the ζ-potential made it possible to describe the stabilisation of the particles and to find the effective volume of the disperse phase ϕ_e and its ionic-electrostatic and solvation constituents.

This resulted in an explanation of the deviation of the rheology of SiO_2 dispersions from Newtonian behaviour corresponding to the Einstein equation

$$\eta=\eta_0(1+2.5\varphi), \quad (8)$$

where η and η_0 are the viscosities of the dispersion and of the dispersion medium and ϕ is the volume fraction of the disperse phase.

Depending on the system parameters and the flow regime, SiO_2 dispersions had thixotropic or dilatant properties, which was explained by the electroviscous effect, i.e. by the influence of the DIL on the deformation process, and also by the presence on the surface of the particles of a solvate layer with a thickness h. The value of h was found graphically[134] using Eqn.(8) in the form

$$\eta_{sp}=2.5\ \varphi_e=k\varphi\ . \quad (9)$$

From Eqn.(9), it is possible to obtain the expression†

$$\frac{k}{2.5}=\frac{\varphi_e}{\varphi}=\frac{\pi(a+h)^3}{\pi a^3}=\left(1+\frac{h}{a}\right)^3, \quad (10)$$

where a is the radius of the disperse particles. As mentioned by Greenberg and Chang[134], the values of h were somewhat too low (1.5–1.7 nm).

The study of the viscous changes in a latex during dialysis led to the discovery of the so-called electroviscous effect, which consists in the fact that the viscosity of the latex increases by a factor of several hundreds as a result of dialysis and returns to its initial value after the addition of an electrolyte[142,143]. This reversible sol $\rightleftharpoons$ gel transformation indicates the occurrence of the $PCS_2 \rightleftharpoons PCS_1$ transition, which takes place in the ion-stabilised latex as the concentration of ions is varied. It has been shown[144] that the density of the electric charge on the surface of latex particles and the ionic strength of the liquid medium have a significant influence on the rheology of dispersions as a consequence of the increase of the effective volume of the particles, which increases their hydrodynamic volume; the relation between the increment of the radius of the particles and the Debye parameter κ has been discussed.

Thus ASL and DIL are the main factors in dilatancy; their role reduces to increasing the effective volume of the disperse phase $\phi_e = \phi + \phi_S$ or, in other words, to decreasing the free volume of the system $\phi_V = 1 - \phi e$. When these layers are fairly large, constrained conditions appear even in dilute dispersions, in conformity with Eqn.(3).

The mechanism of the influence of ASL and DIL consists in the fact that, under constrained conditions, the displacement of the particles relative to one another on shear leads to the overlap of the layers and thei mutual repulsion, which gives rise to a stress whose relaxation depends on many system parameters. The ideas developed in relation to these phenomena have been confirmed by numerous experimental data and considerations put forward by various investigators. Thus a relation has been pointed out between dilatancy and (a) the free volume of the dispersion[56,62,145–151], (b) solvation and adsorption[36,40,45,63,64,131–137], (c) the double ionic layer, the ζ-potential, and the stability of colloidal particles[67,68,119,134,143–146,152–155], (d) the interaction of the particles and the formation of a bond[40,42,59,62,98,121–123,130,134–136,138,143,156–158], and (e) the superposition and repulsion of the ASL and DIL [63,64,121–123,135]; dilatancy has been explained in a number of studies by the dominant effect of repulsion forces[6,45,67,68,119,122,123,138,146,159]. Ideas concerning entropic repulsion have been envoked[45] (although apparently it would be more correct to employ the concept of osmotic pressure[160,161] or, in the general case, the concept of the disjoining pressure[5,81]).

The above principal results of studies designed to determine the factors governing dilatancy, which are by no means complete, are in good agreement with conclusions reached in numerous experimental and theoretical studies of the general characteristics of the rheological behaviour of colloidal structures under different conditions. In addition to the series of studies quoted above (for example Refs.54, 79, 80, 83, 134, 146, 152, etc.), we may also mention investigations[162–168] in which quantitative relations between the rheological and energetic parameters of dispersions have been discussed.

3. Peptisation

The peptisation of aggregates to individual disperse particles has the following consequences: (1) protective surface layers (ASL and DIL) arise on the fresh surfaces; (2) the thickness of liquid layers between the particles diminishes and the distribution of particles becomes more uniform; (3) the overall surface area of the particles increases; (4) the free volume of the dispersion ϕ_V diminishes. The deformation of dispersions unstable as regards aggregation can therefore entail the peptisation of the aggregates under the influence of shear forces[78] with formation of ASL and DIL of definite thickness, which should reduce sharply the values of ϕ_V. Thus peptisation is an important auxiliary factor in dilatancy. On the other hand, the main factors remain ASL and DIL in this case also, since only their formation diminishes the free volume and gives rise to constrained conditions. Naturally, in dispersions which are stable as regards aggregation, there will be either no peptisation at all or, under the influence of the flow, a reversible aggregation and deaggregation process may occur, which will be less pronounced the more stable the system[77–79].

The important role of peptisation and of the uniform distribution of particles in the manifestation of dilatancy in the deformation of various dispersions has been indicated[14,63,71,169–171]. It has been established[172] that weakly disperse suspensions of aggregates and individual PMMA latex particles (ϕ = 0.5) in DBP are dilatant (Fig.23), which has been explained tentatively by the orientation of the particles in the stream and by the formation of a new additional coagulation structure. One should apparently agree with the authors' claim[172] that the peptisation of aggregates of PMMA particles leads to the formation of PCS_2 (of an additional "coagulation" structure# according to Bubis et al.[172]), a decrease of ϕ_V, and the onset of dilatancy.

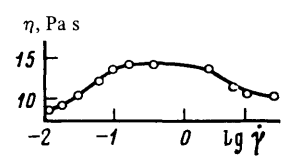


Figure 23. Dependence of the viscosity of a PMMA dispersion in DBP (ϕ = 0.50) on the shear velocity gradient[172].

†Series expansion of the cube of the sum and retention of only the first two terms for $h/a \ll 1$ yields Eqn.(7).

#It is erroneous to refer to colloidal structures of the PCS_2 as coagulation structures. The formation of PCS_2 is a forced process accompanied by an increase in the energy of the system[119].

At the same time the explanation of dilatancy is frequently restricted to a general postulate concerning "changes in the packing of coagulation structures"—network, chain, etc. structures. Thus it has been assumed[153] that the dispersion investigated consists of individual floccules in which colloidal particles form chains. In a shear flow the floccules combine with displacement of the particles from their equilibrium positions. A change in the packing of the particles on dilatancy with formation of a less ordered structure has been noted[145]. The authors of other investigations also believe that dilatancy results in the formation of various "coagulation structures", etc.

One cannot reject the possibility of aggregation and deaggregation processes in a flow[77-80,86], but the hypothesis of such processes must be adequately justified in each specific instance, which is as a rule difficult when rheological data alone are used. Therefore many investigators have endeavoured to employ various modern methods of physics and physical chemistry in rheological research. Here one must note the attempts at a quantitative description of the interparticle interaction forces[67,68,119-123,134,142,145,149], thermodynamic properties[33,34,83,86,137], and physicochemical characteristics[63,79,80,152,164,173] in systems undergoing deformation.

At the same time the modification and improvement of rheological methods are being continued. Methods based on unidirectional and periodic deformations and their superposition have been used[14,88,170,171] in the study of the structures of aerosil dispersions in organic and organosilicon liquids and also of aluminium naphthenate gels. It has been established that, under certain deformation conditions, the dependence of the dynamic modulus of shear G^{I} (the real component of the complex modulus $G^{\times} = G^{I} + iG^{II}$) on the extent of periodic deformation (on the sinusoidal regime) is characterised by a marked maximum; the increase in the stability of the system in this instance is explained by the transition of the coagulation structure as a result of peptisation to a more ordered state (i.e. by the $PCS_1 \rightarrow PCS_2$ transition). Similarly it has been observed[89] that 70% hydrodispersions of kaolin are thixotropic at low frequencies of sinusoidal oscillations and dilatant at high frequencies ($PCS_1 \rightarrow PCS_2$).

It was noted previously that dilatancy degenerates with increase of temperature. However, the results of different investigators have shown that, to a first approximation, there are two temperature ranges in which a dilatant regime passes to a Newtonian or structural-viscous regime. The first range (40–50 °C) corresponds to an appreciable breakdown and rearrangement of the ASL. Thus it has been established[63] that dilatancy of SiO_2 dispersions in solutions of alkyd resins in white spirit disappears below 50 °C as a consequence of the increasing solvent power of the solvent and the decreasing degree of adsorption of the resins. The second range (75–90 °C) corresponds to a sharp increase of the rate of relaxation of the DIL and of the stresses which have arisen as a result of the operation of external forces. The dilatant properties of concentrated aqueous dispersions of SiO_2 [117] and iron oxides[174] as well as, apparently, dilute ion-stabilised PAN latexes[67,68] disappear in this region. Naturally, other variants are also possible. It has been observed[175] that the relative viscosities of dilute bentonite suspensions depend little on temperature, while at high concentrations the viscosity increases appreciably and depends markedly on temperature, which has been explained by structure formation.

An attempt has been made[145,176] to devise a quantitative theory of the dilatant behaviour of dispersions by taking into account the van der Waals attraction forces, the DIL repulsion forces, and the external forces giving rise to shear deformation. A careful analysis of the dimensionless geometrical, energetic, and mechanical parameters of a dispersion undergoing deformation ($\phi = 0.65$) has been carried out[149]; equations describing the rheological properties of disperse systems which thicken and liquefy under the influence of shear deformations have been put forward. Rheological equations for thixotropic-dilatant structures have also been proposed[156,177]. The dependence of the relative viscosities of dispersions of spherical non-interacting particles on the volume fraction has been expressed[178] by the single-parameter equation

$$\eta = \left[1 + \frac{1.25\varphi}{1 - (\varphi/\varphi_{max})}\right]^2, \qquad (11)$$

where ϕ_{max} is the value of ϕ corresponding to close packing. In the presence of ASL or DIL on the surface, ϕ_e replaces ϕ and an equation of type (10) or, when the thickness of these layers is small, Eqn.(7) is used[178].

The following equation is employed for concentrated dispersions of glass spheres ($d \cong 27-118$ μm) in low-molecular-weight polyisobutylene[179]:

$$\eta_r = \left[1 + 0{,}75\left(\frac{\varphi/\varphi_{cr}}{1 - \varphi/\varphi_{cr}}\right)\right]^2. \qquad (12)$$

For monodisperse systems, $\phi_{cr} \cong 0.6$§ and for bimodal systems the dependence of the viscosity on the content of the smallest particles (at a constant overall concentration) passes through a minimum, which is related directly to the thixotropic and dilatant properties of the dispersions. An analogous relation has been observed in Refs.121, 180, 181, etc.

V. DILATANCY OF MICELLAR SOLUTIONS OF SURFACTANTS, SOAP GELS, AND SURFACE MONOLAYERS

Micellar solutions are known to be systems in thermodynamic equilibrium. The micelles have different shapes—usually spherical, cylindrical, or lamellar. The surface of cylindrical micelles is non-isotropic (has no circular symmetry), which can be accounted for by the unusual orientation of the dipolar molecules on the surface[113,182]. The micelles present in solution at not unduly high surfactant concentrations consist of hydrated surfactant molecules; there are comparatively thick liquid layers between the micelles[183].

The results of a study of the viscous properties of 1–15% aqueous solutions of dioctyl sulphosuccinate have been published[108]. At a concentration of 5% and above, the solutions prepared using distilled water are thixotropic (i.e. constitute a PCS_1). On the other hand, when inorganic electrolytes are present ($c_{el} = 1$ *N*), the viscosity of the system diminishes at low rates of deformation and increases at high rates. These rheological anomalies have been explained[138] by taking into account the salting-out effect of ions, which results in the formation of comparatively large micelles separated by hydrate layers (PCS_1), and the breakdown of large micelles into small ones at high rates of deformation, which leads to constrained conditions and the appearance of PCS_2. Thus the transition from the thixotropic to the dilatant flow regime observed in these solutions can be explained satisfactorily by the $PCS_1 \rightarrow PCS_2$ transition (Fig.24). Furthermore, under the conditions of salting-out in surfactant solutions, there is also a possibility of the preferential formation of extended instead of spherical micelles, which enhances the viscoelastic properties[184-186].

§ The value $\phi_{cr} \cong 0.6$ does not correspond to the close packing of monodisperse spheres ($\phi \cong 0.74$). This discrepancy is apparently due to the presence of ASL or DIL on the surfaces of the glass spheres [see Eqn.(6)].

The mechanism of the dilatant increase of viscosity in dilute solutions of hexadecyltrimethylammonium bromide in methylnaphthlene has been explained[187] by the appearance of a network of rod-shaped micelles under the influence of the flow. It has been suggested[138] that the network is formed from the very beginning of the deformation, but at low rates the rupture of the bonds between the micelles predominates (thixotropic liquefaction), while at higher rates the micelles themselves break down, which leads to constrained conditions and the formation of a PCS_2. These solutions have anomalous rheological properties at 22 °C, while at higher temperatures they become Newtonian liquids.

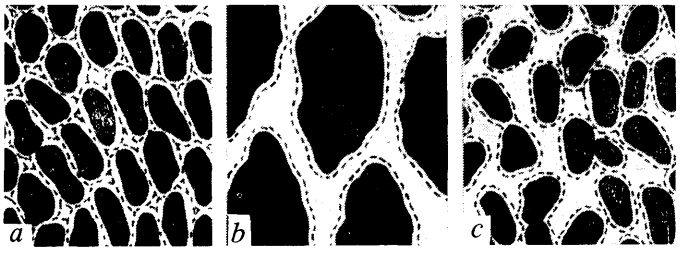


Figure 24. Schematic illustration of the changes in the micellar structure of surfactant solutions after the addition of an electrolyte ($a \rightarrow b$) and with increase of the rate of shear deformation ($b \rightarrow c$).

(a) Dilatancy of Soap Gels

Dilatant thickening has been observed in ammonium oleate[188] and organo-aluminium salt[17,74] gels. An increase in the stability of aluminium naphthenate gels (6%) (both pure and filled with aerosil) in medicinal liquid paraffin as a result of the superposition of harmonic oscillations at a constant rate of shear has been demonstrated[169,189]. It has been noted[190] that the measurement of the dynamic moduli of soap gels itself causes some disruption of the structure. A considerable increase in the stability of hydrocarbon gels of ammonium abietate under the conditions of shear has been observed[191].

In discussing these instances of dilatancy, it is necessary to take into account the microheterogeneous nature of surfactant gels. Presumably, at sufficiently high rates of shear the elements of the gel lattice—floccules consisting of associated surfactant and solvent molecules (ions)—have insufficient time to relax and therefore decompose, which leads to constrained conditions and the formation of structures analogous to PCS_2. This explanation is consistent with the results of a number of studies. Thus a study[192] of the rheological properties of plastic calcium greases, consisting of soap–oil gels, established that (a) the size and shape of the particles of the disperse phase (soap fibres) have a decisive influence on the properties of the grease and (b) a decrease in the size of these particles is accomapnied by an increase of viscosity and stability and also by an increase of the colloidal stability of the system. The common features in the mechanism of the influences of the degree of dispersion, the distribution of grain sizes, and peptisation on the structural-mechanical properties of PCS of various types can be readily seen. Incidentally, calcium greases are optically anisotropic, which shows that the structure is ordered[193].

The results of the investigation of "filled" systems, which are of great theoretical and practical importance, have been published in a number of communications[169,170,189,190,194,195]. The phenomenon of the breakdown of the aluminium naphthenate gel structure in liquid paraffin filled with aerosil has been investigated[170] with periodic deformations and with stabilisation of the structure in unidirectional deformation. It has been established[194] that aqueous bentonite gels, to which a small amount (a fraction %) of non-ionic surfactants has been added, are thixotropic systems; in the presence of ionic surfactants (anionic or cationic) these gels exhibit dilatant properties. It is significant that surfactants, or more correctly the DIL arising on the surface of adsorption layers, are responsible for the change in the properties of bentonite gels¶. On the other hand, the clay particles themselves, being "encapsulated", play an auxiliary role in this process. Such systems can be regarded as intermediate between typical hydrophobic dispersions and micellar solutions. On the other hand, it has been shown[196] that low-tar bitumens with a high content of asphaltenes behave like typical disperse systems, while high-tar bitumens with a low content of asphaltenes have rheological properties similar to those of concentrated polymer solutions. Bitumens with transitional properties are located between these extreme structural-rheological types.

(b) Dilatational Surface Viscosity of Monolayers

A method has been proposed[197] for the determination of the surface viscosities of surfactant monolayers based on the joint dynamic study of the surface pressure and the surface potential; the results of the investigation of the dynamic properties of insoluble elastic and highly elastic monolayers, which permit the determination of the role of the dilatational viscosity in the behaviour of these monolayers, have been published. The behaviour of a liquid drop in another liquid phase has been analysed[198]; it was shown that the period of circulation in the equatorial plane of the drop can be used to calculate the quantity $3k + 2\varepsilon$, where k is the dilatational surface viscosity and ε is the surface shear viscosity. A method for the determination of k has also been proposed in another study[199]†.

VI. DILATANCY OF SOLUTIONS OF HIGH-MOLECULAR-WEIGHT COMPOUNDS

Polymeric molecules frequently form aggregates or associated complexes in solution, such behaviour being usually quite pronounced in solutions of polar polymers and polyelectrolytes. As a result of the interaction of the aggregates, ordered structures may arise, which are analogous, on the one hand, to PCS, and, on the other hand, to liquid crystals[201–208]; this can be accounted for by the common features of the operation of ionic-electrostatic and molecular forces in disperse systems and in polyelectrolyte solutions[99].

¶ *In contrast to this, the non-ionic hydroxyethylated octyl alcohol adsorbed on particles of phthalocyanine pigments sharply decreases the thixotropy of the dispersion as a consequence of the formation of fairly extensive ASL.*[195]

†The dilatational viscoelastic properties of a thick film with a single soluble surfactant have been analysed quantitatively[200].

In a number of recent studies it has been shown that solutions of many polymers are structured. Thus the presence of involved ordered complexes—globular associated species and microgels (the authors[213] believe that these formations can be compared with colloidal particles)—has been demonstrated[209-212] in aqueous solutions of poly(vinyl alcohol) (PVA). It has been observed[214] by thermal, rheological, and morphological methods that very large aggregates of hydrated macromolecules exist in aqueous solutions of polyvinylpyrrolidinone, hydroxyethyl-starch, poly(vinyl alcohol), and poly(ethylene glycol). The aggregation of macromolecules in solutions of different polymers has also been discussed in a series of other studies[215-217]. Rheological studies of a solution of polyisobutylene in liquid paraffin have led to the conclusion[218] that structures made up of polymer chains exist in this solution.

Structured solutions of many polymers have dilatant (antithixotropic) properties[110,111,218-231]. Various factors determining the onset of the dilatant deformation regime have been described in the literature. Some investigators point to the orientation of the structural elements of the polymer, their aggregation and crystallisation, caused by the gradient flux, as well as mixing as fundamental factors in dilatancy[221, 232-237]. Ordered aggregates of macromolecules, strongly interacting with the solvent, constitute a kind of hydrates oriented in the flow[209-212,238-242]. Freshly formed gel fibres have an analogous structure[243]; the crystalline nature of fibrils containing the solvent has been noted[240,244-246]. It has been claimed in a number of studies that the principal condition for the occurrence of dilatancy is low solubility of the polymer and the consequent presence of associated complexes and aggregates of molecular chains (see Refs. 226, 230, 232, etc.). It has been shown[247] that the existence of a fluctuation network in solutions of methyl methacrylate–methacrylic acid copolymers is responsible for antithixotropy both under the conditions of simple shear and in complex (predominantly longitudinal) flow deformations.

The data presented permit the conclusion that the increased viscosity of polymer solutions under the conditions of shear is a consequence of the peptisation of the associated chain species and chain aggregates and of the appearance of constrained conditions, under which deaggregated formations–partly decomposed aggregates and individual macromolecules as well as their separate units—interact. When the degree of structure formation in the solution is low, complex and structure formation intensify in the first deformation stage[224]. At higher rates there is also a possibility of the peptisation of more stable complexes, leading to constrained conditions in dilatancy[138].

The ideas developed here are consistent with experimental data and with the conclusions of other investigators. Thus the formation of a second structure under the conditions of shear deformations after the partial breakdown of the first structure in polymer solutions has been discussed[218]. Evidently the second structure arises as a result of the peptisation of the first structure with formation of uniformly distributed solvated microfibrils under constrained conditions. The increase of viscosity in the initial state of the deformation of solutions of a number of polymers has been explained[248-250] by orientational effects. The observed relative expansion of fibrous polymer gels in the extension process has been attributed[248] to a rearrangement of their structure.

The peptisation of aggregates and microgel particles in polymer solutions can be illustrated by an example from the technology of paper manufacture. The grinding of a freely flowing paper mass by a roller reduces mainly to the dispersion of large fibrous particles until very fine hydrated fibres (fibrils) are obtained. For a high degree of grinding (for "fat" or "slimy" grinding), the mass becomes gel-like with an increased viscosity, which is due to the increase of the overall surface area of the fibrils and the decrease of ϕ_v.[251] In this case the freely disperse system is converted into PCS_2 as a result of peptisation. To complete the analogy, one can imagine that after fat grinding the fibrilled mass undergoes further dispersion up to "molecular" peptisation with formation of a "structured solution" possessing dilatant properties and resembling the usual dilatant polymer solutions[5].

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The common features in the rheological behaviour of PCS and polymer solutions, determined by the following common characteristics of the interaction of micro-objects, may be noted.

1. PCS_2 are dilatant as a consequence of the dominant operation of repulsion forces in the system, or, in other words, the manifestation of the positive disjoining pressure $\Pi_2 > 0$; PCS_1 are thixotropic and are characterised by a negative disjoining pressure $\Pi_1 < 0$.

2. In polymer solutions the peptisation or deaggregation of structural elements (complexes, associated species) under conditions involving the stabilisation of the ASL or DIL deaggregation products leads to a decrease of ϕ_v, a more uniform distribution of the polymer, and constrained conditions. This is possible when the polymer particles are adequately solvated or protected by ionic layers and the repulsion forces predominate, i.e. $\Pi_2^1 > 0$, which is responsible for dilatancy. If the deaggregation products in solution are not resistant to mutual adhesion, i.e. $\Pi_1^1 < 0$, then in the breakdown process the deformation of structures of one kind will be accompanied by the appearance of those of another, denser kind; the "network continuity" will then be infringed and the viscosity will correspondingly diminish.

The phenomenon of dilatancy has been considered in this review in the simplest form where the increase of the resistance to shear is determined mainly by the properties of the liquid layers separating the micro-objects. However, it is frequently complicated by various concomitant aggregation processes of different kinds, which have been enumerated in the second section. Furthermore, regardless of external influences, syneresis takes place spontaneously in disperse systems, while various processes involving the deaggregation of dissolved polymers, which may be intensified on deformation, occur in solutions of high-molecular-weight compounds[218, 252-254]. As a result of this, the processes occurring in the flow can be of a complex type whose determination is the next primary task of rheology. In particular, in view of the large particle size (of sand or other substances) and close packing, which hinders the movement of the particles during shear, classical dilatancy is a limiting if not an exceptional case. Here too the operation of common factors (ASL and DIL) is manifested, but under conditions of major constraint determined by the low value of ϕ_v (or by the ratio of the volume concentration of the disperse phase to the maximum attainable close packing, approaching unity[56]).

Consideration of the mechanism of the dilatancy of colloidal structures raises the question of the invariance of the rheological characteristics of non-Newtonian liquids. It is found that the flow parameters, determining the onset of the dilatant flow regime, depend on the deformation conditions[146,179]. Bearing this factor in mind, Strivens[146] notes that the dilatant effect observed on deformation is a kind of instrumental artifact. Further study of the energetic and kinetic aspects of the interaction of micro-objects will make it possible to establish the relation between the microparameters of the dispersion and its integral characteristics, which constitutes the basis of the development of methods for the

rational regulation of the structural-mechanical properties of dispersions and will also permit the construction of a quantitative theory of dilatant-thixotropic transformations in colloidal structures.

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