Rheology of Emulsions

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Rheology of emulsions

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ABSTRACT

The review is devoted to the historical and modern understanding of rheological properties of emulsions in a broad range of concentration. In the limiting case of dilute emulsions, the discussion is based on the analogy and differences in properties of suspensions and emulsions. For concentrated emulsions, the main peculiarities of their rheological behaviour are considered. Different approaches to understand the concentration dependencies of viscosity are presented and compared. The effects of non-Newtonian flow curves and the apparent transition to yielding with increasing concentration of the dispersed phase are discussed. The problem of droplet deformation in shear fields is touched. The highly concentrated emulsions (beyond the limit of closest packing of spherical particles) are treated as visco-plastic media, and the principle features of their rheology (elasticity, yielding, concentration and droplet size dependencies) are considered. A special attention is paid to the problem of shear stability of drops of an internal phase starting from the theory of the single drop behaviour, including approaches for the estimation of drops' stability in concentrated emulsions. Polymer blends are also treated as emulsions, though taking into account their peculiarities due to the coexistence of two interpenetrated phases. Different theoretical models of deformation of polymer drops were discussed bearing in mind the central goal of predictions of the visco-elastic properties of emulsions as functions of the properties of individual components and the interfacial layer. The role of surfactants is discussed from the point of view of stability of emulsions in time and their special influence on the rheology of emulsions.

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Contents

1. Introduction

Emulsions, i.e. dispersions of liquid droplets in a continuous liquid medium, are very interesting objects for rheological investigations. During the last century, studies of emulsions under deformation have been the topic of vast and systematic theoretical and experimental works. Many outstanding scientists and engineers took part in these investigations. Persistent and unceasing interest in the comprehension of nature and peculiarities of the rheological properties of emulsions is determined by the challenge given by numerous and unexpected effects observed in the flow of emulsions. This interest is also strongly and permanently motivated by the problems of industry, which prõduces and consumes many hundred thousand tons of emulsions of various contents, properties and functions. It is the abundance of chemical compounds and the variation of their nature in composing these multi-component materials that are the fundamental reasons for unexpected and new effects in the behaviour of emulsions.

A special and rather interesting line in the studies of emulsions is their behaviour in the presence of solid components. It is known that this might be an original way for stabilizing emulsions. Nowadays, this possibility becomes even more attractive bearing in mind the involving

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of nano-particles in emulsion recipe and entering the world of nano-technology for emulsions.

Thousands of publications are devoted to emulsions, and therefore the following questions are of primarily importance:

- What are general features of the rheological properties of emulsions?
- What are those basic physical properties of liquid components in emulsions, which determine their behaviour — viscosity and elasticity, possibility to relax, stability in time and resistance to applied forces in deformations?
- What is the role of interfacial rheology?

This review pretends by no means to mention and list all publications related to rheology of emulsions. Meanwhile, the maybe even more ambitious goal is the attempt to understand the most characteristic and general features of emulsions of very different types with the aim of giving drawing a picture of the state of knowledge and leading directions of developments in this field. This approach should be based on the most important theoretical results and representative experimental data. Discussing the state of art in the rheology of emulsions, the present manuscript intends to treat the problems in the universal terms of continuum mechanics and rheology failing to use any qualitative and technological estimates because only the approach based on some general principles provides the chance of reaching the adequate interpretation of the behaviour of a matter.

It is worth mentioning that the analysis of rheological properties of emulsions suggests itself either similarity or contradictions with the behaviour of suspensions, i.e. of dispersion of solid particles in a matrix liquid. This is quite natural because if we move from the side of emulsions, then suspensions can be treated as the limiting case of emulsions when the viscosity of dispersed droplets becomes unlimitedly high. Therefore, the two fundamental milestones, which are genetically related to suspensions, represent the background of theory and treatment of experimental data for emulsions.

Firstly, this is the Einstein law [1] for the limiting case of the concentration dependence of viscosity of dilute dispersions, $\eta(\varphi)$:

$$\eta(\varphi) = \eta_0(1 + 2.5\varphi). \tag{1}$$

The other version of its formulation is written for a reduced viscosity, η_r:

$$\eta_r \equiv \frac{\eta - \eta_0}{\eta_0} = 2.5\varphi. \tag{1a}$$

As one can see, this linear relationship is valid in the limit of very low concentrations where fluid dynamics or any other interactions between dispersed particles are absent. It is difficult to find more frequently cited equation, as almost all publications in the field of rheology of dispersions of any type start with it.

Secondly, there is the Stokes equation [2] for the velocity U_{St} of a falling hard sphere of radius R in a continuous liquid medium (of viscosity η_0), the movement being provided by the density difference $\Delta\rho$ of the sphere material and the liquid medium, in which it moves:

$$U_{St} = \frac{2\Delta\rho g R^2}{9\eta_0} \tag{2}$$

where g is the gravitational acceleration.

Most likely, it is useful to note that the physical sense of both equations is very close, which is a consequence of the general momentum conservation law equations (the Navier–Stokes equations), which are solved for slow movement (i.e. for the domain of low Reynolds numbers, $Re \ll 1$) for an infinite space occupied by a viscous liquid [3]. The Reynolds number is expressed here via the drop diameter d:

$$Re = \frac{Vd}{v}, \tag{3}$$

where V is the velocity of a drop or a stream flowing round a drop, and v is the kinematic viscosity, i.e. viscosity η_0 divided by the density of the continuous medium.

As said above, both Eqs. (1) and (2) were initially obtained for the dispersions of solid spheres but not for emulsions. However the correlation of experimental results related to emulsions by these equations is always useful and even necessary. They present the limiting situation when the viscosity of drops in an emulsion is much higher than the viscosity of the matrix liquid, and the concentration of drops is so low that they do not influence the dynamics of the flow around them.

Coming back to emulsions, the following list of questions should be considered and (if possible) answered.

- What is the input of viscosity of a liquid forming drops? What happens in the transition from non-deforming hard spheres to liquid drops? A transient situation of slight deformable but not yet fluid particles (e.g. flow of blood where dispersed droplets are red cells) is of special interest.
- What happens (like in the case with suspensions) if the concentration increases, and it is incorrect to neglect the mutual influence of the flow dynamics around different dispersed particles, and it becomes necessary to take their interactions into account?
- What is the role of surfactants, which are most often used for the stabilization of emulsions?
- What is the role of drop size and size distribution?
- What is the relationship between the deformation of liquid drops in a flow and orientation of appearing anisotropic structures, and how do these structure effects influence the rheological properties of an emulsion as a whole?
- Do drops remain stable in the flow or – as apposed to dispersions of solid particles – can they be destroyed, and what are laws of their break-up provided by the action of external forces?
- What happens in the transition to highly concentrated emulsions which unlike suspensions of hard particles can exist at concentrations exceeding the limit of closest packing?
- What is special for emulsions formed with not purely viscous liquids but with visco-elastic materials, such as mixtures of polymer melts?

The above lists of questions are only the basic problems. An investigator should answer them first of all, if one pursues the goal of looking inside the nature and tries to describe the properties of emulsions quantitatively. Just these questions will be discussed in the present review, and no extensive survey of theoretical deviations neither of the many different emulsions in practice is given.

2. Viscosity of dilute emulsions — limiting case

A movement of liquid droplets (as well as solid particles) inside a fluid medium under isothermal conditions can occur due to two reasons: Brownian molecular fluctuations and action of dynamic forces in flow. The ratio of these factors is determined by the dimensionless factor, the Peclet number, Pe, which is expressed as

$$Pe = \frac{\eta\dot{\gamma}}{k_B T / R^3} \tag{4}$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, k_B is the Boltzmann constant, T is the absolute temperature, and R is the radius of a particle (either liquid or solid).

The Peclet number is evidently the relationship between characteristic stresses, provided by dynamic ($\eta\dot{\gamma}$) and diffusional ($k_B T/R^3$) displacements. If $Pe \gg 1$, the diffusion (or Brownian) movement can be neglected and the fluid dynamic process can be analyzed. As one

can see, *Pe* depends strongly on the particle size (proportional to the cube of *R*). So, molecular movements become noticeable for rather small particles only. They should be taken into consideration in the transition to the nano-size drops.

Below those situations will be discussed exclusively if molecular movements can be neglected (i.e. the particles are large enough to allow neglect Brownian motion). Thus, only fluid dynamics problems will be treated: the behaviour of a drop under action of forces appearing as a result of relative movement of a drop and the surrounding liquid.

First of all let us discuss the movement of liquid drops of viscosity η_{dr} inside another liquid of viscosity η_0. The general approach to solve this problem is analogous by its methodology to the approach to the theoretical analysis that resulted in the Stokes equation for the movement of a solid sphere in a viscous fluid. However, the possibility of deformations inside a moving fluid body created some special features in the problem under discussion.

Hadamard [4] and Rybczynski [5] have independently and almost simultaneously obtained a solution to the problem. The final formula (called the Hadamard–Rybczynski equation) gives the expression for the steady velocity, *U*, of a settling/rising liquid drop in an infinite liquid medium under the action of the density difference $\Delta\rho$, and reads:

$$U = \frac{2\Delta\rho g R^2}{3\eta_0} \frac{\eta_0 + \eta_{dr}}{2\eta_0 + 3\eta_{dr}} = \frac{2\Delta\rho g R^2}{3\eta_0} \frac{1+\lambda}{2+3\lambda} \qquad (5)$$

where $\lambda = \eta_{dr}/\eta_0$ is the ratio of viscosities of the two liquids.

This equation is valid under the following limitations:

- the flow is laminar and proceeds at low Reynolds numbers ($Re \ll 1$);
- outer boundaries of space, where the flow takes place, do not exist and the velocity "at infinity" equals zero;
- time effects are absent and the flow is assumed as stationary (and steady);
- no dynamic or any other interactions between drops exist, i.e. perturbations of the flow produced by one droplet in no way influences the dynamic situation around any other drop.

The further development of the theory is related to the consecutive refusal from these limitations and it is reasonable to analyze Eq. (5).

It is evident that if the condition $\eta_{dr} \gg \eta_0$ is fulfilled (i.e. if the viscosity of a liquid in a droplet becomes much higher than viscosity of a continuous medium), a drop becomes solid-like. In this case, Eq. (5) passes into the Stokes law (2) for the movement of solid spheres in a viscous fluid, i.e. the natural transition from emulsions to suspensions takes place. It is instructive to compare the velocity of a liquid drop with "Stokes velocity" U_{St}. As easily seen, the ratio U/U_{St} is equal to

$$\frac{U}{U_{St}} = \frac{3(\eta_0 + \eta_{dr})}{2\eta_0 + 3\eta_{dr}} = \frac{3(1+\lambda)}{2+3\lambda}. \qquad (6)$$

This ratio is always larger than 1, which means that the velocity of a drop settling or rising in an emulsion should be higher than that of a solid particle under the same driving force ($\Delta\rho = \text{const}$).

This result has the following physical explanation. The fluid flow at the phase boundary decreases the rate of deformation in the surrounding medium and thus decreases the intensity of the energy dissipation due to viscous friction, which is equivalent to the decrease in the apparent viscosity of an emulsion.

While the correctness of the Stokes law is out of question, the attitude to the Hadamard–Rybczynski equation is a bit more complicated. Even the first experimental studies showed that the situation is rather contradictory. Indeed, early studies [6–8] demonstrated that the velocity of a settling/rising drop corresponds exactly to the Stokes

equation for solid particles but not to the Hadamard–Rybczynski equation for liquid drops. However, the results of subsequent studies [9] carried out with very accurately prepared emulsions have showed that the velocity of a liquid drop is really higher than that of a solid sphere. As it will be discussed below, the keywords here are "accurately prepared" and the role of the cover layer has been found to be decisive [10].

The general explanation of the observed peculiarities of the behaviour of fluid drops goes back to the early publication of Boussinesq [11]. He proposed that a layer with special properties exists or appears at the drop surface. These properties are described by some two-dimensional shear viscosity η_s (modern methods of measuring 2D rheological properties of interfacial layers are considered in [12]). If so, the velocity of a settling/rising liquid drop should be described by the following equation (cited from [13], where an accidental numerical error in the original publication was corrected):

$$U = \frac{2\Delta\rho g R^2}{3\eta_0} \frac{\eta_0 + \eta_{dr} + \frac{2\eta_s}{3R}}{2\eta_0 + 3\eta_{dr} + \frac{2\eta_s}{3R}}. \qquad (7)$$

The conception of the 2D (surface) viscosity shows that the volume-to-surface ratio plays an essential role in the dynamics of a drop. If the drop is small, it behaves as a solid-like body. In the opposite case, volume effects dominate and the situation approaches to the limit described by the Hadamard–Rybczynski equation.

The main value of the Boussinesq conception consists in the idea of the special impact of a surface layer, which influences the properties of a drop as a whole, though it is every likely that the dominating role belongs not to the surface viscosity but to the elasticity of the interfacial layer provided by the energy of surface tension. This is the reason why the observed behaviour of drops depends on the methods of sample preparation for the respective experimental investigations.

The problem of the movement of a liquid droplet in a continuous medium is in essence equivalent to the estimation of the apparent viscosity of emulsions containing non-interacting drops. Indeed, the emulsion viscosity was calculated with the same theoretical approach as of a suspension's viscosity. Therefore, the obtained result is actually the generalization of the Einstein equation. Taylor [14] solved the present problem in a rigorous formulation and received the following equation for the concentration dependence of the emulsion viscosity in the linear approximation:

$$\eta_r = 1 + 2.5 \frac{2\eta_0 + 5\eta_{dr}}{5(\eta_0 + \eta_{dr})}\varphi = 1 + \frac{1 + 2.5\lambda}{1+\lambda}\varphi. \qquad (8)$$

It is not difficult to estimate the boundary cases.

At $\eta_{dr} \gg \eta_0$ (emulsion transforms to suspension) the Einstein law given by Eq. (1) is fulfilled. In the opposite case, at $\eta_{dr} \ll \eta_0$, the emulsion becomes a foam-like body and in this situation

$$\eta_r = 1 + \varphi. \qquad (9)$$

Further development of this approach is based on the conception of the existence not only of the 2D surface shear viscosity η_s, but also so the dilatational viscosity η_d, which characterizes the resistance of an interfacial layer to 2D extension. The result of this approach goes back to Oldroyd [15] who examined the situation of the combined action of both viscosities. The final equation in this case reads:

$$\eta_r = 1 + \frac{\eta_0 + 2.5\eta_{dr} + \frac{2\eta_s + 3\eta_d}{3}}{\eta_0 + \eta_{dr} + \frac{2(2\eta_s + 3\eta_d)}{5R}}\varphi. \qquad (10)$$

Its generic link with Eqs. (7) and (8) is quite evident. It means that the Oldroyd equation presents the most general case covering the theories of Taylor and Boussinesq. Eq. (10) is evidently the most general rigorous solution to the viscosity problem of dilute emulsions formed

by two Newtonian liquids in a linear approximation (linear dependence of viscosity on concentration).

It is noteworthy to remind that dispersed drops in dilute emulsions have always a spherical shape. This is why problems devoted to studies of more complicated non-spherical fluid particles relate to the non-stationary behaviour of emulsions. They will be considered in the next sections in connection with the discussion of the transient states and shapes of drops in emulsions.

3. Rheological behaviour of concentrated emulsions

The term "concentrated emulsion" covers the wide concentration domain of intermediate concentrations. Its boundaries are: from one side, the limit of dilute emulsions with a linear dependence of viscosity on concentration (neglecting inter-drop interactions), and from the other side, the concentration of closely packed spherical drops (drops remain spherical but it is impossible to add even a single drop without deformation of the others). Actually, this is the same domain as for concentrated suspensions: the boundary from the low concentration side corresponds to the absence of any type of interactions between particles, and the upper boundary is determined by the state of closest packing.

Like in the case of suspensions, the central theoretical problem is the understanding and description of inputs of mutual influence of the flow around neighbouring particles (either solid or liquid). In other words, it is necessary to find the second virial coefficient A_2 at the squared concentration member in a power series function for the $\eta(\varphi)$ dependence, with the Einstein factor 2.5 at the linear member leaving untouched.

The effect of insoluble surfactants and the drop deformation on the hydrodynamic interactions and on the rheology of diluted emulsion are the subject of investigations by numerous teams. For example for diluted emulsions with mobile surfaces, Danov (see details in Section 7) derived an interesting new relationship that takes into account the Gibbs elasticity, and bulk and surface diffusion and viscosity.

Many authors examined this problem, primarily for suspensions. For emulsions, the dynamic analysis was firstly made by Batchelor [16] who received that $A_2 = 6.2$.

For suspensions, one can find different values of A_2 lying in the range between 5 and 15. Meanwhile it is worth mentioning that the size of droplets was not taken into account neither in theoretical studies nor in experimental works carried out with model systems, and the only total concentration was included in the argumentation. It is unlikely to be true as a general case because it is well known that the viscosity of suspensions does depend on the average particle size, as well as on the size distribution, especially when fine particles are discussed.

Several authors obtained more complicated results for the concentration dependence of the emulsion viscosity $\eta_r(\varphi)$ in the range of intermediate concentrations by a rigorous analysis of the dynamic equations. According to [17]:

$$\eta_r = 1 + \frac{5.5\left[4\varphi^{7/3} + 1 - \frac{84}{11}\varphi^{2/3} + \frac{4}{K}\left(1 - \varphi^{7/3}\right)\right]}{10(1 - \varphi^{10/3}) - 25\varphi(1 - \varphi^{4/3}) + \frac{10}{K}(1 - \varphi)(1 - \varphi^{7/3})}\varphi \tag{11}$$

and according to [18]:

$$\eta_r = 1 + \frac{2\left[5\lambda - 5((\lambda - 1)\varphi^{7/3}\right]}{4(\lambda + 1) - 5(5\lambda + 2)\varphi + 42\lambda\varphi^{5/3} - 5(5\lambda - 2)\varphi^{7/3} + 4(\lambda - 1)\varphi^{10/3}}\varphi \tag{12}$$

where, as before, the λ factor represents the ratio of viscosities of liquids forming the drop, η_{dr}, and the continuous medium, η_0, respectively: $\lambda = \eta_{dr}/\eta_0$.

It is shown [19] that Eq. (11) fits well (and even better than Eq. (12)) experimental data for many model emulsions of the "oil-in-water" type, at least in the range up to $\varphi \approx 0.6$.

Numerous attempts to find theoretically based expressions for the concentration dependence of the emulsion viscosity are known other than power series, because the latter approach requires the introduction of independent coefficients in the series.

The approach proposed in [20] is especially interesting in this aspect. It is a version of the generalization of the Taylor model. The final equation for the concentration dependence of viscosity is:

$$\left(\frac{\eta}{\eta_0}\right)^{2/5}\left[\frac{2\eta + 5\eta_{dr}}{2(\eta_0 + \eta_{dr})}\right]^{3/5} = (1 - \varphi)^{-1}. \tag{13}$$

This equation fits quite satisfactorily the viscosity of many emulsions in a wide concentration range.

Pal [21] proposed another approach for the function $\eta_r(\varphi)$ based on a rather formal method of generalization of the well known equations valid in the low concentration range. According to this approach, the type of an emulsion ("water-in-oil" or "oil-in-water") is irrelevant, which becomes clear when recalling that this approach is nothing else but a method for fitting experimental data. Moreover the size of droplets was not considered as well. Two " models" were proposed, expressed by the following equations.

Model I

$$\eta_r\left[\frac{2\eta_r + 5\lambda}{2 + 5\lambda}\right]^{1/2} = \exp\left[\frac{2.5\varphi}{1 - (\varphi/\varphi^*)}\right] \tag{14}$$

Model II

$$\eta_r\left[\frac{2\eta_r + 5\lambda}{2 + 5\lambda}\right]^{1/2} = [1 - (\varphi/\varphi^*)]^{-2.5\varphi^*} \tag{15}$$

As easily seen, Eq. (15) generalizes Eq. (8). However a new factor φ^* is introduced which corresponds to the limit of the closest packing of drops in the space (as in suspensions), although it was used as a free fitting factor.

It is not difficult to estimate the limiting situations for both models. Indeed, in the transition to the domain of dilute solutions, one can expect that the Einstein law is fulfilled upon the unlimited growth of viscosity $\varphi \rightarrow \varphi^*$, just as in the case of concentrated suspensions of solid particles.

The important peculiarity (and advantage) of both models consists in the absence of free (fitting) parameters except φ^*. This parameter has a clear physical meaning in considering a possible structure of the suspension. For emulsions, this is an upper limit of the domain of intermediate concentrations. Closing this limit, drops in emulsions can fill the space without changing their spherical shape.

Both the above mentioned models describe rather well experimental data for various real emulsions in a wide concentration range [21], although their structure underlines the assumption of similarity in the behaviour of emulsions and suspensions.

Indeed, a successful attempt of describing the concentration dependence of the emulsion viscosity, $\eta_r(\varphi)$, by means of the well known two-terms Vand equation with the second virial coefficient equal to 7.349 was achieved many years ago [22] and a more complex equation in form of a power series provides good correlation with experimental data in a wide concentration range [23]. It is worth mentioning that this equation was originally proposed and used for the viscosity of suspensions.

Finally, the comparison of the concentration dependence of the emulsion viscosity [24] with the results of rigorous calculations for the viscosity of suspensions [25] for various emulsions has been made. In this study, the viscosity of the continuous medium was changed by 100 times, and consequently, the parameter $\lambda = \eta_{dr}/\eta_0$ changed
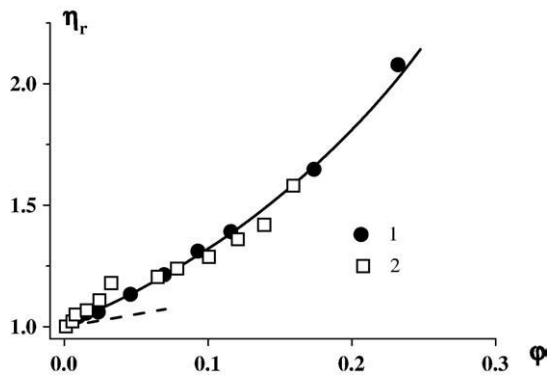
Fig. 1. Comparison of experimental data of the concentration dependence of different emulsions with some theoretical predictions. ($1 - \eta_0 = 0.997$ cP, $\eta_{dr} = 12$ cP; $2 - \eta_0 = 104$ cP, $\eta_{dr} = 12$ cP). The curve presents a concentration dependence of the viscosity calculated for suspensions, the dotted line is the Taylor asymptote. (From [24], Fig. 8, with kind permission of Elsevier B.V.).

from 0.115 up to 12, and all points for the emulsion viscosity were perfectly well located on the general curve built for the viscosity of emulsions (Fig. 1). This result seems remarkable because it clearly demonstrates that fluid drops in emulsions can behave like solid spheres in suspensions.

The analysis of experimental data related to viscosity measurements requires the estimation of the impact of a surfactant, which creates a layer at the surface of the droplets. If the thickness of this layer is of the same order as the size of a drop, the apparent diameter appears larger than the real diameter of the drop itself. Taking this factor into account, it appeared possible to prove that the model of suspension of solid spheres adequately describes the viscosity of emulsions (in the domain of Newtonian flow at low shear rates) [26].

The conclusion of the above discussed experimental results can be formulated in the following manner: emulsions in flow (at least at low Reynolds numbers) behave quite similar to dispersion of solid particles. The solid-like behaviour of drops can be explained by the formation of an elastic interfacial layer at the drop surface, and this elastic cover changes radically the boundary conditions between the two fluids and prevents deformations of the liquid inside the drops.

It should also be mentioned that the development of powerful modern computational methods allows to obtain rigorous quantitative predictions for the concentration dependence of the emulsion's viscosity (see e.g. [27,28]) including the effect of flow in confined conditions [29].

The increase of the concentration of drops in emulsions results not only in increased viscosity at low shear rates (i.e. Newtonian viscosity), but also in the appearance of strong non-Newtonian effects, a shear
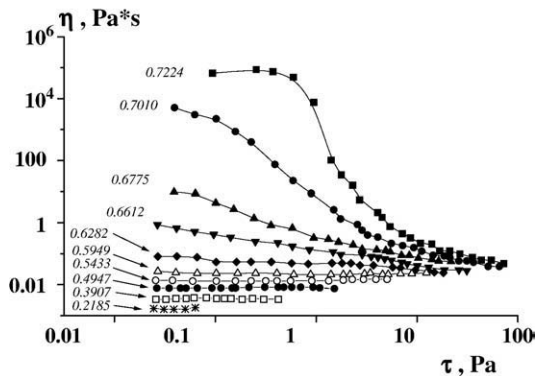
rate dependence of the apparent viscosity. Experimental data shown in Fig. 2 are a typical and very characteristic example of that effect.
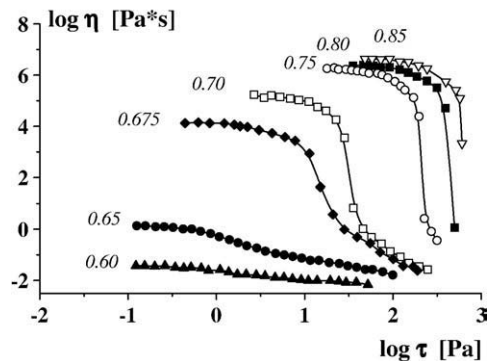
As one can see from Fig. 2, quite remarkable and even sharp transitions from a Newtonian (or almost Newtonian) behaviour to an anomalous flow with strongly pronounced non-Newtonian effects occurs mainly when approaching the upper boundary of the domain of intermediate concentrations.

Fig. 3 is another rather impressive example for the changes in the character of rheological properties just close to the upper boundary of the concentration domain under discussion, i.e. when approaching the state of the closest packing of spherical drops. The sharp transition takes place in a narrow concentration range where a radical change in rheological properties of the emulsions is observed.

As seen from Figs. 2 and 3 the approach to the limit of high concentration and transition beyond the closest packing of non-deformed spherical drops leads to principle changes in the rheological properties of emulsions: Newtonian viscous flow is replaced by a visco-plastic behaviour with jump-like (up to seven orders of magnitude) decrease of the apparent viscosity in a narrow range of stresses. An upper limit of the domain of Newtonian flow still exists. Such type of rheolgical behaviour is typical for multi-component systems with a coagulate structure formed by the dispersed phase [31]. The jump in the apparent viscosity at some shear stress is the reflection of the rupture of the structure, and this stress is treated as the yield stress. The existence of the yield stress will become even more evident upon further increase of concentration into the domain of highly concentrated, so-called "compressed" emulsions, which will be discussed in the next section.

The increase in concentration also enhances the influence of the drop size on the rheology of emulsions. As mentioned above, the drop size influences the volume-to-surface area ratio: the increase of diameter leads to a more pronounced effect of the flow inside the drops. This phenomenon becomes even more significant when approaching to the upper boundary of the domain of intermediate concentrations. Fig. 4 illustrates this effect. The experimental data show figures were obtained for emulsions with polydisperse drops, the effect of which is evident. In the low concentration range (the left part of the figure) the drop size is irrelevant while in the range $0.6 < \varphi < 0.75$ (the right part of the figure) the average size of droplets strongly influences the viscosity.

Also other rheological effects become possible at high concentrations (in the concentration domain under discussion, i.e. at $\varphi < \varphi^*$). One of such effects is the viscous thixotropy [32] because the interfacial layers in the closely arranged drops can produce some kind of structure, which is destroyed by deformation and restores at rest. The interaction between drops and evolution of their shape in flow can also result in visco-elastic effects. This conception was rigorously formulated in a classical publication [33] and then further developed (see e.g. [34]).

Fig. 2. Flow curves of a model "oil-in-water" emulsion (Average size of drops is 4.6 μm) in a wide concentration range. (From [19], Fig. 3, Set 4, with kind permission of Elsevier B.V.).

Fig. 3. Flow curves of "water-in-oil" emulsions when approaching the concentration limit corresponding to the closest packing state of spherical drops. Aqueous phase comprises water with 0.5% NaCl; Oil phase is cyclomethicon. (From [30], with kind permission of Prof. Lapasin).
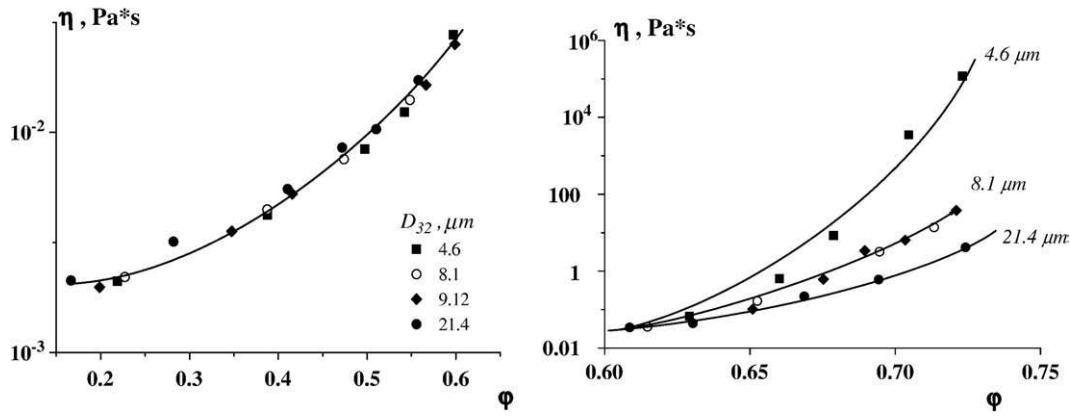
Fig. 4. Concentration dependences of the viscosity of emulsions for different average sizes of drops (size is shown at the curves). (From [19], Fig. 1, with kind permission of Elsevier B.V.).

A drop in shear flow transforms into a prolong particle (ellipsoid) with the principle equatorial radii R_{max} and R_{min}. The degree of elongation (or asymmetry) is characterized by a dimensionless factor D expressed as

$$D = \frac{R_{max} - R_{min}}{R_{max} + R_{min}}. \tag{16}$$

The D value for a non-deformed sphere is evidently zero.

As a result of deformations, the D value reaches a value D_0, and after the flow is stopped the reverse process takes place and the value of D returns from D_0 to zero. When the deformations are not too large, the restoration follows the Maxwell model of relaxation with a characteristic relaxation time θ:

$$D = D_0 e^{-t/\theta}. \tag{17}$$

According to the Oldroyd model, this characteristic relaxation time θ can be expressed by

$$\theta = \frac{\eta_0 R}{\sigma} \frac{(3 + 2\lambda)(16 + 19\lambda)}{40(\lambda + 1)}. \tag{18}$$

Eq. (16) definitely shows the driving force of the restoration process, the surface tension σ. The area of the drop surface increases due to deformation and this is the source of additional stored energy.

Oldroyd also received the equation for a retardation time, which does not coincide with the relaxation time, as follows from the theory of linear visco-elasticity. Thus, the reason of visco-elasticity in the flow of emulsions is the droplet deformation under the action of shear stresses, and the mechanism of restoration related to surface tension.

The Oldroyd model also predicts an important result called "similarity rule" [35]. According to this rule, the frequency dependence of the complex viscosity $\eta^*(\omega)$ should be equivalent to the shear rate dependence of the apparent (non-Newtonian) viscosity $\eta^*(\dot{\gamma})$ of the emulsions in steady flow:

$$\eta^*(\omega) = \eta(\dot{\gamma}). \tag{19}$$

The first difference of normal stresses $(\tau_{11} - \tau_{22})$ practically coincides with the doubled value of the imaginary part of the complex viscosity $\eta''(\omega)$ multiplied by frequency:

$$\tau_{11} - \tau_{22} \cong 2\omega\eta''(\omega). \tag{20}$$

Eq. (19) is the well known *Cox–Merz rule* for visco-elastic polymer melts [36], and Eq. (20) was theoretically obtained [37] for visco-elastic polymer melts too (see for details [38]).

Thus, the similarity rule appears to have a general value for different media regardless of the nature of their elasticity. Its validity is not restricted to polymeric substances described in numerous publications on polymer rheology. One can expect that this rule works always if elasticity (or relaxation phenomena) appears due to whatever reason. The Oldroyd model says that non-Newtonian effects appear due to the same reasons.

A confirmation of the similarity rule is given in [35] by experimental data obtained for "two-phase solutions" of biopolymers. Such solutions (emulsions) are surely visco-elastic, though in that case this effect might be explained by the dynamics of polymer chains. However the similarity rule was convincingly demonstrated in the range of shear rates (frequencies) covering more than four orders of magnitude.

4. Highly concentrated emulsions as visco-plastic media

The tendency to increasing the concentration of a dispersed phase (drops) is explained by the fact that just this phase contains components, for which an emulsion has been created bearing in mind its application, while the continuous phase is nothing more than a carrier for these useful-in-application properties and therefore represents the ballast.

Emulsions at a concentration of the dispersed phase exceeding the limit of the closest packing of spherical drops (without any deformation), φ^*, are called *highly concentrated*. The parameter φ^* corresponds to the concentration of the closest packing of spherical particles in space. Depending on the size distribution and arrangement of drops in space, the limit value of φ^* is about 0.71–0.75.

Some examples of application fields of highly concentrated emulsions are cosmetic industry, production of some food stuffs, liquid explosive compositions and so on.

Creating highly concentrated emulsion (with $\varphi > \varphi^*$) can be realized by deformation of spherical droplets via compression of a dispersion resulting in the transformation of spherical drops into particles of different tightly packed polygonal shapes occupying the space.

The general thermodynamic approach to understanding the nature and properties of highly concentrated emulsions was proposed by Princen [39]. According to his approach, later developed in many publications, highly concentrated emulsions are created by application of outer pressure that compresses drops and transforms them from spheres to polygons. By its physical nature, this outer pressure is equivalent to the osmotic pressure Π, acting inside the thermodynamic system. The work produced by this pressure when creating a highly concentrated emulsion is equal to the stored energy given by the increase of droplet surface area S due to changes in shape. This equality is written as:

$$-\Pi dV = \sigma dS \tag{21}$$

and shows that work produced by the osmotic pressure for decreasing the volume of the system ΠdV equals to the work used for creating additional new surface dS (here σ is the interfacial tension).

Substituting the expression for concentration leads us to the final equation for the osmotic pressure as a function of concentration φ and change of surface area S (reduced by the volume, V):

$$\Pi = \sigma \varphi^2 \frac{d(S/V)}{d\varphi}. \tag{22}$$

The stored surface energy serves as a source of elasticity of the system as a whole (i.e. highly concentrated emulsion), which is observed in shear deformations [40–43]. The experimental evidence of this conception is seen in close correlation between concentration dependencies of the shear elastic modulus G and osmotic pressure Π, as shown in Fig. 5 [40]. The experimental data in this figure are reduced by the value of the Laplace pressure (σ/R). Moreover, not only a qualitative correlation but also even equality of these values was observed, though the theory does not require it and the reasons for this equality are not evident.

Using a reduction factor (σ/R) reflects the proposed conception of elasticity of highly concentrated emulsions as the consequence of the increase of surface energy upon compression of a drop as developed by Princen as well as by Mason et al. [40]. This approach presumes that both parameters, G and Π, should be inverse proportional to the drop size. When speaking about the concentration dependence of elasticity, the argument in the concentration dependencies should be the product $\varphi^{1/3} (\varphi - \varphi^*)$ or $\varphi(\varphi - \varphi^*)$, as discussed in [44] and [41,42], respectively. The difference between the two approaches is not principle from an experimental point of view, because highly concentrated emulsions exist inside a rather narrow concentration window, practically from 0.71 till 0.92. However, another point is important: any parameter characterizing highly concentrated emulsions as solid-like "mild" elastic media are approaching zero at $\varphi \to \varphi^*$ from the high concentration side. In other words, solid-like properties of emulsions can be observed in the concentration domain $\varphi > \varphi^*$.

Indeed numerous direct measurements presented in literature demonstrate that the values of φ^* lie in the range between 0.71 and 0.74. This range corresponds to the closest packing of spherical particles bearing in mind that they can be polydisperse. Further below, some experimental data will be shown, which illustrate the role of concentration.

The above cited conception of elasticity of highly concentrated emulsions looks rather transparent and even evident. However some publications mentioned that real values of the elastic modulus sometimes appear much higher (for example for protein stabilized emulsions)
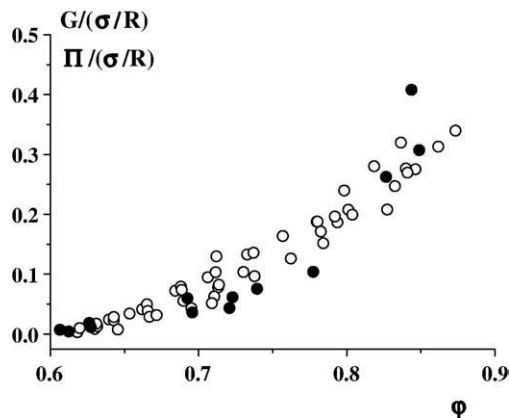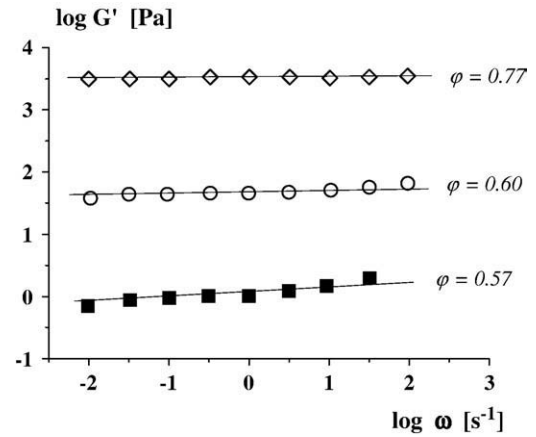

Fig. 6. Frequency dependencies of the elastic modulus for model emulsions of different concentrations − monodisperse droplets of poly(dimethyl siloxan) in water, according to Mason et al. [41], Fig. 5.

than predicted by this theoretical model [45–47]. Thus, other conceptions explaining elasticity of highly concentrated emulsions are possible and necessary.

Meanwhile, it is indisputably that highly concentrated emulsions can be treated as "mild" elastic materials with a concentration dependent elastic modulus. Therefore direct measurements of elastic properties of emulsions are of primary interest, and these properties have been measured in a very wide frequency range for different systems [39,48–54].

A typical and rather obvious example of the results of these measurements is presented in Fig. 6. One can see that the elastic modulus is constant in a very wide frequency range covering several orders of magnitude. Such kind of behaviour is standard for ideal elastic materials, the elastic modulus of which must be independent of frequency. Hence, in a first approximation, highly concentrated emulsions can be classified as linear (in a mechanical sense) elastic materials. Mason [42] marked that the elastic modulus increases at very high frequencies only (see diagram in Fig. 7) and treated this effect as a mechanical glass transition of an emulsion as a visco-elastic material.

These results by far do not exhaust the rheology of highly concentrated emulsions. The matter of fact is that these emulsions demonstrate strongly non-linear visco-elastic, as well as viscous behaviour.

An indication of the non-linearity of visco-elastic properties is the observed amplitude dependence of the elastic modulus at any deformation frequency. High deformations (or high stresses) lead to "softening" of the material as seen from the decreased modulus

Fig. 5. Correlation between the elastic modulus G (open circles) and osmotic pressure Π (filled circles) for highly concentrated emulsions. (According to Lacasse et al. [40], Fig. 1).
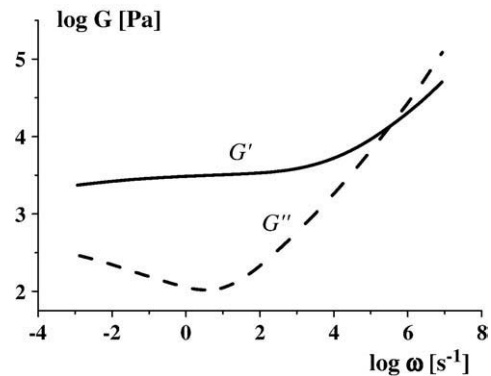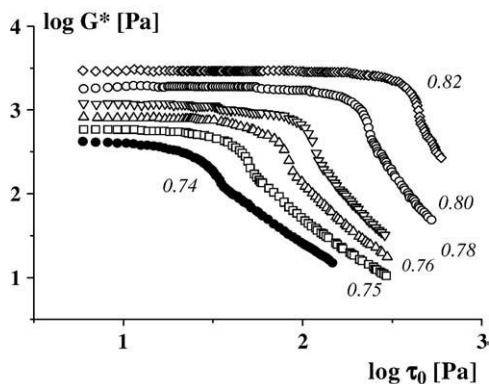

Fig. 7. Complete frequency dependence of the dynamic modulus components for a model emulsion − monodisperse droplets of poly(dimethyl siloxan) in water. $\varphi = 0.98$, $R = 500$ nm. (From [42], Fig. 4, with kind permission of Elsevier B.V.).

Fig. 8. Non-linearity of viscoelastic properties of highly concentrated (cosmetic grade) "water-in-oil" emulsions at large amplitude of deformation. (From [55], Fig. 1, with kind permission of Springer Science + Business media).

Fig. 9. Flow curves of highly concentrated "water-in-oil" emulsions demonstrating the existence of the yield stress (used as liquid explosives), different concentrations of a dispersed phase — shown at the curves. (From [54], Fig. 7b, with kind permission of Springer Science + Business media).

upon increasing the amplitude of deformation [55,56]. An example of this phenomenon is shown in Fig. 8. Such kind of behaviour is characteristic to different structurized colloidal systems: the growth of the deformation amplitude in periodic oscillations leads to a destruction of the inner structure and, as a consequence, to the decrease of the elastic modulus [56].

It is rather interesting to compare the amplitude dependencies of the elastic (storage) modulus G' and the loss modulus G'' under large deformations. As was said above, highly concentrated emulsions behave like elastic media, and hence $G' > G''$ in this amplitude domain. However along with increasing amplitude a solid-like to liquid-like transition takes place and the deformation γ^*, at which $G' = G''$, can be considered as quantitative measure of this transition representing the point of rupture of the material structure [57]. It was noticed that $\gamma^* \approx 0.1$ for monodisperse emulsions, while for polydisperse emulsions γ^* is much lower and of the order of 0.01–0.02. This effect might reflect the peculiarities in structure of mono- and polydisperse emulsions. Meanwhile, the value of γ^* for monodisperse droplets of a poly (dimethyl siloxane) is no more than 0.004 [57]. Large amplitude oscillatory shear experiments can be used as a useful tool to probe the non-linearity of different media [58].
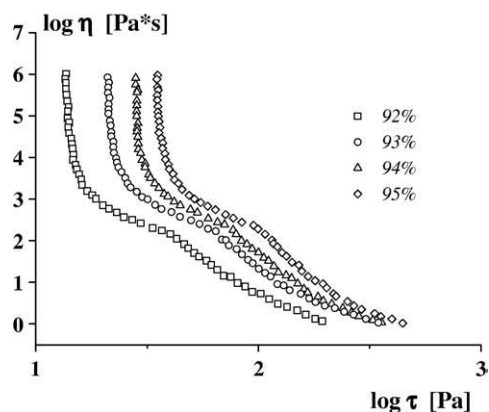
The reverse effect has also been observed: structure formation with increasing amplitude of deformations in oscillations [59]. This is an analogue of anti-thixotropy — the growth of viscosity with increasing rate of deformation.

Upon the application of constant stress (or shear rate) highly concentrated emulsions flow like any other liquids demonstrating strong non-Newtonian behaviour, which becomes possible beyond some stress threshold, which obviously has the meaning of a yield stress, τ_Y. Typical complete flow curves of highly concentrated "water-in-oil" emulsions (used as liquid explosives) are shown in Fig. 9 for several systems with varying the concentration of the dispersed phase.

As seen the yield stress remarkably increases even at rather slight increase of the dispersed phase concentration. Flow of highly concentrated emulsions is impossible at stresses below the yield stress ($\tau < \tau_Y$). Therefore the domain of "upper Newtonian viscosity" described for these materials should be treated as an artefact obliged to a long transient region of deformations before the steady state flow is reached. This is an example of "rheopectic" behaviour as was proven in [60].

A scheme of generalizing the characteristic peculiarities of the evolution of rheological properties of emulsions in the transition from dilute (at $\varphi \ll 1$) to highly concentrated emulsions (in the domain $\varphi > \varphi^*$) is shown in Fig. 10.

The transition into the domain of highly concentrated emulsions is accompanied by changes in the type of concentration dependencies of rheological properties and the influence of the droplet size. An argument, which is reasonable to use in discussing concentration de-
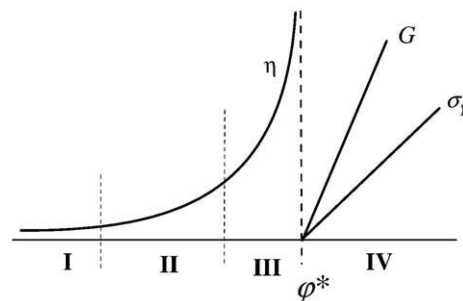
pendencies of rheological properties is the difference in concentration in respect to the concentration of closest packing of spherical droplets, i.e. the difference ($\varphi - \varphi^*$). Typical concentration dependencies of the elastic modulus G, and yield stress τ_Y, are shown in Fig. 11.

The $\tau_Y(\varphi)$ dependence is not presented in the original publication [54], but it can be easily reconstructed from their Fig. 7. The dependence $G(\varphi)$ presented in Fig. 10 was recalculated from data given in [54] in form of $G/\varphi^{1/3}$ according to the theory presented in [44]. The transition to the dependencies of absolute values of G and τ_Y allows us to establish that the critical concentration φ^* is the same for both considered functions, $G(\varphi)$ and $\tau_Y(\varphi)$.

The presentation of concentration dependencies of G and τ_Y in Fig. 11 as linear functions of the argument ($\varphi - \varphi^*$) is not in contradiction to the conception of Princen discussed above. According to Princen [44], the argument should be $\varphi^{1/3}(\varphi - \varphi^*)$. Meanwhile, the argument obtained in [40] was assumed as $\varphi(\varphi - \varphi^*)$. However the narrow range of concentrations and possible experimental errors do not lead to unambiguous conclusions about the "correct" choice of the argument.

The problem of the influence of droplet size in the domain of highly concentrated emulsions was considered in [61] where it was demonstrated that the viscosity of emulsions of smaller droplets is higher than that of emulsions formed by larger drops. Besides the non-Newtonian behaviour is much more strongly expressed for dispersion of fine droplet, as illustrated in Fig. 12.

Fig. 10. General peculiarities of rheological properties of emulsions in the whole concentration range of the dispersed phase. I — domain of dilute emulsions — Newtonian liquids with $\eta = const$; II — domain of intermediate concentrations — emulsions are liquids with weakly pronounced non-Newtonian behaviour; III — domain of relatively high concentrations — non-Newtonian effect is strongly expressed and thixotropic and viscoelastic effects are possible; IV — domain of highly concentrated "compressed" emulsions — visco-plastic materials with obvious yield behaviour and wide frequency range of elasticity with constant shear modulus.
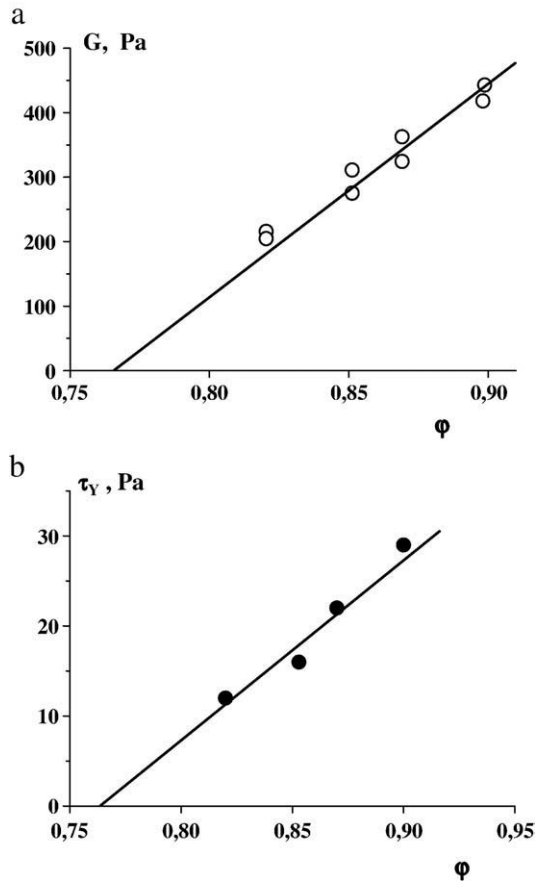
Fig. 11. Concentration dependencies of elastic modulus G (a) and yield stress $\tau_Y(\delta)$. (From [54], Figs. 15 and 16, with kind permission of Springer Science + Business media).

However, judging from the shape of the observed curves, these dependencies more likely belong to the domain III than IV in Fig. 10, because no visible yielding behaviour is visible in these curves. Though the data refer to rather high concentration, nevertheless the concentration is below the φ^* threshold due to the wide polydispersity of the studied samples.

More definite information on the role of droplet size in the domain IV is presented in [51,54]. It is doubtless that the droplet size influences the viscosity of emulsions, confirmed by numerous experimental studies. However, it is rather difficult to formulate any definite quantitative
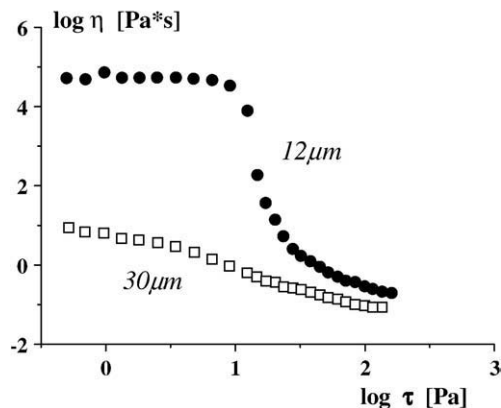
conclusions because it is not clear how to choose viscosity values from non-Newtonian flow curves for their comparison. Strategies based on modulus and yield stress measurements are more definite. Surely, it would be more instructive to have data for monodisperse droplets. To our regret, such results are unknown and we focus on data obtained for polydisperse samples. A typical example is shown in Fig. 13.

It is well seen that the dependence of modulus on average droplet size D_{23} is satisfactory approximated as a reciprocal squared function:

$$G = aD_{32}^{-2} \tag{23}$$
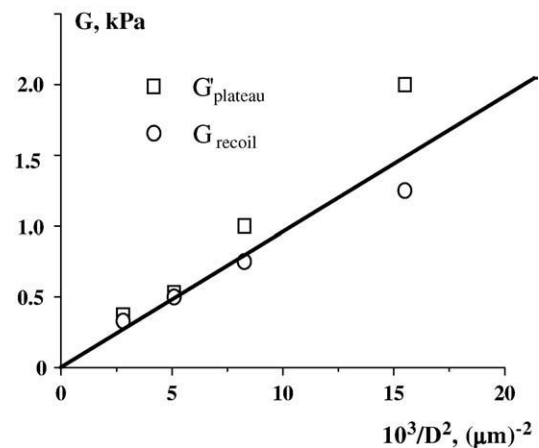
where a is an empirical factor.

It is worth mentioning that according to the generally accepted Princen–Mason model the dependence of G vs. D was always considered as reciprocal linear (but not squared) as it follows from the basic conception of elasticity of highly concentrated emulsions. Just this concept allows normalizing the modulus by the Laplace pressure (σ/R).

Thus, experimental data as well as the theoretical conception predict that the solid-line behaviour of highly concentrated emulsions enhances along with decreasing droplet size, though the quantitative character of the size factor remains disputable.

The boundary conditions for moving highly concentrated emulsions through a channel are also one of their important rheological features. The problem is formulated as follows: does the standard hypothesis of wall stick (zero velocity at the solid wall), which is universally accepted in solving any boundary problems in fluid dynamics, remain valid for emulsions?

A possibility of wall sliding is rather evident for the movement of suspensions because boundary conditions can be changed due to their interaction with the wall. Numerous experimental studies (see e.g. [62,63]) carried out by changing from a smooth to a rough surface or by varying the ratio between surface area and volume of a sample (using different gaps between stationary and rotation surfaces in rotational devices or the diameter of a capillary) have proven that wall slip in the flow of colloid dispersions is possible.

Meanwhile the answer about the possibility of wall slip in the flow of emulsions is not so obvious. Doubts are connected with the structure of emulsions, which, in opposite to suspensions consist of fluid components and for any of them the hypothesis of wall stick can be valid. However – in opposite to this argument – we have to accept that drops of the dispersed phase in an emulsion behave as quasi-solid particles, as was discussed in previous sections, and wall slip for such "quasi-suspensions" is quite possible.

Fig. 12. Flow curves of emulsions with fine (average size 12 μm) and coarse (average size 30 μm) droplets, at the same concentration of the dispersed phase $\varphi = 0.76$. (According to Pal [61], Fig. 2c).

Fig. 13. Dependence of the elastic modulus on the average droplet size for highly concentrated emulsions. The modulus values were obtained by two corresponding methods — as the plateau in the frequency dependence of the modulus, and from elastic recoil after cessation of loading with constant stress. (From [54], Fig. 16, with kind permission of Springer Science + Business media).
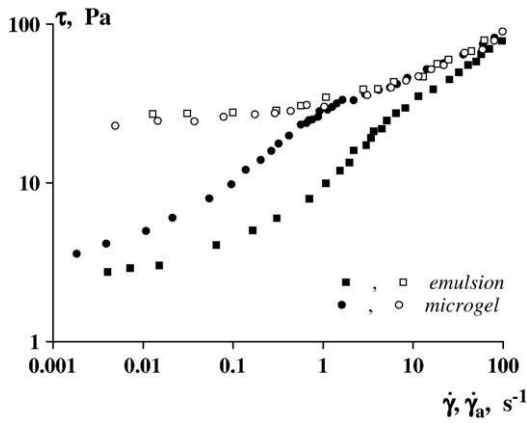
Fig. 14. Flow curves of an emulsion (squares) in comparison with a microgel dispersion (circles) at the same viscosity above the yield stress. Filled symbols reflect the effect of wall slip, open symbols present true flow curves. (From [70], Fig. 9, with kind permission of Springer Science + Business media).

Wall slip was really observed in the flow of mayonnaise (a typical emulsion) in a rotational viscometer [64]. The author of the review [65] stated that wall slip is a necessary effect in flow of emulsions, and there is a solid body of experimental facts confirming this conception [66]. A strong effect of slip of 80% water dispersion in thickened Vaseline was also observed in the flow of this emulsion in a rotational viscometer with smooth surfaces [67]. An even stronger effect of wall slip was described for shear deformations of foams [67]. It is reasonable to think that their rheology is similar to the rheology of emulsions when zero viscosity of dispersed droplets is assumed.

Moreover direct measurements of velocity profiles carried out by the method of dynamic light scattering [68] showed that wall slip is undoubtedly present in channel flow of dilute emulsions ($\varphi = 0.20$) as well as of highly concentrated ($\varphi = 0.75$) ones. These effects were quite independent of the flow curves of emulsions because dilute emulsion showed a Newtonian viscosity while the concentrated one behaved in a non-Newtonian manner.

Independent direct measurements of velocity profiles in channel flow of a classical model system (droplets of poly(dimethyl siloxane) in water in the concentration range from 50 to 78.5 vol.%) and an industrial product (mayonnaise) carried out by NMR-velocimetry have also led to the conclusion that wall slip is an obligatory component in shearing emulsions [69].

In the light of this discussion, the results of parallel studies of flow of a typical highly concentrated model emulsion (silicon oil-in-water at concentration $\varphi = 0.77$) and microgel particle suspension are rather significant [70]. The results of the comparison are shown in Fig. 14. As it can be seen, wall slip strongly increases an apparent shear rate $\dot{\gamma}_a$ in comparison to the real (volume) shear rate $\dot{\gamma}$ in the range below the yield stress where true flow is impossible. It is interesting to note that the effect of wall slip proved to be even stronger for emulsion than for a suspension. The explanation of this effect was connected with the

smaller size of dispersed drops in emulsions (1.5 μm) as compared to particle's size in suspensions (220 μm).

Direct measurements of the wall velocity showed that V_s is proportional to the squared shear stress in the flow of dispersions of "mild" elastic particles in the range of a solid-like behaviour [70], $V_s \propto \tau^2$, however, no influence of the volume-to-surface area ratio (varied by changing the gap in a rotational rheometer and the diameter of a capillary) on the flow of highly concentrated explosive emulsions was observed [54,60]. This is possible if wall slip is absent or negligible only. The absence of wall slip was also confirmed by a large-scale application experiment testing an industrial set-up for calculating the transportation characteristics of pipe-lines [71]. It is quite possible that the absence of wall slip in these tests is explained by the method of measurements, because flow curves were measured in a device with artificially roughened surfaces that excluded wall slip, and the pressure in the industrial pipe-line was so high that bulk flow prevailed over possible wall slip.

5. Deformation and break-up of droplets in emulsions during flow

Deformation of drops in flow precedes their break-up. Therefore, initially it is necessary to monitor how the deformation of liquid drops occurs in a flow.

There are many publications demonstrating the mechanism and stages of deformation of liquid drops in shear and/or elongation flows preceding break-up. Data of this kind are obtained either by direct optical methods using a high-speed camera or by numerical modelling. Fig. 15 (according to [72]) is an example of numerical results of such kind (see also [73]).

The problems of quantitative understanding of how morphology of drops in a viscous liquid medium is changing and what the impact on the rheological results of drop deformations is, were the subject of vigorous theoretical and experimental investigations during the last 20 years.

Stresses acting on a liquid drop transform its shape in such a manner that it becomes an ellipsoid with the principle maximal R_{max} and minimal R_{min} semi-axes. Then, as was already said in Section 3, the morphology of a drop is characterized by a dimensionless factor — the degree of anisotropy D, described by Eq. (16).

In addition it is important to know the orientation of a drop determined by its angle of inclination, θ, of the principle axis in relation to the direction of flow.

The driving forces of deformation are shear stresses, while interfacial tension is the resistance force supporting the shape of a drop. Therefore the realized morphology of a drop is determined by the ratio of these forces expressed through the Capillary number Ca:

$$Ca = \frac{\eta_0 \dot{\gamma}}{\sigma / R} \tag{24}$$

where η_0 is the viscosity of the continuous medium, $\dot{\gamma}$ is the shear rate, σ is the interfacial tension, and R is the drop radius.

The fundamental linear approximation for calculating the degree of anisotropy is based on the classical Taylor model for the viscosity of
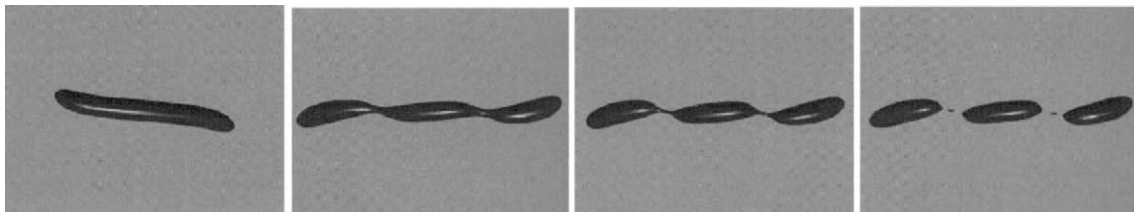
Fig. 15. Sequence of stages of deformation of a liquid drop in flow of an emulsions. Numerical modelling. $Ca = 0.4$; $Re = 2$. (From [72], Fig. 11, with kind permission of Springer Science + Business media).

dilute emulsions [74]. In this approach, the degree of anisotropy of deformed drops is expressed by

$$D = \frac{16 + 19\lambda}{16(\lambda + 1)} Ca, \tag{25}$$

Deformation of drops in a liquid flow is really determined by the viscosity of the continuous phase. This conception was confirmed in a rather original way — by an inverse calculation of the viscosity from monitoring the shape of a drop in flow, the drops being covered by surfactants for increasing their stability [75].

The expression for the anisotropy of drops in another approximation based on the model for a moderately concentrated emulsions taking into account dynamic interaction between drops (see Section 3) is written as [76]:

$$D = \left[\frac{16 + 19\lambda}{16(\lambda + 1)}\right]\left[1 + \frac{5(2 + 5\lambda)}{4(\lambda + 1)}\varphi\right] Ca. \tag{26}$$

The correctness of this equation was investigated and supported in [77], though for equi-viscous emulsions only ($\lambda = 1$) but different concentrations of the dispersed phase. It was shown that a good correlation exists between theoretical predictions and experimental results, though coalescence of droplets and vibration around some average position happened in the domain of moderate concentrations.

A rather successful method was used in generalizing experimental results obtained for different concentrations. The approach used for this purpose was based on the modification of a standard expression for the Capillary number. This was done by changing constant viscosity of a continuous phase η_0 for the "mean field" viscosity, the latter was assumed as the viscosity of an emulsion as a whole, η_{em}. This method was firstly proposed in [78] for the analysis of the break-up of droplets in a shear flow of concentrated emulsions (see below).

In this approach a modified ("mean field") Capillary number is written as

$$Ca_m = \frac{\eta_{em}\dot{\gamma}}{\sigma / R}. \tag{27}$$

This approach provided a possibility to present all experimental values of drop anisotropy as a function of shear rate for emulsions of different concentrations as a unique function of the modified Capillary number Ca_m, described by the Taylor Eq. (25). The result shown in Fig. 16 looks quite convincing, although for a single value of λ only.

However it was noticed in [79] that the viscosity calculated by the model given in [18] (see Eq. (12)), is always overestimated in com-

parison with experimental data. It means that this model is not completely adequate to the real behaviour of emulsions, as it was already mentioned in Section 3.

Palierne proposed the solution of the problem of deformation and orientation of liquid drops in flow for the linear range of periodic oscillations [80]. In other words, he investigated the dependence of visco-elastic properties of emulsions on the characteristics of the system and frequency. Then the generalization of the theory for the non-linear domain of mechanical behaviour of emulsions was proposed in [81]. A complete model of visco-elastic behaviour of the emulsion of two immiscible liquids was developed in [82,83]. Final analytical results (though related to the domain of moderate concentrations and not taking into account possible droplet coalescence and brea-up) can be found in [84,85]. These studies do not treat only the linear domain of deformations but non-linear effects as well, covering high shear rates and large amplitude periodic deformations.

A clear connection between the morphology of emulsions (i.e. the shape of droplets and their orientation in flow) and the whole complex rheological behaviour was established in a series of publications [80–85] for various flow geometries. The final results were obtained in an analytical form, though they are rather complicated. As an example, only the expression for shear stresses τ for a steady flow is given below, as it illustrates the input of the main factors — shear rate and interfacial tension (presented via the Capillary number), ratio of viscosities of both phases λ and concentration φ (though in the domain of moderate values). The final formula for the dependence $\tau(Ca)$ is:

$$\tau = \frac{2KCaf_1f_2^2}{3(Ca^2 + f_1^2)} \tag{28}$$

where the factors f_1 and f_2 reflect the role of λ and are expressed in the following manner:

$$f_1 = \frac{40(\lambda + 1)}{(3 + 2\lambda)(16 + 9\lambda)}; \tag{29a}$$

$$f_2 = \frac{5}{3 + 2\lambda}. \tag{29b}$$

One can easily see that these factors are close to the coefficients obtained earlier (see Eq. (18) in Section 3).

The factor K represents primarily the influence of concentration on viscosity. Its analytical expression is given by:

$$K = \left(\frac{6\sigma}{5R}\right)\frac{(\lambda + 1)(3 + 2\lambda)\varphi}{5(\lambda + 1) - 5(2 + 5\lambda)\varphi}. \tag{30}$$

The cited publications also give analytical expressions for the first and second differences of the normal stresses in shear flow, describe the stress evolution in transient regimes of deformations, and the frequency (in the linear domain) and amplitude (at large deformations) dependencies of the complex elastic modulus.

A problem of calculating droplet deformations in a flow of viscous liquid was rigorously formulated in [86]. This deformation consists in the transition from spherical to ellipsoidal shape. The exact solution of this problem (but without taking into account interfacial tension) was obtained in [87]. At last, in [88] the authors proposed a complete solution of the problem including the influence of all factors influencing the shape of a drop. One can estimate the quality of the solution referring to Fig. 17 where the calculated values of the anisotropy of a drop (found as the D values according to Eq. (16)) and its orientation θ as functions of the Capillary number Ca are compared with experimental data.

Deformation of drops in a flow (transition from spherical to ellipsoidal shape) surely influences the viscosity of an emulsion [89]. This is confirmed by direct measurements of a model system – emulsion of
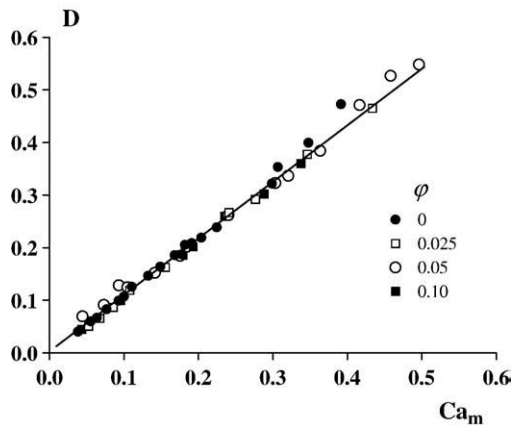
Fig. 16. Dependence of the anisotropy of a droplet in flow of emulsions of different concentrations plotted in terms of the modified ("mean field") Capillary number. The straight line corresponds to the dependence $D(Ca_m)$, calculated by Eq. (25) after change of Ca to Ca_m. (From [77], Fig. 8, with kind permission of Springer Science + Business media).
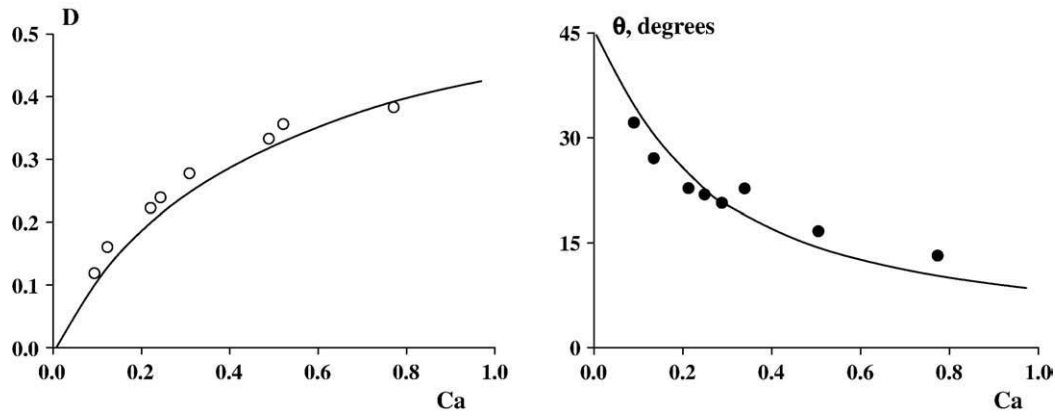
Fig. 17. Comparison of the theoretical predictions for the liquid drop deformation (*left*) and orientation (*right*) in a viscous liquid flow ($\lambda = 3.6$) with experimental data (*points*). (From [88], Fig. 6, with kind permission of Springer Science + Business media).

water droplets in a rather viscous alkyd resin – in the domain of low shear rates where no noticeable deformation of droplets takes place. The concentration dependence of emulsion viscosity was found to be very close to the concentration dependence of suspension viscosity, as it was discussed in Section 2 [90]. However the situation changes radically at high shear rates where droplets are strongly deformed due to low values of the viscosity ratio λ. As a result, a non-Newtonian flow was observed and the concentration dependence of viscosity was described (at high shear rates) by the empirical formula:

$$\eta = \eta_0(1 - \varphi), \tag{31}$$

As one can see, the viscosity of an emulsion becomes less than the viscosity of the continuous medium.

As usual, the problem of calculating the deformation of liquid drops in a flow is considered without taking into account inertia (i.e. at very low Reynolds numbers). However, estimations show that the increase of the Reynolds number enhances the impact of inertia, which in turn leads to stronger deformations of a drop and consequently to the growth of stresses in an interfacial layer [72,91]. It also influences the stability of drops, which – as will be discussed below – is determined by surface stresses.

The possibility of drop break-ups is governed by the fact whether outer forces (stresses) applied to a drop exceed the forces (stresses) stabilizing its shape. As was mentioned earlier, the stability of a drop is supported by a surface force characterized by the Laplace pressure (σ/R), where σ is the surface tension and R is the radius of a drop. Outer stresses are created by a flow around the drop. They are determined by the product ($\eta_0\dot{\gamma}$), the shear stress, where η_0 is the viscosity of a continuous medium, and $\dot{\gamma}$ is the rate of deformation (in shear).
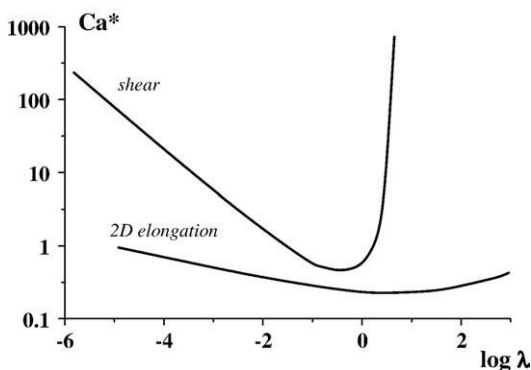
The ratio of the discussed factors is the Capillary number *Ca* (see Eq. (24)).

The determining factor for drop stability is a critical value of the Capillary number *Ca**, which follows from theoretical calculations and experimental data and depends on the ratio of viscosities of the drop and continuous phase: $\lambda = \eta_{dr}/\eta_0$.

The values of *Ca** decrease with the increase of λ in the domain $\lambda < 1$. As result in one of the earlier publications [92] the following quantitative approximation for the function *Ca**(λ) at rather small values of λ is proposed:

$$Ca* = 0.054\lambda^{-2/3}. \tag{32}$$

More complete results were obtained by Grace [93], who examined not only simple shear but also two-dimensional extension (kinematically equivalent to pure shear) deformations. His final results are presented in Fig. 18 for the full range of λ values.

The two following results are of special interest. Firstly, there is some minimal limit of *Ca** = 0.4 approximately corresponding to the equality of viscosities of drop and matrix liquid ($\lambda = 1$). Secondly, drops do not break down in laminar flow at all in the domain $\lambda > 4$ (the right side of Fig. 18). It corresponds to drops of high viscosity.

The results of systematic investigations of the problem of break-up of single drops are presented in Fig. 19 for a simple shear deformation. The break-up condition was defined as the limit of their deformations (see above). It was assumed that when a deformation results in some steady state of a drop, then this rate of deformation is less than that corresponding to the critical value *Ca**. When the calculations show that drop deformations becomes continued unlimitedly, which means

Fig. 18. Dependence *Ca** (λ) for the full range of λ values in simple shear and two-dimensional extension flow. (According to Grace [93], Fig. 14a).
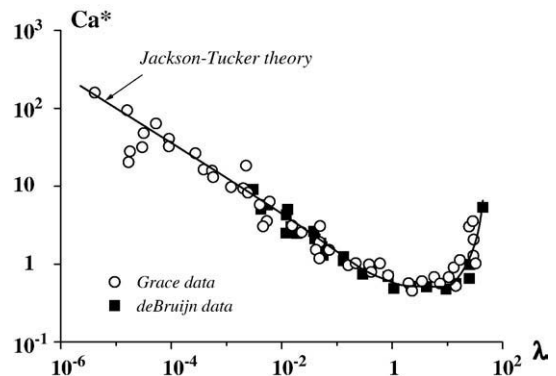

Fig. 19. Correlation of theoretical predictions for the *Ca** (λ) dependence for laminar simple shear and experimental data (points). (From [88], Fig. 14b, with kind permission of Springer Science + Business media).

that the drop brakes, then the corresponding Ca is larger than Ca^*. As one can see in Fig. 19, the theoretical predictions are in full agreement with experimental data in a wide range of λ values spanning over six orders of magnitude [88].

The critical conditions for droplet break-up change when the continuous medium is not purely viscous but visco-elastic. Indeed, surface stresses at the interface can vary and are a function of the Reynolds number and simultaneously of the Weissenberg number (the ratio of characteristic times of outer action and inner relaxation). Numerical modelling demonstrated that the critical values of the Capillary number really increase with increasing Weissenberg number (enhancement of elasticity of a continuous medium) [94].

The above discussed theoretical results and experimental data referred to a single drop or the limiting case of dilute dispersions where any dynamics or interactions can be neglected. However, the largest interest from a theoretical and applied point of view is connected with the break-up or coalescence of drops in concentrated emulsions, but the use of any approach for dilute emulsions and experimental data in Ca^* vs. λ coordinates do no allow to draw a general picture [78]. The critical values Ca^* were found to lie below the lowest limit (cf. Fig. 19) and are strongly concentration dependent. A generalization of experimental results can still be reached by modifying the definitions for Ca^* and λ, substituting the viscosity of the continuous medium η_0 by the viscosity of the emulsion η_{em}. The expression for such modified ("mean field") Capillary number was given above by Eq. (27), and the corresponding modified viscosity ratio λ_m is written as

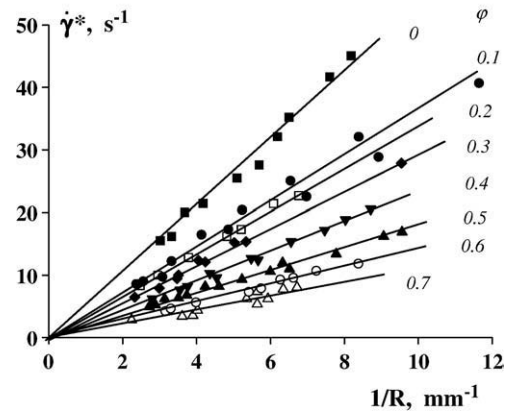$$\lambda_m = \frac{\eta_{dr}}{\eta_{em}}. \tag{33}$$

The results of experimental studies discussed in terms of the function $Ca_m^*(\lambda_m)$ are shown in Fig. 20 for emulsions in a wide concentration range (up to $\varphi = 0.7$). As one can see, this approach allows us to obtain the generalized characteristics of drop break-up in a laminar shear flow of emulsions at different concentrations.

The influence of concentration is especially evident from Fig. 21, where the critical shear rate $\dot\gamma^*$ (for the condition of break-up) is presented as a function of the reciprocal droplet radius for emulsions of different concentrations. The higher the concentration, the lower is the shear rate required for the break of a drop. It is evident that this result is subjected to the increase of stresses in the transition to higher concentrations of an emulsion.

The relationship $\dot\gamma^* \propto R^{-1}$ is a consequence of the definition of the critical Capillary number, but the coefficient in this dependence is different varying with the concentration (and consequently, with the viscosity) of the emulsion.
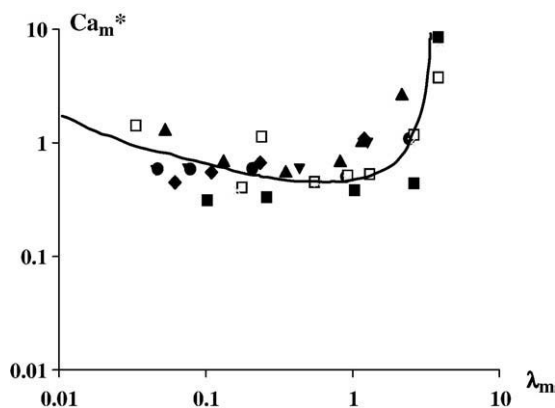
Fig. 21. Dependence of the critical shear rate corresponding to droplet break-up on droplet size in emulsions of different concentrations of the dispersed phase. (From [78], Fig. 5, with kind permission of Springer Science + Business media).
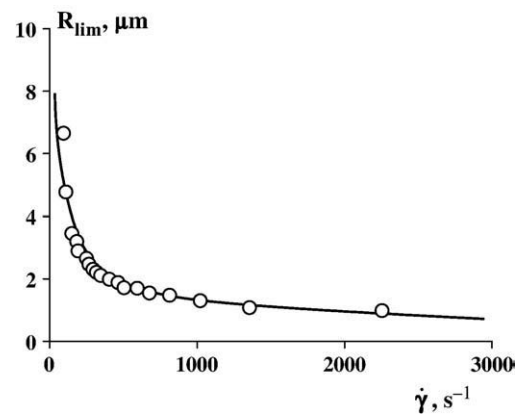
The drop break-up at a given shear rate can continue up to some limiting size R_{lim}, because the Capillary number decreases with the decrease of radius and finally it becomes less that the critical value Ca^*. This conception is illustrated in Fig. 22. The dependence of R_{lim} on the shear rate $\dot\gamma$ is described by a parabolic law (solid line in Fig. 22) and the following scaling law becomes valid [95]:

$$R_{lim} = C\frac{\sigma}{\eta\dot\gamma}. \tag{34}$$

The factor C appeared to be of the order of 1, and this also reflects the critical value of the Capillary number.

Droplet break-up in concentrated emulsions ("emulsification") can proceed in steady shear as well as in the mode of periodic oscillations if deformations go beyond the limit of the linear domain [96]. In this case, the drop break-up leads to a quite noticeable growth of the elastic modulus. This result is in accordance with the dependence of the modulus on the droplet size, as it was discussed above (see Fig. 13).

It is essential that all theoretical (model) conceptions and experimental results discussed above relate to laminar flows. The transition to higher velocities and the transition to a turbulent regime of flow change the situation substantially and make the picture of drop break-up in emulsions more complicated. The basic problem consists in methods of a quantitative characterization of turbulent flows by themselves, i.e. large fluctuations of local velocities and stresses inherent to turbulent flows.

Fig. 20. Condition of drop break-up for different concentrations (φ varied from 0 to 0.7). Experiments were performed for a model emulsion — silicon liquid drops in water. (From [78], Fig. 7, with kind permission of Springer Science + Business media).

Fig. 22. Dependence of drop size decrease as result of laminar shearing of an emulsion on shear rate. Experimental data were obtained for a model system: silicon liquid drops in water ($\varphi = 0.7$). A solid line corresponds to the scaling law, Eq. (34). (According to Mason [95], Fig. 3).

It is generally accepted that there are two different modes of turbulent flow — "inertial turbulent" (TI) and "viscous turbulent" (TV) regimes. The difference between them is related to the ratio of characteristic sizes of a liquid droplet and a turbulent vortex [97,98]. The minimal droplet size in the TI regime depends on the ratio of dynamic pressure fluctuation (break-up of a droplet) and surface tension, while the break-up of drops in the TV regime occurs under shear stresses acting via the continuous medium.

I was shown in [99] that the maximum size of a stable drop in the TI regime $d_{\text{TI,max}}$ can be expressed in the following manner:

$$d_{\text{TI,max}} = A_1 \left(\varepsilon^{-2/5} \sigma^{3/5} \rho_c^{-3/5} \right) = A_1 d_k \tag{35}$$

where A_1 is the front-factor of the order of 1, ε is the intensity of energy dissipation characterizing the dynamic situation in a flow, and ρ_c is the density of the continuous phase. The term in brackets designated as d_k is a characteristic length.

The maximal size of a drop in the TV regime, $d_{\text{TV,max}}$, is determined by the viscous shear stresses:

$$d_{\text{TV,max}} = A_2 \left(\varepsilon^{-1/2} \eta_0^{-1/2} \rho_c^{-1/2} \sigma \right) \tag{36}$$

where the constant $A_2 \approx 4$, η_0 is again the viscosity of the continuous medium.

These formulas are valid for low-viscosity drops. A generalization for emulsions, in which drops are dispersed in a phase of arbitrary viscosity, interrelates parameters of the emulsion and flow conditions [100–105]:

$$d_{\text{TV,max}} = A_3 \left(1 + A_4 \frac{\eta_{dr} \varepsilon^{1/3} d_{\text{TV,max}}^{1/3}}{\sigma} \right)^{3/5} d_k \tag{37}$$

where A_3 and A_4 are constants, η_{dr} is the viscosity of the liquid dispersed drops. Note, d_k is again the characteristic length, which enters in Eq. (35). The results of experimental investigations confirm that the dependence of the droplet size on determining factors for the TI regime are well described by Eq. (35) with a coefficient $A_1 = 0.86$ (see Fig. 23). The comparison of theoretical predictions and experimental data for the TV regime provides also quite good results (Fig. 24). In this case, the coefficients in Eq. (37) are as follows: $A_3 = 0.86$ and $A_4 = 0.37$.

The theory of droplet break-up is typically focused on the final equilibrium state of droplets, but also the kinetics of the break-up process is of interest. This kinetics in a turbulent flow regime was con-
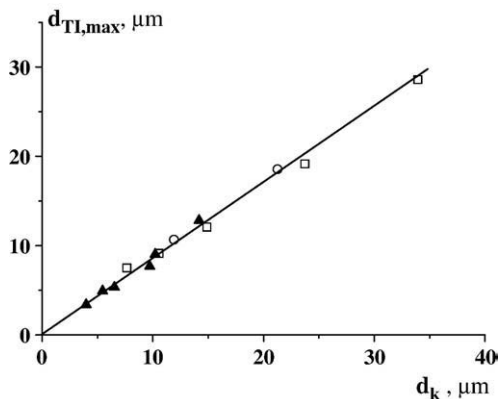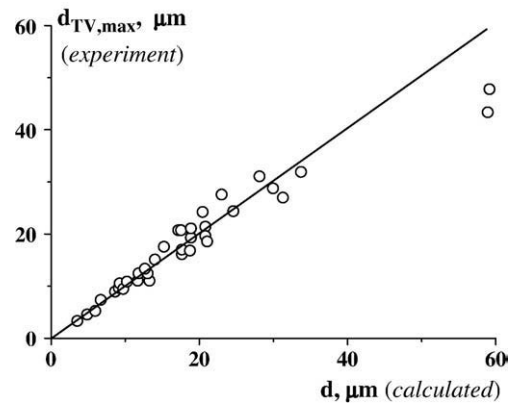

Fig. 24. Correlation between experimental and predicted values of the maximum drop size formed in the TV regime. Experimental points were obtained for a large number of different emulsions. (From [99], Fig. 7, with kind permission of Elsevier B.V.).

sidered in [106], where a kinetic scheme and an experimental method for the determination of the kinetic constant were proposed. The kinetics of drop break-up can be described by means of a single additional constant k_{br}, depending on the drop size d:

$$k_{dr}(d) = B_1 \frac{\varepsilon^{1/3}}{d^{2/3}} \exp \left[-B_2 \left(\frac{d_k}{d} \right)^{5/3} \left(1 + B_3 \frac{\eta_{dr} \varepsilon^{1/3} d^{1/3}}{\sigma} \right) \right] \tag{38}$$

where B_1, B_2, B_3 are fitting coefficients. The experiments carried out with a large number of objects confirmed the validity of the proposed calculation scheme and allowed the authors to find the values of constants in Eq. (38). However, it is worth mentioning that break-up of drops in the flow of emulsions leads to the formation of a large number of droplets of different sizes. Therefore, these droplets should be characterized by their maximum size as well as by the size distribution and the average size. It seems most reasonable that the size distribution is described by the Gaussian distribution function. However, direct measurements showed that the real droplet size distributions can be very different and depend on the viscosity of the droplets [107].

6. Blends of polymer melts as emulsions

Polymer blends are very important technological materials of modern industry because the addition of a polymer to another can create a material of principally different properties. The classical example of introducing rubber particles into a PS matrix gave a completely new material — high impact PS with quite different application properties in comparison with its components.

Many original papers, reviews, books and technical reports are devoted to the analysis of various aspects of polymer composition and their applications. Only two examples are referred to [108,109]. The present discussion touches a rather narrow problem in this vast field of problems related to polymer blends and represents a possibility to treat polymer blends as emulsions where one polymer is dispersed in the other. Note, only blends of polymeric melts (i.e. liquids) will be considered here.

Two different polymers are not compatible with each other in a noticeable concentration range, as a general rule. This means that they do not form solutions even if their monomers and low-molecular-weight analogues do. Rare exceptions are such pairs as PET/PBT, PS/poly(phenylene oxide), PMMA/ poly(vinyledene fluorine). In practically all other cases two polymers in a blend create emulsions.

The transition from a compatible system to an emulsion as the result of phase separation and coalescence of droplets leads to tremendous changes in the rheological (and in particular visco-elastic)

Fig. 23. Dependence of the maximum drop diameter on the term entering Eq. (35) for the TI flow regime. The emulsion was formed by hexadecane drops in water. The slope of the straight line is at $A_2 = 0.86$. Different labels correspond to various surfactants used as stabilizers. (From [99], Fig. 5, with kind permission of Elsevier B.V.).

properties of the material. Fig. 25 illustrates this effect on the basis of relaxation spectra of a blend PS/poly(vinylmethyl ester). Only one sharp peak (a relaxation maximum) is observed at 120 °C. This peak corresponds to the PS phase, in which the second component is solved. The components become incompatible at 150 °C and it is reflected by two independent peaks [110]. The existence of a single or of two relaxation maxima is a direct evidence of the phase state in a system (blend).

The general question can be put: are polymer blends analogous by their structure and properties to emulsions of low-molecular-weight components? A formal analogue between these two types of systems undoubtedly exists. Moreover, as it will be shown below, many principle features of emulsions are quite acceptable in the discussion of polymer blends. However, polymer blends have some principle peculiarities, which require their treatment as a rather special class of emulsions. Several significant points should be stressed here.

Firstly, polymer blends do not stay in the molten state for a long time in real technological conditions but they are subjected to large deformations. Viscosities of both components in a polymer blend are very high in comparison with regular emulsions. Therefore, a dispersed phase rather rarely separates off in form of spherical particles. A dispersed phase usually generates prolonged agglomerates, which can be sometimes self-organized in a continuous phase, so that in many cases it is impossible to say, which component represents the dispersed particles and which one the continuous phase.

The structure of polymer blends can be presented by the following simple picture in Fig. 26. One can see that a dispersed phase exists in form of (almost) spherical droplets in narrow concentration ranges, while both phases create domains of uncertain shape in the broad central range of concentrations.

Secondly, polymeric materials are visco-elastic media and their bulk visco-elasticity has the same importance as the elasticity of interfacial layers. Thirdly, polymers are not soluble in each other. But relatively short parts of the polymeric chains ("segments") are mobile and similar to the diffusivity of low-molecular-weight analogues. Therefore these segments can diffuse into each other forming an intermediate transient layer with continuous (but not sharp) changes in concentration of both components [111,112]. Such interfacial layer (in which segmental solubility of the components is realized) has properties different from those of the two pure phases, and this effect should be taken into account in the analysis of the behaviour of polymer blends. And finally, surfactants are rather rarely introduced into polymer blends, although the compatibility of two polymers is artificially improved by adding special compounds — *compatibilizers*, which give an additional and significant input into the properties of polymer blends.
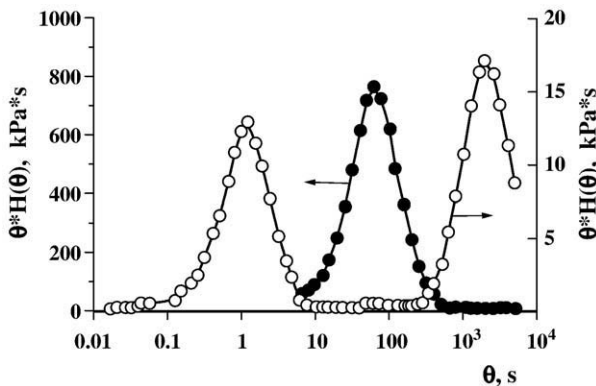

Fig. 26. Evolution of the blend structure as a function of concentrations of both components in transition from one boundary situation ("black" droplets are dispersed in a "white" material) to the opposite case ("white" droplets are dispersed in a "black" matrix) via the transient state of uncertain morphology of both phases.

Block-copolymers consisting of components of a blend are often used as compatibilizers. The basic idea of this approach is that each block in a copolymer is compatible with one of the components in the blend. So, one can expect that this method provides a continuous transition from one phase to the other which cannot be reached for low-molecular-weight liquids.

Surely, the general conceptions concerning drop deformations in a flow as well as ideas about the concentration dependence of viscosity can be applied to polymer blends. However, an independent problem is the estimation of the visco-elastic properties of these blends, bearing in mind that a polymer blend should be treated as a three components system with special properties of the interfacial layer.

The viscosity of a blend consisting of incompatible polymers, e.g. PIB/PDMS, can be quite satisfactorily described by Eq. (13) [113]. This blend is a typical polymeric emulsion: the lower concentrated component exists the form of spherical droplets and phase inversion takes place at the concentration ratio 50:50. However, even when only a minor amount of a compatibilizer (0.5% of a PIB-PDMS block polymer) is added to this blend, this modification provides a much better compatibility of the components and, as a result, the viscosity sharply increases, and also the relaxation time, complex elastic modulus and elasticity of the blend increase. Besides, the addition of a compatibilizer prevents coalescence of the droplets. A general explanation of these effects is based on the concept that a compatibilizer is completely adsorbed onto the surface of the dispersed droplets providing them a solid-like character. Such systems behave like a liquid containing a quasi-solid filler, which means that the viscosity of the liquid matrix with solid particles can be described by the equations proposed for typical suspensions. In other words, the situation here is quite similar to the above described emulsions of low-molecular-weight liquids stabilized with typical surfactant (see Section 3).

Let us assume that the visco-elastic properties of components of a blend are described by the frequency dependencies of the complex modulus, $G_1'(\omega)$ and $G_2'(\omega)$ of the two components. Then the question arises what relaxation properties of a blend are? The closest answer is the additive supposition of the inputs of both components. In this approach, the frequency dependence of the elastic modulus of a blend $G_{bl}(\omega)$ can be written as

$$G_{bl}'(\omega) = w_1 G_1'(\omega) + w_2 G_2'(\omega) \tag{39}$$

where w_1 and w_2 are the weights of both components in the blend.

However, numerous experimental studies showed that this simplest supposition is not adequate. This is easily grasped because the equation does not take into consideration the existence of the transient layer, which undoubtedly gives its input into visco-elastic properties of a blend. One of the more successful attempts to describe the visco-elastic properties of polymer blends is the Yemura–Takayanagi equation [114], which is related to standard conceptions of viscosity of emulsion of low-molecular-weight liquids:

$$\eta_{bl}^*(\omega) = \eta_0^* \frac{3\eta_0^* + 2\eta_{dr}^* - 3\left(\eta_0^* - \eta_{dr}^*\right)\varphi}{3\eta_0^* + 2\eta_{dr}^* + 2\left(\eta_{dr}^* - \eta_0^*\right)\varphi} \tag{40}$$

Fig. 25. Normalized relaxation spectra $\theta H(\theta)$ compatible (at 120 °C — filled circles) and incompatible (at 150 °C — open circles) mixtures of two polymers. (From [110], Fig. 14, with kind permission of Springer Science + Business media).

where η_{bl}^* is the dynamic viscosity of the blend, η_0^* is the dynamic viscosity of the polymer forming the continuous phase, η_{dr}^* is the dynamic viscosity of the polymer representing the droplets with φ as its concentration. Another version of their approach is a relationships for the frequency dependence of the dynamic modulus taking into account volume compressibility of a blend via the Poisson coefficient. However, these calculations were proposed not for melts but for mixtures of solid polymers where it is incorrect to neglect their compressibility.

Modern conceptions in understanding rheological properties of polymer blends are based on the fundamental publication of Palierne [80], which has been already cited in the previous section in discussing the drop deformation in a liquid flow. The same approach can be applied to polymeric visco-elastic emulsion if one component forms drops in a continuous matrix of the other. These drops are transformed to ellipsoids and this leads to a change in deformation of a drop, in the intermediate layer as well as in the surrounding medium.

As was discussed above in Section 5, a rigorous theory of drop deformation in the linear domain of visco-elasticity was proposed in [80]. This theory gives the following expression for the complex elastic modulus of a blend $G_{bl}^*(\omega)$ of two visco-elastic liquids as result of the sphere-to-ellipsoid transformation:

$$G_{bl}^* = G_0^* \frac{1 + 3\varphi H(\omega, R)}{1 - 2\varphi H(\omega, R)} \tag{41}$$

where the function $H(\omega,R)$ in Eq. (41) is given by

$$H = \frac{4\frac{\sigma}{R}\left[2G_0^*(\omega) + 5G_{dr}^*(\omega)\right] + \left[G_{dr}^*(\omega) - G_0^*(\omega)\right]\left[16G_0^*(\omega) + 19G_{dr}^*(\omega)\right]}{40\frac{\sigma}{R}\left[G_0^*(\omega) + G_{dr}^*(\omega)\right] + \left[2G_{dr}^*(\omega) + 3G_0^*(\omega)\right]\left[16G_0^*(\omega) + 19G_{dr}^*(\omega)\right]}. \tag{42}$$

When we simplify the model by assuming only a single-relaxation time (as discussed in Section 3, Eq. (18)), the following formulas for the components of the complex modulus are obtained

$$G'(\omega) = \frac{3Kf_2^2(\omega\theta)^2}{3\left[f_1^2 + (\omega\theta)^2\right]}; \tag{43a}$$

$$G''(\omega) = \frac{3Kf_2^2(\omega\theta)}{3\left[f_1^2 + (\omega\theta)^2\right]} \tag{43b}$$

where the parameters K, f_1 and f_2, and the relaxation time θ were defined further above. This approach really gives satisfactory results for the PIB/PDMS blends [115], but attention has to be paid to the fact that this study was devoted to low-molecular-weight analogues of these polymers, which behave as Newtonian liquids. This is possibly the reason why the simple single-relaxation-time approximation was satisfactory.

A more complicated case of the blend of the same polymer pair (PIB/PDMS) with an added compatibilizer [116] demonstrated the diversion between experimental values of the dynamic modulus G'_{exp} and the values G'_p predicted by the Palierne model, which was explained by the input of visco-elasticity of the interfacial layer, and formulated by the following equation

$$G'_{exp} = G'_p + G'_{int\,er} \tag{44}$$

where the parameter $G'_{int\,er}$ was just introduced as responsible for the properties of the intermediate layer. In this equation, the visco-elasticity of a blend is treated as the additive sum of elasticity contributions of both polymeric components and the interfacial layer [113]. Fig. 27 illustrates the quality of theoretical predictions by the Palierne model and demonstrates that the theory proposes rather good pre-
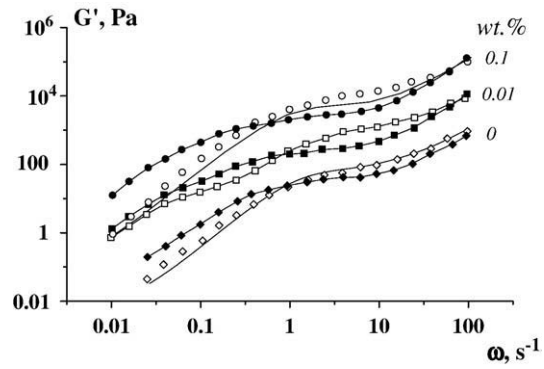

Fig. 27. Frequency dependencies of the storage modulus for a PIB/PDMS blend (points). Open points correspond to the state of the system after shearing at 480 Pa, and filled points reflect data after shearing at 30 Pa. Pairs of curves were obtained for blends with different contents of a compatibilizer (shown at the curves) and are shifted upwards by one order of magnitude to avoid superposition of points. (From [113], Fig. 3, with kind permission of Springer Science + Business media).

dictions of the frequency dependencies of the storage modulus. We can also see from this figure, that the prehistory of deformation usually does not influence the rheological properties of emulsions of low-molecular-weight liquids, but it does for polymeric blend. This phenomenon is completely related to the morphology of the dispersed droplets, which is reached in previous deformations and stored due to the high viscosity of the continuous polymeric phase.

The applicability of models for deformable drops of polymer blends requires a special analysis from case to case in order to find out if each polymer is characterized by its own relaxation spectrum. The generalization of Palierne's model allows obtaining a complete equation for the complex dynamic modulus [116]. This analysis additionally includes the mechanism of visco-elastic relaxation of the interfacial layer and also the possibility of an arbitrary size distribution of drops described by some function $v(R)$. All in all, this represents a complicated and closed analysis of the problem, leading to the basic final equation for the frequency dependence of the complex dynamic modulus of the blend $G_{bl}^*(\omega)$ in the following form:

$$G_{bl}^*(\omega) = G_0^* \frac{1 + 3\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}v(R)dR}{1 - 2\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}v(R)dR} \tag{45}$$

where the functions $E(\omega,R)$ и $D(\omega,R)$, though too cumbersome to be reproduced here, contain the visco-elastic characteristics of all components of a system: dynamic moduli of the continuous phase $G_0^*(\omega)$ and dispersed drops $G_{dr}^*(\omega)$, as well as a function presenting the visco-elastic properties of the interfacial layer, and a function describing the droplet size distribution $v(R)$.

The analysis by this complete model of experimental data showed that the visco-elastic properties of the interfacial layer are quite adequately presented by a single-relaxation time assuming a Maxwell model. Moreover, it appeared that at least in the first approximation, the simplest single-relaxation-time model satisfactory describes the visco-elastic properties of the components of a blend, the values of relaxation times being different for the continuous phase and dispersed drops. Also, it was proven that the whole size distribution $v(R)$ could be substituted for a single volume-averaged radius of drops. This rather simplified model quite adequately describes the experimental dependencies $G_{bl}^*(\omega)$ for PS/PMMA blends in a wide frequency range. The parameters of the model were chosen by a fitting method of the experimental data by the calculated curves. Surface tension was also one of the free parameters in the procedure of optimization.

The calculations confirm that the rheological properties of the interfacial layer are practically purely elastic (with low viscous losses).

If we treat an emulsion as a system containing monodisperse particles, Eq. (45) can be written in a simpler form:

$$G_{bl}^* = G_0^* \frac{1 + 3\varphi \frac{E(\omega,R)}{D(\omega,R)}}{1 - 2\varphi \frac{E(\omega,R)}{D(\omega,R)}}. \tag{46}$$

This equation for the complex dynamic modulus was used in [117], and it was shown that the visco-elastic properties of the interface have a major effect onto the properties of a blend in the real case of two in-compatible polymers. The comparison of calculations with experimental data, according to the conclusions of [117], is presented in Fig. 28.

It is also worth mentioning that the effect of the prehistory of deformation on rheological properties of the blend was observed in [117] and direct structural studies confirmed that this effect was related to the morphology of the blend.

The data presented in Fig. 28 clearly demonstrate that neglecting the effect of the interfacial layer (dotted lines) leads to an underestimating of the real values of storage modulus, which is especially evident in the low frequency domain. Fitting of the quantitative predictions of the model of deformable ellipsoids to experimental data showed good agreement in a wide frequency range only when taking into consideration the surface modulus of elasticity of the interfacial layer, G_s. Moreover, there is a direct correlation between the concentration of a diblock copolymer of both components of the blend as compatibilizer and the elastic modulus of the interfacial layer. Fig. 29 illustrates this correlation with the argument being the coverage of dispersed droplets by the compatibilizer. This figure also demonstrates the role of shear deformations in structure formation: with increasing the time of deformation (up to the limit of steady values) the coverage of the dispersed droplets increases and, consequently, the modulus of interfacial elasticity become higher. Note, that the G_s values are related to the length unit but not to the area and their dimension is N/m.

The above discussed experimental data as well as experimental data of other authors (see e.g. [118]) and their comparison with theoretical predictions prove that the rheological properties of the interfacial layer should be necessarily taken into consideration in addition to the elasticity directly relayed to drop deformation, the latter being treated in many publications as the only mechanism governing the properties of emulsions. This approach opens the possibility to give quantitative estimations of the impact of a compatibilizer. This approach allowed not only to describe correctly the visco-elasticity of polymeric blends but also to predict the probability of drop coalescence in a shear field too.

It is interesting to note that the method of compatibilizing does not strongly influence the rheological properties of blends. An example
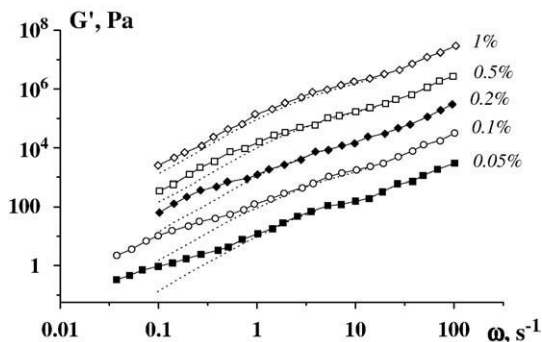

Fig. 29. Dependence of the elastic modulus of the interface layer (2D structure) on the content of the compatibilizer. The abscissa presents the number N of compatibilizer molecules at 1 cm² of the surface area of dispersed particles. Numbers at the curves designate the concentration of a compatibilizer in the blend. Circles mark results obtained after preliminary shear at a shear rate of 4.8 s⁻ up to the deformation of 3000 units. Squares reflect results obtained after shearing at 1.2 s⁻ till the steady (stationary) state was reached. (From [117], Fig. 8, with kind permission of the Springer Science + Business media).

leading to this conclusion is the comparison of the rheological properties of the pair PP/PS where compatibilizing was reached either by a chemical method (introduction of compounds with active chemical groups interacting with both components of the blend) or by simple physical mixing [119].

As a result of this discussion, we can conclude that the theoretical models describing rheological properties of emulsions are valid for both emulsions of low-molecular-weight liquids and for polymeric blends. However two special points for polymeric systems have to be emphasized, firstly, the existence of a multi-component relaxation spectrum, and secondly, the strong impact of the pre-history of deformations. The latter effect is evidently explained by the structure and morphology relaxation due to the high viscosity of the medium. Moreover, the theoretical models have been compared with experimental data for blends, in which the morphology of the dispersed droplets was close to the spherical or ellipsoidal shape. Theoretical models work well just in these cases. It is difficult to suppose that these models would give satisfactory results when a dispersed phase forms a prolonged domains of uncertain shape (as in the central part of Fig. 26) or moreover if both components form continuous phases. These situations are unlikely to be described by the above discussed models. A lot of photos of these uncertain morphological forms existing in polymer blends can be found in the scientific literature. The possibility of a quantitative description of rheological properties of such systems looks rather questionable.

Many publications devoted to polymeric blends contain parallel examination of their morphology and rheological properties. This represents a solid ground for correlations between the structural and mechanical properties of polymer blends (emulsions) and allows an extension to transient modes of deformation. An instructive example of such investigations is the study of drop shape transformations in a PP/PS blend along the deformation curve of constant shear rate mode including a pre-stationary domain with shear stresses passing through a maximum, as well as a periodic multi-step deformation mode with alternating shear and rest [120].

All these experimental studies clearly demonstrate that the shape of dispersed drops continuously change and are transformed into fiber-like structure of the self-reinforcing type at high rates of deformation [121]. In such cases, the viscosity of a blend can be calculated by a model proposed in [122]:

$$\eta = \eta_0 \left[1 + \left(\frac{1}{\lambda} - 1 \right) \varphi \right]^{-1}. \tag{47}$$

Fig. 28. Viscoelastic properties of PI/PDMS blends with different contents of a compatibilizer (block-copolymer of the components of the blend). Each subsequent curve is shifted upward by one order of magnitude to avoid superposition of points. Solid lines correspond to the model taking into account an interface layer, while dotted lines were calculated without this factor. (From [117], Fig. 5, with kind permission of Springer Science + Business media).
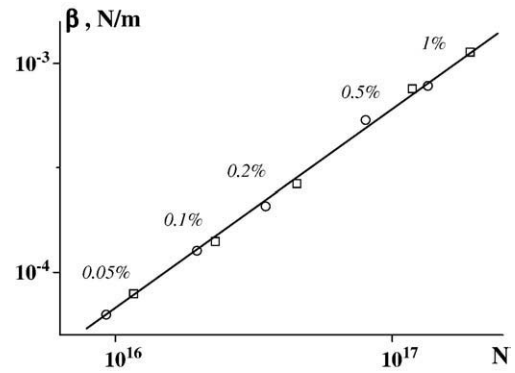
This equation was applied to polymer blends in the range of high shear rates, though for the given Eq. (46) underestimates the viscosity values in comparison with real values [123]. It appeared that this case was quite well described by the simple rule of logarithmic additivity for the viscosity of the blend η_{bl}:

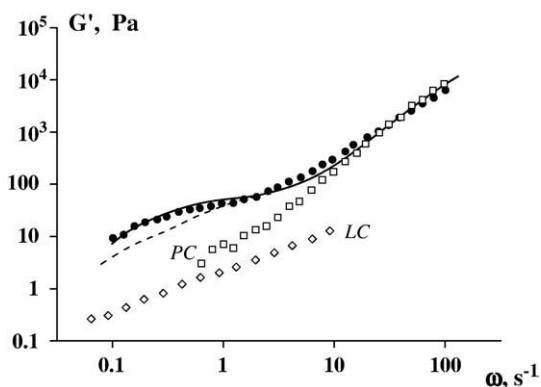$$\lg \eta_{bl} = \varphi_1 \lg \eta_1 + \varphi_2 \lg \eta_2 \qquad (48)$$

where φ_1, η_1 and φ_2, η_2 are volume shares and viscosities of both co-existing phases, respectively.

Finally, there is a special case of rheology of polymer blends in shear when the dispersed phase is a liquid-crystalline (LC) polymer. Systems of this kind are of great technical interest, because by varying the content of a LC polymer it appears possible to construct materials with particular characteristics, such as high strength and perspective optical properties. Such materials and fields of applications are described for example in [124,125].

Naturally the anisotropy of LC liquids (with their sharp tendency to orientation) leads to a non-standard behaviour of drops with the formation of original structures and polydomain morphology [126–128]. One can also suppose that the rheological properties of such systems would be quite different from those of other blends. Up to date numerous studies devoted to investigations of the rheology of LC and regular thermoplastic polymer blends are known due to their technological importance. The main role of a LC polymeric additive relates to the remarkable decrease of viscosity of a blend [126,127,129]. Of course this effect is connected with the fibrillization of the LC component, which leads to a domination of the orientation of macromolecules of a thermoplastic polymer in a flow and consequently to a decreased effect of intermolecular entanglements [130–132].

In [133,134] it was shown that the application of emulsion models proposed for blends of ordinary thermoplastic polymers to blends containing a LC component is possible if the characteristic size of the LC domains is much less than the size of dispersed drops. In this situation, one can neglect the structure peculiarities of the dispersed phase. Apparently, the approach of Ericksen based on the conception of rheology of anisotropic media is better founded for such systems [135].

The results of the dynamic modulus calculations based on Palierne's model and the model taking the anisotropy of the LC domains into account are presented in Fig. 30 in comparison with experimental data for a blend, in which a PC melt is the matrix and a LC polymer forms the dispersed phase. As one can see the correction related to peculiarities of the rheological properties of the LC polymer is not very high though its introduction allows a better fitting of the experimental data. This figure is also interesting as striking evidence for much higher values of the elastic modulus of a blend in comparison with the moduli of both components in a low-frequency domain. The effect of the LC component is pronounced just in this domain while the properties of the thermoplastic matrix dominate at high frequencies.

The fact that the difference between the calculations for isotropic and anisotropic models of dispersed drops is not very large and possibly caused by the low deformation. At the same time, one can expect that for large deformations, and in particularly in flow, the impact of anisotropy of a LC polymer on the rheological properties of a blend would be much stronger. Thus, it is reasonable to think that the general quantitative understanding of the rheology of such polymeric emulsions is still pending.

Studies of uni-axial extensions of molten polymer blends deserve special emphasis. As a rule, the extension mode in such studies is well controlled and accompanied by observations of the structure. The main fact found is the effect of the non-affine deformation of dispersed drops. The relationship between the draw ratio of a blend as a whole and the deformation of separate drops depends on the viscosity ratio of the components in the blend [136–139].

A possibility to estimate the effect of interfacial tension in uni-axial extension of multi-component polymers was mentioned in [140] where the behaviour of a multi-layered (up to 100) parallel array of different polymers on a plane was studied. It becomes evident that the rheological properties upon extension are definitely influenced by the existence of interfacial interactions. Later, this approach was developed for mixtures of incompatible polymers [141–145]. The process of extension was treated in the framework of purely mechanical arguments, noting that mixing of polymers of even close architecture (linear PE and PE with a small number of long chain branchings) leads to quite perceptible changes in the rheological behaviour of a blend [146]. It is interesting to note that the analysis of elastic recovery of blend samples after extension is based on the conception of surface tension as the driving force in the transition from the extended morphology to spherical drops [141–144]. The results of the rheological analysis allow the estimation of the interfacial tension.

Like in shear, also in extensional deformation emulsions including the LC phase demonstrate unusual rheological effects in comparison with blends of regular thermoplastic polymers. The LC polymer plays primarily the role of a plasticizer decreasing the viscosity of a blend. The effect of fibrillization of a LC component was pronounced in the extension of such blend (demonstrated for PP/LC in [147]) and this is favourable for mechanical properties of the final product. The introduction of a compatibilizer promotes the involvement of a thermoplastic matrix in the process of orientation and it leads to the increase of the rigidity of a blend in extension flows.

It is evident that blends of ordinary thermoplastic polymers (e.g. PET or PP) with a LC component demonstrate non-Newtonian properties in elongation flow. The character of a non-linear behaviour might be different: depending on the elongation ratio and/or deformation rate, viscosity as well as rigidity of a blend can increase or decrease [132,148]. It is unlikely that at present we can estimate general quantitative regularities of the behaviour of emulsions of this type — blends of flexible-chain and LC polymers.

In conclusion of this section, it is worth to note that the flow of emulsions in some special geometries, precisely where the space for flow is commensurable with the size of the emulsion drops in (i.e. when flow takes place in so named — *micro-confined* conditions) the effect of spontaneous formation of regular (dissipative) structures characteristic for unsteady state of a system was observed [149]. Surely the properties of such structures should be very unusual in comparison with the rheological properties of regular emulsions.

Fig. 30. Comparison of experimental data (filled symbols) with the results of calculations for the frequency dependencies of viscoelastic properties of the PC/LC polymer blend according to the Palierne model (dotted line) and the model taking into account the anisotropy of a LC polymer (solid line). The frequency dependencies of the dynamic modulus for both components (PC and LC) of the blend are also shown (open symbols). (From [135], Fig. 4, with kind permission of Springer Science + Business media).

7. The role of surfactants: stability and aging

As has been seen from the discussions of Sections 2–6, surfactants and/or compatibilizers play an important, if not a decisive role in the

rheological behaviour of emulsions at any concentration. Aggregation stability of droplets is determined mainly by the nature and concentration of a surfactant in the system creating and stabilizing the emulsion. Thermodynamically, a surfactant is adsorbed at internal interfaces and decreases the interfacial tension. In some cases, it can result even in the formation of equilibrium colloid systems. Besides, the impact of stabilizing internal surfactant layers consists in providing repulsive forces (energetic barrier) between droplets. The increase of the surfactant concentration up to a certain limit is favourable for the stability of an emulsion providing constancy of its properties with time. Therefore it is reasonable to discuss principle regularities of the influence of a surfactant (interfacial adsorption layers) on the rheology of emulsions.

The influence of concentration of a dispersed phase at the same concentration of a surfactant is shown in Fig. 31. One can see that the increasing polymer concentration results in an appreciable increase in viscosity at low shear rates.

The increased emulsions viscosity caused by the low-molecular-weight surfactant stabilizer immobilizes (loss of mobility) the continuous phase due to the formation of micelles at high surfactant concentration [151]. If high-molecular-weight surfactants (e.g. proteins) are used, the increase in viscosity can be explained by the adsorption of polymer molecules and the formation of structurized interfacial layers [45,47].

Rheological properties of adsorbed layers of a surfactant definitely influence the rheology of an emulsion as a whole. To our regret, there are no adequate methods for the study of adsorbed layers just inside emulsions. Therefore the standard objects for investigations are model systems at stationary flat hydrocarbon/water interfaces [12,152,153].

The following physical phenomena are substantial for understanding the properties of an adsorbed layer on the droplet surface in emulsions. Firstly, as a rule, surfactants adsorb at droplet surfaces from the continuous phase (according to the Bancroft rule, the phase in which an emulsifier is more soluble constitutes the continuous phase though some exceptions can exist). Therefore a system as a whole appears non-stationary and the kinetics of adsorption should be taken into consideration. Secondly, the surfactant layer should not be treated as solid-like. This layer contacts with a solution and stores some mobility. As a result, the surfactant concentration is changing in flow and some kind of surface flow down the droplet rear part happens. Therefore the surfactant concentration is inhomogeneously distributed along the droplet surface.

The analysis of the simplest model for a single drop in a dilute emulsion stabilized by a surfactant shows [154] that there are three dimensionless parameters playing a key role in the process of flow. The first one is the viscosity ratio in both phases $\lambda = \eta_{dr}/\eta_0$. The second one is

Fig. 31. Flow curves of aqueous emulsions of acidic microbial polysaccharide for two concentrations of the dispersed phase (shown at the curves). Surfactant − silicon oligomer. (From [150], Fig. 1a, with kind permission of Springer Science + Business media).

the ratio of surface (2D) viscosity expressed as a sum $\eta_{surf} = (2\eta_s + 3\eta_d)$ (like in the Oldroyd Eq. (10)) to volume viscosity of the continuous phase. This ratio can be called the Boussinesq number $Bo = \frac{\eta_{surf}}{R\eta_0}$, where R is the droplet radius. And finally, the third factor takes into account the elasticity of the interfacial layer and diffusion of a surfactant expressed via the ratio $Gi = Re_{Gs}/2\eta_0 D_{eff}$, where $E_{Gs} = \left(\frac{d\sigma}{d\ln S}\right)_\Gamma$ is the surface elasticity modulus (the Gibbs effect), S is the area of the surfactant interfacial layer (area of the droplet surface), Γ is adsorption, and D_{eff} is the apparent diffusion coefficient of the surfactant.

A final expression for the apparent viscosity of an emulsion η_r obtained with the assumption of a visco-elastic interfacial layer and diffusional adsorption dynamics reads [154]:

$$\frac{\eta_r}{\eta_0} - 1 = \left(1 + \frac{3}{2}<\varepsilon>\right)\varphi \tag{49}$$

where $<\varepsilon>$ is the mobility parameter of the interfacial layer averaged over all droplets, which depends on all above listed dimensionless factors. It can be expressed for every droplet in the following way

$$\varepsilon = \frac{\lambda + \frac{2}{5}(Gi + Bo)}{1 + \lambda + \frac{2}{5}(Gi + Bo)}. \tag{50}$$

The introduction of this parameter allows estimating the relative impact of various factors on the viscosity of dilute emulsions stabilized by a surfactant. Eq. (49) with the given expression for ε transforms into the Oldroyd equation at $Gi \to 0$ ($E_{Gs} \to 0$), i.e. when the interfacial elasticity is negligible.

A quantitative estimation show that the ratio between the viscous and elastic properties of an interfacial layer for real systems (ionic and non-ionic surfactants and proteins) is such that its elasticity should not be neglected. This is true especially for interfacial layers of insoluble surfactants where the apparent coefficient of diffusion is low and consequently the factor G is high. Just this reason explains the solid-like character of liquid drops covered by a surfactant and moving through a liquid continuous medium at low velocities (low Reynolds numbers), as was discussed above in Sections 1 and 2.

The rheology of interfacial layers becomes important with increasing droplet size [155]. Large drops deform in a shear field (see Section 5) and the viscosity of the corresponding emulsion becomes dependent on the rheological properties of the interfacial film. With respect to concentrated emulsions, the deformation of droplets can happen due to their dense packing. A solid-like behaviour (elasticity) of highly concentrated emulsions is the results of the counteraction of adsorbed surfactant layers against the increase of the equilibrium interfacial tension upon the increase of the surface are of already compressed droplets in shear [42]. Both, shear and dilational elasticity can give their input into the overall elasticity of an emulsion, as was demonstrated experimentally for proteins [47].

However, the discussion of rheological properties of different surfactants and the influence of various factors on these properties including the intermolecular interaction in surface layers is a separate problem going beyond the aim of this overview. Nevertheless, it is worth mentioning that there is undoubtedly an interrelation between the rheology of interfacial surfactant layers and the stability of emulsions because the latter is determined mainly by the elasticity (thermodynamic factor) and viscosity (kinetic factor) in droplet interactions (see, e.g. [156–158]).

The chemical structure of a surfactant is of primary practical interest. First of all, the efficiency of a surfactant depends on the hydrophilic–lipophilic balance. For example, if an amphiphilic polymer (for example a modified hydroxy ethyl cellulose) is used as surfactant, then emulsions with different rheological properties – from a low viscous liquid up to a gel-like product – can be obtained depending on the ratio of hydrophilic and hydrophobic substituted groups [159,160]. Proteins as emulsifiers are especially important for applications in food industry.
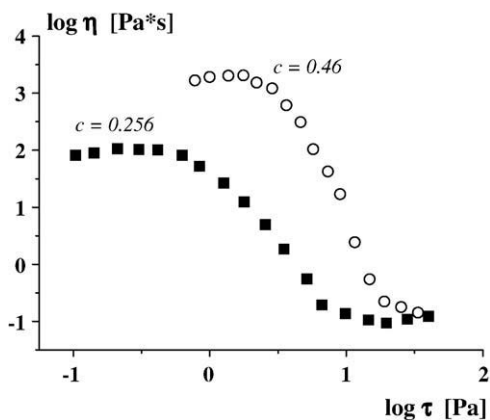
Many papers have been devoted to emulsions stabilized by caseinates (Na-caseinate) providing a respective elasticity [46]. The introduction of inorganic ions (calcium) and low-molecular-weight alcohols (ethanol) leads to the loss of elasticity and elimination of the non-Newtonian behaviour of emulsions. Generally speaking, the rheological properties are determined by the structure of the adsorption layers and their tendency to form structures in the continuous phase [161, 162]. Highly concentrated emulsions containing simultaneously proteins and low-molecular surfactants of different natures are of special interest. Upon the increase of the molar ratio [surfactant]/[protein] the polymeric stabilizer is substituted by a low-molecular-weight surfactant in the interfacial layer, which results in a sharp drop of the yield stress, decrease of the viscosity and suppression of the elasticity of the emulsion system. This effect was demonstrated for bovine serum albumin substituted by Tween-80 [53,158] and explained by the possibility of the polymer to form gel-like or even liquid-crystalline-like structures with strongly expressed elastic properties at the droplet surfaces.

The existence of such interfacial layers allows us to treat emulsion as a three-phase system, in which the third phase is for example a stabilizing protein layer [163]. It is also necessary to mention that the effect of ionic and non-ionic surfactants is similar upon the increase of their concentration in protein containing emulsions [164,165]. The possibilities of modifying the emulsion's rheological behaviour are greatly diverse due to the nature of surfactants. As an example, the addition of polysaccharides to caseinates allows us to produce emulsions with improved strength and elasticity, reached by the formation of intermolecular complexes between the components [166].

Emulsions stabilized by highly dispersed solid particles are a special domain. These particles can be matched by polar and non-polar liquids as well and because these particles can assemble at the interface. Effects of such kind are known for a long time as Pickering emulsions [167]. Emulsions of this type can be formed by different pairs of liquids. e.g. kerosene/water, decane/water, olive oil/water. Even 1% of solid particles (ferric oxide or hydroxyde, clay, gypsum, quartz, carbon black) are enough to influence the emulsion viscosity noticeably, which increases with the increase of the solid particles' concentration. The efficiency of a solid stabilizer depends on different factors, including size and shape of particles, their concentration, wettability and their interaction at the interface [168,169].

In reality, the high stability and rheological properties of Pickering emulsions are determined by a mutual interaction of solid stabilizers and low-molecular-weight surfactants. For example, hexane-in-water emulsions ($\varphi = 30\%$) stabilized by bentonite particles (1–5%) and hexadecyl trimethyl ammonium bromide (0.01%) demonstrate solid-like properties manifested by a constant storage modulus in a wide frequency range, a loss modulus always lower than the storage modulus over the entire linear domain of the mechanical behaviour [170].

The particle size of a solid stabilizer is important and the rule is: stabilization is possible only if solid particles are smaller than emulsion droplets. Too small particles (with size less than 0.5 nm) comparable in dimension with molecules are subjected to Brownian motion and cannot retain at interfaces and do not form a stabilizing structure [171].

Structure formations in emulsions can proceed at low solid particle concentrations if their size is on a nano-meter scale. Then a solid-like network appears typical for "mild" elastic bodies. An example illustrating the role of the size of solid particles is shown in Fig. 32 [172]. The crucial role of the particle size is quite evident: the transition to smaller particles results in a strongly expressed non-Newtonian flow characteristic for structurized systems.

In the case under discussion, low-molecular-weight silicon-organic oligomers ($\varphi = 0.6$) form emulsions when dispersed in water. Structure stabilization was provided by silica particles when present in addition to a standard surfactant. As one can see, the particle size is crucial: a small decrease in size (from 20 to 10 nm) leads to a radical
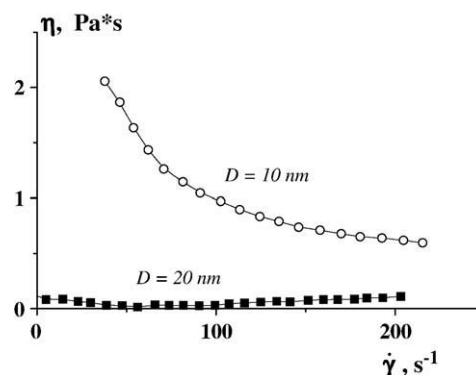

Fig. 32. Flow curves of aqueous emulsions of silicon-organic oligomer with addition of 1 wt.% nano-particles of silica. $\varphi = 0.6$. (From [172], Fig. 2, with kind permission of Elsevier B.V.).

change in the rheology of the system. The shape of the flow curve clearly reflects the formation of a 3D network structure destroyed upon shear. The results of measured frequency dependence of the elastic modulus are even more convincing, as the elastic modulus of the system containing 10 nm particles is independent of frequency which is characteristic for elastic materials. Thus, there is a direct similarity in the behaviour of structurized systems and highly concentrated emulsions as described in Section 4.

Very small amounts of fine solid particles represent an effective method of stabilization for emulsions consisting of polymer pairs. In this case, the solid particles act as "bridges" joining emulsion droplets, so that finally the formation of clusters of droplets in the disperse phase is observed. This effect was demonstrated for the PIB-in-PDMS system, where fumed silica was used as a solid stabilizer [173].

The addition of carbon nanotubes to aqueous emulsions of a monomer (insoluble in water) provides a stable system, which opens the possibility for the synthesis of nano-porous and electro-conductive materials [174].

Emulsions are principally thermodynamic non-equilibrium systems due to a surplus in free surface energy. The instability of emulsions influences their rheological behaviour either during deformation or with time. This means that the evolution of rheological properties with time can be a simple and convenient experimental method for controlling the state of an emulsion.

The aging of emulsions leads to changes of their rheological properties with time. Initially, droplets coagulate; aggregates appear with liquid of the continuous phase immobilized inside. This process results in an increase in viscosity at low shear rates. Coalescence leads to a decrease of the number of droplets per unit volume and this inevitably results in an evolution of the rheological properties of the emulsion due to aging. The behaviour of a model oil-in-water system stabilized by either Na- or Ca-caseinate is the simplest example [175]. If Ca-caseinate is used as surfactant, the emulsion stability increases with protein concentration from 0.5 to 2.0%, while droplet coagulation and a 3D network formation is observed with time if Na-caseinate is used at the same concentration.

It appears natural, that coagulation and aggregate formation influences the viscosity of emulsions. A quantitative description of the influence of aggregate formation on the emulsion viscosity is based on a generalization of Eqs. (13)–(15) [176]. The variation of the free parameter φ^* plays the key role in this generalization as it reflects the degree of coagulation. By varying φ^*, it becomes possible to describe numerous experimental data. It is also supposed in [176] that the correct choice of the dependence of φ^* on the shear rate allows to describe the non-Newtonian flow curves of emulsions.

The effect of shear (shear rate or shear stress) does not only destroy aggregates, but it is also important to note that individual
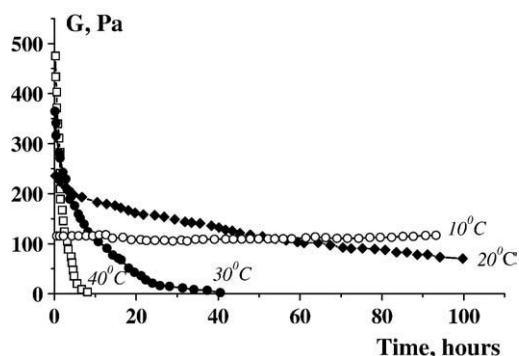
Fig. 33. Decrease of the dynamic modulus with aging as the result of coalescence of droplets in an emulsion at different temperatures. (From [48], Fig. 4, with kind permission of Elsevier B.V.).

droplets by themselves can be unstable in a hydrodynamic field. This concern has been discussed in Section 5.

A rather instructive example for the study of emulsion aging is via measuring the dynamic elastic modulus of highly concentrated emulsions with time, as presented in Fig. 33. Here inverse emulsions (water droplets in a fluorinated oil with non-ionic surfactant as stabilizer) were studied. As one can see, the decrease rate of the modulus strongly accelerates at increased temperature. Direct experiments proved that the mechanism of this process consists in the coalescence of droplets.

The example of an inverse emulsion (water-in-dodecane) stabilized by Span-80 is also quite demonstrative (Fig. 34). The role of the concentration of the disperse phase is clear. Its increase leads to the accelerates the decrease of the storage modulus, again explained by droplet coalescence.

The mechanism of aging described in [178,179] is rather different because aging is due to a special peculiarity of the content in highly concentrated inverse emulsions. The droplets of the disperse phase comprise over-cooled highly concentrated inorganic salts in water. Therefore, not only the emulsion itself but also the state of the disperse phase is unstable. Just slow crystallization of the over-cooled solution explains the increase in rigidity (increase of the yield stress, viscosity and elastic modulus) of the emulsions with time, inverse to the results presented in Figs. 33 and 34. It was shown that a direct correlation between the degree of crystallinity (reached at a definite time) and the yield stress as a typical measure of the rheological properties of an emulsions exists for a wide range of composition of highly concentrated emulsions of this type.
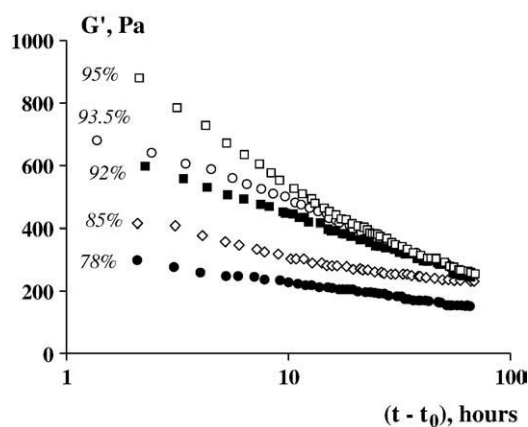
Fig. 34. Decrease of the storage modulus with time as a consequence of "aging" of highly concentrated emulsions. (From [177], Fig. 1, with kind permission of Springer Science + Business media).

8. Conclusion

It is unrealistic to imagine everyday life (and possibly life at all) without emulsions. It is already sufficient to remember the huge number of food products (milk, mayonnaise, numerous creams, pastes, musses), the great number of cosmetic and pharmaceutical stuffs, the basics of photo technique, binders and solvents in buildings, greases and cooling recipes in metal cutting machines, materials of road construction (mixture of bitumens), lacquers and paints, crude oil and many other products which are all emulsions. A new modern level of investigation and application of emulsions is represented for example by the use of sub-micrometer components (nano-composites) in creating new medicinal formulations. Therefore the great and continuously growing interest in understanding the fundamental regularities of the behaviour of emulsions is quite natural. There is also the permanent tendency to creating new emulsions for solving these or those applied problems.

Physicist–theoreticians, experts in fluid mechanics, professionals in colloid chemistry, organic chemists creating new compounds, applied engineers working for reaching concrete goals — all of them are dealing with emulsions. Among other characteristics, the rheological properties of emulsions occupy their adequate place. These properties determine parameters of different technological processes in the production and application of emulsions as well as such almost invisible factors like "quality" of emulsions for different applications. Characteristics of crude oil and oil products, lotions and ointments, pigments and food products are estimated exactly in rheological terms expressed sometimes in rigorous parameters and sometimes by qualitative measures.

At present, we know a lot about the structure and rheology of emulsions. The central goal here is the prediction of the emulsion properties based on the properties of its components. This problem is discussed by creating mechanical models. Their behaviour is considered by methods of continuum mechanics. The rigorous formulation and the way of solution are based on the analysis of the dynamic Navier–Stokes equations. Modern computer technique allows solving such problems with any desirable accuracy. As a general rule, theories are quite trustworthy when experimental results are well fitted by the theoretical predictions.

The situation with highly concentrated ("compressed") emulsions at concentrations beyond the limit of closest packing of spherical particles is even more complicated. Some thermodynamic arguments connected with the conception of osmotic pressure and the increase of the stored surface energy are useful terms in understanding rheological properties of such emulsions.

However such favourable picture has two principle limitations. Firstly, it is necessary to realize clearly, which properties of an emulsion are essential and what is the structure of an emulsion. The latter is especially true in relation to the impact of intrinsic interfacial layers. Secondly, the situation is rather evident if we speak about emulsions formed by two Newtonian liquids, while the situation becomes more difficult and uncertain when we speak about mixtures of two incompatible non-Newtonian liquids, for example two visco-elastic polymeric components. The theoretical models proposed for such blends are quite adequate when such compositions are treated as analogues of emulsions formed from low-molecular-weight liquids with droplets of spherical shape. The situation becomes much more ambiguous when the structure of a molten blend is not as simple as proposed by the model. It happens when both components form continuous phases or one of the components forms fibrils under deformation or if one of the components has anisotropic properties.

A separate problem in discussing the rheology of emulsions is their stability, which is understood in two ways: stability against the action of mechanical forces, and stability with time called "aging". Especially in aging, a better analysis is based on a colloid-chemical approach connected with interfacial interactions and the impact of surfactants becomes dominating. In this approach, the bulk rheology plays a

secondary role as a method of monitoring changes in the material. The problems in this field are frequently of great importance and attract therefore permanent attention.

At any rate, it is quite obvious that today's knowledge about emulsions of different compositions and structures does not explain all problems and for future investigators there is a lot of interesting and useful things to find out about these omnipresent objects.

List of symbols

A_1, A_2, A_3, A_4	constants
A_2	second virial coefficient
B_1, B_2, B_3	fitting coefficients
Bo	Boussinesq number
C	factor
Ca	Capillary number
Ca^*	critical value of the Capillary number
D	dimensionless factor
D_{23}	average droplet size
D_{eff}	apparent coefficient of diffusion
d	diameter
d_k	characteristic length
$d_{TI,max}$	maximal size of a drop in the TI regime
$d_{TV,max}$	maximal size of a drop in the TV regime
$D(\omega,R)\ E(\omega,R)$	functions
E_{Gs}	surface modulus of elasticity (the Gibbs effect)
f_1, f_2	factors
G	elastic modulus
G'	elastic (storage) modulus
G''	loss modulus
G'_{exp}	experimental values of dynamic modulus
G'_p	dynamic modulus values predicted by the model
$G'_{int\ er}$	dynamic modulus of an intermediate layer
$G'_{bl}(\omega)$	elastic modulus of a blend
$G^*_{bl}(\omega)$	complex elastic modulus of a blend
$G^*_0(\omega)$	dynamic modulus of a continuous phase
$G^*_{dr}(\omega)$	dynamic modulus of dispersed phase
G_s	surface or interfacial modulus of elasticity
G	gravitational acceleration
$H(\omega,R)$	function
K	factor representing the influence of concentration on viscosity
k_B	Boltzmann constant
Pe	Peclet number
R	radius
Re	Reynolds number
S	surface area
T	absolute temperature
t	time
U	steady velocity
U_{St}	velocity of fall-out
V	volume
V	velocity
V_s	wall velocity
w_1, w_2	weigh shares
Γ	absorption
$\dot{\gamma}$	shear rate
ε	intensity of energy dissipation
$<\varepsilon>$	value of the mobility parameter
η	viscosity
η_0	viscosity of continuous medium
η_{dr}	viscosity of liquid of drops
η_r	reduced viscosity
η_s	surface or interfacial shear viscosity
η_d	surface or interfacial dilatational viscosity
η_{surf}	ratio of surface or interfacial viscosity
$\eta^*(\omega)$	complex viscosity
$\eta(\dot{\gamma})$	apparent (non-Newtonian) viscosity
η_{em}	viscosity of emulsion
η_{bl}	viscosity of a blend
η^*_{bl}	dynamic viscosity of a blend
η^*_0	dynamic viscosity of polymer forming continuous phase
η^*_{dr}	dynamic viscosity of polymer of droplets
θ	relaxation time
λ	ratio of viscosities of two liquids: of a continuous medium and drops
λ_m	modified viscosity ratio
Π	osmotic pressure
ρ	density
ρ_c	density of liquid of continuous phase
σ	surface or interfacial tension
τ	shear stress
τ_Y	yield stress
υ	kinematic viscosity
φ	concentration of dispersed phase
φ^*	limit concentration of dispersed phase
ω	frequency

The following acronyms are used for designation of polymers:
PE — polyethylene;
PP — polypropylene;
PC — polycarbonate;
PS — polystyrene;
PI — polyisoprene;
PMMA — poly(methyl metacrylate);
PIB — polyisobutylene;
PET — poly(ethylene terephthalate);
PBT — poly(butylene terephthalate);
PDMS — poly(dimethyl siloxane).

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