

DEFINITIVE

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY

**TERMINOLOGY AND SYMBOLS IN
COLLOID AND SURFACE CHEMISTRY
PART 1.13. DEFINITIONS,
TERMINOLOGY AND SYMBOLS FOR
RHEOLOGICAL PROPERTIES**

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PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

MANUAL OF SYMBOLS AND TERMINOLOGY FOR PHYSICOCHEMICAL QUANTITIES AND UNITS.
Appendix II : Definitions, Terminology and Symbols in Colloid and Surface
Chemistry.

Part 1.13 SELECTED DEFINITIONS, TERMINOLOGY AND SYMBOLS FOR RHEOLOGICAL PRO-
PERTIES

Approved by the Interdivisional Committee on Nomenclature and Symbols, 1978.
Prepared for publication by H. van Olphen & J. Lyklema on behalf of IUPAC Com-
mission I.6 on Colloid and Surface Chemistry of the Division of Physical
Chemistry (see Note a.).

1.13 RHEOLOGY

Rheology is the study of the flow and deformation of matter under the influ-
ence of a mechanical force. It is concerned particularly with material beha-
vior which cannot be described by the simple linear models of hydrodynamics
and elasticity. Some of these departures are due to the presence of colloid-
al particles or to the influence of surfaces. Some of the simple terms and
concepts of rheology are of sufficient importance to colloid and surface
chemistry to deserve inclusion in this manual.

The recommendations in this document should be considered a subset of a com-
plete set of recommendations on terminology in the field of rheology and
fluid dynamics in general, which has not yet been developed. The present
subset is a selection of those terms which are of particular interest to
colloid and surface chemists, and which can be defined in a relatively ele-
mentary fashion. Another subset of terms relating to elastic deformations,
viscoelasticity, creep flow, etc. is equally important for the audience men-
tioned, but cannot be properly defined without referring to the fundamental
equations on fluid mechanics. Therefore, its development will be postponed
until the complete set has been established.

Rheology may be conveniently divided into *bulk rheology*, in which effects
due to the surface of the system can be neglected, and *surface rheology*, in
which such effects are predominant. It should be noted that in surface rheo-
logy the neglect of bulk behavior is permissible only in exceptional circum-
stances, such as for very thin films surrounded by a gas.

Note a. While this paper was prepared, membership of Commission I.6 was as follows:
K.J. Mysels, USA; R. Haul, Fed.Rep.of Germany; J. Lyklema, The Netherlands;
R.L. Burwell Jr., USA; R.S. Hansen, USA; V.B. Kazansky, USSR; C. Kemball, UK;
R.M. Barrer, UK; G. Ertl, Fed.Rep.of Germany; J. Haber, Poland; P. Mukerjee,
USA; E. Ter Minassian-Saraga, France; I.I. Tretiakov, USSR; H. van Olphen,
The Netherlands; E. Wolfram, Hungary; D.H. Everett, UK; W. Schirmer, German
Democratic Republic.

The section on Bulk Rheology incorporates some suggestions made as a result
of a review by members of the International Committee on Rheology, an Asso-
ciate Organization of IUPAC (R.S. Marvin, chairman 1972-1976).

The Commission acknowledges the contributions of M. van den Tempel in draft-
ing the section on Surface Rheology.

1.13.1 BULK RHEOLOGY

Viscosity is a material property relating *stress* and *rate of strain* in a fluid flowing in a fashion such that the distance between volume elements changes with time. Stress expresses the force per unit area acting across an imaginary plane in the fluid. Strain is the relative change of position of the volume elements. Rate of strain is determined by all spatial derivatives of the components of velocity.

A. Newtonian behavior

A *Newtonian fluid* is one in which the components of the stress tensor are linear functions of the first spatial derivatives of the velocity components. These functions involve two material parameters (taken as constants throughout the fluid, although depending on ambient temperature and pressure):

(1) the *shear viscosity*, η , often termed simply *viscosity* since in most situations it is the only one considered, relates the shear components of stress and those of rate of strain at a point in the fluid by :

$$\sigma_{xy} = \sigma_{yx} = \eta(\partial v_x/\partial y + \partial v_y/\partial x) = 2\eta\dot{\gamma}_{xy}$$

where $\dot{\gamma}_{xy}$, the shear component of rate of strain,

$$\dot{\gamma}_{xy} = \frac{1}{2}(\partial v_x/\partial y + \partial v_y/\partial x)$$

Corresponding relations hold for σ_{xz} and σ_{yz} ; σ_{xy} is the component of stress acting in the y -direction on a plane normal to the x -axis; v_x, v_y, v_z are the components of velocity (Note b.).

(2) the *volume viscosity* or *dilatational viscosity*, ζ , enters into equations at any point where the flow involves a change in volume, i.e. is dilatational. If the deformation is purely dilatational, the average of three normal stress components is:

$$\sigma = (1/3)(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = -p + \zeta(\partial v_x/\partial x + \partial v_y/\partial y + \partial v_z/\partial z)$$

where p is the hydrostatic pressure at the point considered in the absence of motion. By the usual convention, the normal components of stress and the pressure act in opposite directions.

Shear stress, being defined in terms of forces acting across imaginary planes in a material, cannot be measured directly. It must be inferred from measurements made at a surface of the material, and its calculation implies some assumptions about the rheological properties and the homogeneity of the material studied. The constitutive equation relating stress and rate of strain is, properly speaking, an abstraction. When a fluid is termed "Newtonian", this means that its flow behavior is consistent with the above definition.

The full constitutive equation for a Newtonian fluid, from which the above relations follow, is equivalent to six scalar equations, which hold at every point in the fluid. Only a few idealized problems can be solved exactly. One is that of *simple shear*, i.e. the case of a fluid between two large parallel plates (to permit ignoring edge effects) of area A , separated by a distance h . If one plate moves relative to the other with a constant velocity V , requiring a force F acting in the direction of movement, and the density, pressure, and viscosity throughout the fluid are constant, the Newtonian equation can be coupled with the equations of motion and of continuity to show that the velocity gradient in the fluid is constant ($= V/h$), and that $F/A = \eta V/h$. This idealized case (*simple shear*) is sometimes used to define shear viscosity. If V and F are in the x direction and h in the y direction, then $2\dot{\gamma}_{xy} = V/h$ and $\sigma_{xy} = F/A$. Accordingly, in *simple shear*, the *shear rate* D is defined as $D = 2\dot{\gamma}_{xy} = dV/dy$ and the *shear stress* F/A as σ_{xy} .

The following are some additional terms and symbols describing Newtonian behavior:

ϕ	= $1/\eta$: fluidity
ν	= η/ρ	: kinematic viscosity
η_s, η_m		: viscosity of the solvent or the continuous medium
η_r	= η/η_s	: relative viscosity or viscosity ratio
η_i	= $(\eta - \eta_s)/\eta_s$: relative viscosity increment
		Note: this is a new term. The use of the former term "specific viscosity" is discouraged.
η_i/ρ_D		: reduced viscosity or viscosity number, where ρ_D is the mass concentration of the dispersed phase.
$[\eta]$	= $\lim_{\rho_D \rightarrow 0} (\eta_i/\rho_D)$: intrinsic viscosity or limiting viscosity number
η_{1n}	= $[\ln(\eta/\eta_s)]/\rho_D$: inherent viscosity or logarithmic viscosity number (the symbol η_{inh} is often used).

Note b. Alternative definitions omit the 2 and $\frac{1}{2}$ respectively. The possibility is left open, that in the final complete set of definitions this alternative will be recommended.

For dispersions of charged particles, components of the viscosity connected with the charge of the particles are referred to as *electroviscous effects*.

B. Non-Newtonian behavior

The definitions below of various types of non-Newtonian viscosity are stated in terms of simple shear (i.e. scalar) relations. This can be justified in part by the fact that they are used almost exclusively in cases of flow involving no change in volume. But even with this limitation, some of the properties, such as the yield stress which is a special case of a more general tensor yield condition, may vary with the type of flow.

If steady flow occurs only above a certain finite stress, it is called *plastic flow*. *Consistency* is a general term to describe the property of a material by which it resists permanent change of shape.

For systems showing *non-Newtonian* behavior when measured in steady simple shear, the *shear dependent viscosity*, η , is a coefficient equal to σ/D at a given value of D ; η_0 is the *limiting viscosity at zero shear rate*, and η_∞ the *limiting viscosity at infinite shear rate*; $[\eta_0]$ is the *limit of intrinsic viscosity at zero shear*. The *differential viscosity*, η_Δ , is the derivative of stress with respect to the rate of shear at a given shear rate.

The ratio of stress to rate of strain, calculated from measurements of forces and velocities as though the liquid were Newtonian, is termed *apparent viscosity*, η_{app} . If the liquid is actually non-Newtonian, the apparent viscosity depends on the type and dimensions of the apparatus used.

If viscosity is a univalued function of the rate of shear, a decrease of the viscosity with increasing rate of shear is called *shear thinning* and an increase of the viscosity *shear thickening*. Shear thickening is often accompanied by an increase in volume of the system, which is referred to as *dilatancy*. This term has formerly been used for the phenomenon of shear thickening.

The *yield stress*, σ_0 or τ_0 , is the shear stress at which yielding starts abruptly. Its value depends on the criterion used to determine when yielding occurs. Many colloidal dispersions show *Bingham flow* which is characterized by a σ - D diagram as shown in figure 1. At rates of shear greater than that at point A, the following relation applies:

$$\sigma - \sigma_B = \eta_\Delta D$$

σ_B (or τ_B) is called the *Bingham yield stress*.

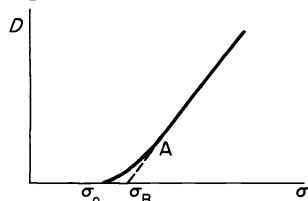


Figure 1. σ - D diagram, characterizing Bingham flow.

The following terms describe some time- and shear history dependent rheological phenomena.

The application of a finite shear to a system after a long rest may result in a decrease of the viscosity or the consistency. If the decrease persists when the shear is discontinued, this behavior is called *work softening* (or *shear breakdown*), whereas if the original viscosity or consistency is recovered this behavior is called *thixotropy*. The time in which a certain viscosity or yield stress is reached after discontinuation of the shear is the *time of thixotropic recovery* or the *time of solidification*. These times depend on the values of viscosity or yield stress chosen by the experimenter. *Rheopexy* describes the phenomenon in which the time of solidification, after discontinuation of a relatively high shear rate, is shortened by applying a small shear rate.

Terms which describe the opposite behavior, i.e. the fact that shear results in either a permanent or reversible increase of viscosity or consistency with time are *work hardening* (opposite of work softening) and *anti-thixotropy* (opposite of thixotropy).

1.13.2 SURFACE OR INTERFACIAL RHEOLOGY

In general, surface or interfacial rheology involves two-dimensional analogs of the models used in three-dimensional rheology. Thus, phenomena of surface dilatation concern changes in area rather than in volume. Whereas bulk rheology deals primarily with deformations involving shear, dilatational deformations prevail in surface rheology. In surface dilatation one may start at zero area or end up with zero area, whereas in bulk processes zero volume cannot occur. Another difference is that in bulk rheology purely viscous behavior is often encountered, whereas in surface rheology it is rare. In surface rheology *viscoelastic phenomena* involving both viscous and elastic aspects are predominant and have to be considered.

The interface between two fluids can always support a pressure difference, Δp , which produces a stress normal to the surface, provided the surface has the proper curvature, given by the *Laplace equation*:

$$\Delta p = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

where γ is the surface or interfacial tension, static or dynamic as the case may be (cf. 1.2.1) and r_1, r_2 are the two principal radii of curvature. Thus, for a flat interface there can be no pressure difference, and the following discussion will be restricted to such interfaces. The interface between two fluids may or may not be able to support a tangential shear stress and/or a tangential dilatational stress.

For steady state deformations one can define a *surface shear viscosity* η^S , and an *area viscosity* or *surface dilatational viscosity* ζ^S . In a Cartesian system with the x axis normal to the surface, they are defined by the equations:

$$\eta^S = \frac{\sigma_{xy}}{\partial v_y / \partial v_x} \quad \text{and} \quad \zeta^S = \Delta\gamma / \frac{d(\ln A)}{dt}$$

where σ_{xy} is the shear component of the surface stress tensor, v_y is the y component of the surface velocity vector, A is the surface area, t is the time, and $\Delta\gamma$ is the difference between the (steady state) dynamic surface tension and the equilibrium surface tension. In general, as in bulk rheology, these viscosities are dependent on the rates of deformation and past history of the surface. They are constant only if the behavior is Newtonian.

For surfaces at which no adsorption occurs, η^S and ζ^S are zero. In practice, the interfaces between two pure immiscible liquids often approach this behavior. Surfaces at which adsorption occurs, including spread monolayers, generally show a surface dilatational viscosity, since this is related to the finite rate of re-establishment of equilibrium surface tension. In addition, such surfaces may or may not possess significant surface shear viscosity.

In analogy to the customary treatment of viscoelasticity in bulk, the ratio of the surface shear stress to the corresponding surface shear strain is defined as the surface shear modulus, G^S :

$$G^S = G^{S'} + iG^{S''}$$

Here, $G^{S'}$ represents the elastic component of the response, and $G^{S''}$ the dissipative or viscous component.

For a simple harmonic motion of angular frequency ω , the *dynamic surface shear viscosity* $G^{S''}$ follows from

$$G^{S''} = G^{S''} / \omega$$

The *surface dilatational modulus* is defined by:

$$K^S = K^{S'} + iK^{S''}$$

with the *dynamic surface dilatational viscosity*:

$$\zeta^S = K^{S''} / \omega$$

For small deformations these quantities are often independent of the extent of deformation, but generally depend on the frequency.

Motions of the surface are coupled with those of the subsurface fluid or fluids, so that movements of the liquid normally produce stresses in the surface and vice versa. The movement of the surface and of the entrained fluid(s) caused by surface tension gradients is called the *Marangoni effect*.

When only one fluid has a significant viscosity, coupling between surface and subsurface fluid motion can be described by the force balance equation for a surface element and a liquid velocity distribution v_x, v_y, v_z :

$$\eta \left[\frac{\partial v_x}{\partial z} \right]_{z=0} = K^S \frac{\partial^2 \xi}{\partial x^2} + G^S \frac{\partial^2 \xi}{\partial y^2}$$

Here ξ is the x component of the displacement of the surface element, and η the complex bulk shear viscosity. An analogous equation can be written for v_y . These equations are basic to the measurements of surface rheological properties.

Shear properties can be measured by subjecting the surface to a state of stress in which every element deforms without changing its area. Similarly, surface dilatational properties are best measured in a purely isotropic dilatation. There are, however, many systems having significant dilatational properties in which surface shear resistances are negligibly small (although the reverse is not likely to be encountered) and for such systems dilatational properties can be measured by extending the surface in one direction only. Otherwise, the analysis of experimental results on surface behavior in which both shearing and dilatation are significant (as in the canal viscometer) is extremely difficult.

Although rheological phenomena can be described in terms of an excess viscosity (or elasticity) associated with the interfacial layer (cf. 1.2.3), the resulting surface properties will depend in general on the detailed geometrical arrangement and not only on the nature of the surface and on its motion.