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Rheology of Liquid Detergents

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I. INTRODUCTION

Liquid detergent products span the entire rheology spectrum from low-viscosity Newtonian fluids to semisolid pastes, as demonstrated in Figure 4.1. Consumers can readily purchase the product form most in keeping with their preferences throughout the personal and household care product lines. For example, shampoos can be easily found that are low-viscosity Newtonian solutions, viscoelastic dispersions, or highly elastic gels. Similarly, laundry detergent products range in consistency and form from low-viscosity Newtonian liquids, to viscous pastes, to solid tablets. Developing these products to yield the desired shelf life and rheology stability is a complex task considering the number of components included in final commercial formulations.

Research scientists and engineers involved in successful development and manufacture of commercial products have different rheology needs. Advanced technology emphasis may be on fundamental studies of interactions of product

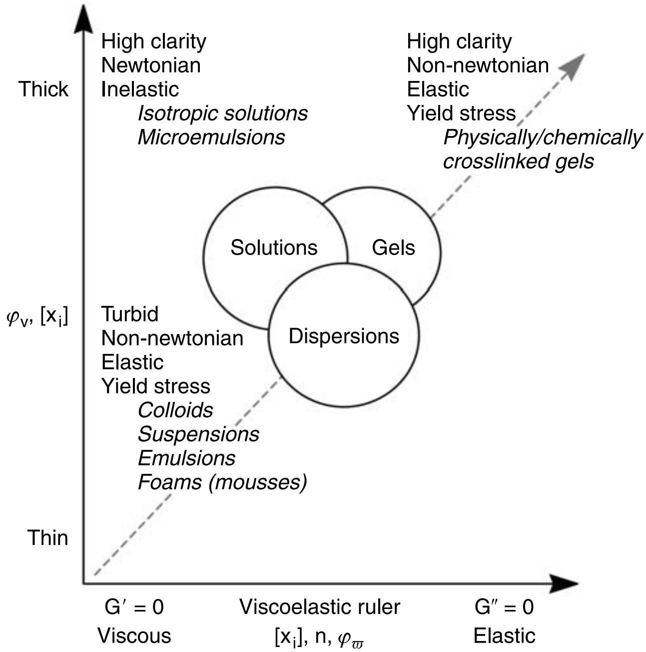


FIG. 4.1 Liquid detergent product delivery forms and rheology spectrum. (Courtesy of Fluid Dynamics, Inc.)

ingredients and phase behavior of multicomponent surfactant systems, for example, while product formulators may need to benchmark rapidly the rheology of market prototypes and competitive products. Testing conditions for process engineers may extend rheology measurements to high shear rates and temperatures in keeping with process conditions for surfactants and/or product manufacture. Further, quality control professionals generally require test protocols for finished goods at factory locations. In response to these highly diversified needs, instrument manufacturers have produced a broad range of rheometers and viscometers.

From R&D to quality control, rheology measurements for each phase of the product development life cycle involve raw materials, premixes, solutions, dispersions, emulsions, and full formulations. Well-equipped laboratories with stress- and strain-controlled oscillatory/steady shear rheometers and viscometers can generally satisfy most characterization needs. When necessary, customized systems are designed to simulate specific user or process conditions. Rheology measurements are also coupled with optic, thermal, dielectric, and other analytical methods to further probe the internal microstucture of surfactant systems. New commercial and research developments are briefly discussed in the following sections.

Rheology is frequently cited in patents, often as a claim, and Section II provides examples of liquid detergent patents recently issued where rheology is cited as a key property. Instruments and methods used for product characterizations in several patents are included. Section III highlights new developments in rheology measurements, also listing several patents for new rheology measurement technology, since there have been dramatic advances in the science of rheology over the past decade. Examples of the flow behavior of commercial detergent products, including laundry detergents, shampoos, dishwashing liquids, and dentifrices, are included in Section IV and selections of fundamental rheology studies in surfactant systems are presented in Section V.

This chapter is intended to expand on the chapter of the same title in the first edition of this book [1]. An overview of the rheology of liquid detergents, including dispersions, suspensions, gels, and surfactant systems, is included in that chapter.

II. PATENT SURVEY OF LIQUID DETERGENT FORMULATIONS

Personal and household care detergents have applications ranging from hard surface cleaners, to body washes, to dental pastes and gels. Products used by consumers need to be poured, pumped, squeezed, or sprayed while maintaining constant rheology profiles throughout the shelf life. Since rheology is a performance and consumer perceived property, patents describe compositions and manufacturing procedures needed to achieve desirable rheological properties and shelf life stability. This applies also to surfactants and admixtures during detergent manufacture, since these fluids need to be easily processed.

A representative catalog of recent patents is provided in Table 4.1 in chronological order. Each of these patents focuses attention on flow properties of key raw materials or full formulations. For high- and low-pH formulations, patents describe rheology modifiers meeting the demands of these difficult systems. Various rheology modifiers are also disclosed for the purpose of targeting specific rheology requirements. Several of the patents listed in Table 4.1 are discussed in the following sections.

A. Home Care Products

Numerous patents have been granted for automatic dishwasher detergents, hard surface cleaners, and laundry detergents. Of special interest are patents concerning liquid compositions containing bleach, due to the problems encountered with the rheology and chemical and physical stability of these complex systems. Increasingly, patents describe “thickened” compositions and specifically cite viscoelastic behavior. A stable perfumed bleaching composition is described in U.S. Patent 6,248,705 for hard surface cleaning having a pH less than 2. The perfume cited is

TABLE 4.1 Summary of Patents Relating to Rheology of Liquid Detergents

Patent number and date	Assignee and inventors	Title
U.S. 6,576,602, June 10, 2003	Procter & Gamble Company M.A. Smerznak, W.A.M. Broeckz, I. Goderis, R. Jones, D. Parry, J. Kahn, J. Wevers	Nonaqueous, particulate-containing liquid detergent compositions with surfactant-structured liquid phase
U.S. 6,506,716, January 14, 2003	Procter & Gamble Company P. Delplancke, F. de Buzzaccarini, A. Fredj, P. Reddy, R. oswell, E. Sadlowski	Aqueous, gel laundry detergent composition
U.S. 6,331,291, December 18, 2001	W.R. Glace, R.L. Ibsen, G.A. Skoler	Dentifrice gel/paste compositions
U.S. 6,313,085, November 6, 2001	Cognis Deutschland GmbH C. Le Hen-Ferrenbach	High-concentration flowable anionic surfactant mixtures containing alkyl ether sulfates and alkyl sulfates
U.S. 6,306,916, October 23, 2001	Henkel Kommanditgesellschaft auf Aktien A. Ansmann, R. Kawa, G. Strauss	Pearly luster concentrate with Newtonian viscosity
U.S. 6,294,511, September 25, 2001	Clorox Company B.P. Argo, C.K. Choy, S.L. Nelson	Thickened aqueous composition for the cleaning of a ceramic surface and methods of preparation thereof and cleaning therewith
U.S. 6,274,539, August 14, 2001	Procter & Gamble Company M.L. Kacher, D.P. Wallace, F.S. Allouch	Light-duty liquid or gel dishwashing detergent compositions having controller pH and desirable food soil removal, rheological, and sudsing characteristics
U.S. 6,274,546, August 14, 2001	Henkel Kommanditgesellschaft auf Aktien D. Legel, J. Penninger, T. Voelkel	Stable high-viscosity liquid detergents

U.S. 6,271,187, August 7, 2001	Ecolab Inc. C.A. Hodge, C.J. Uecker	Hand soap concentrate, use solution, and method for modifying a hand soap concentrate
U.S. 6,271,192, August 7, 2001	National Starch &Chemical Investment Holding Co. E.W. Verstrat, J.S. Maxim, Jr., J. Rosie	Associative thickener for aqueous fabric softener
U.S. 6,277,798, August 21, 2001	Procter & Gamble Company P.E. Russell, N.J. Phipps	Cleansing compositions containing water-soluble gel-forming nonionic surfactant
U.S. 6,258,859, July 10, 2001	Rhodia, Inc. M. Dahayanake, J. Yang, J. G. Niu, P.-J. Derian, R. Li, D. Dino	Viscoelastic surfactant fluids and related methods of use
U.S. 6,248,705, June 19, 2001	Procter & Gamble Company S. Cardola, L. Pieroni, R. Scoccianti	Stable perfumed bleaching compositions
U.S. 6,268,324, July 31, 2001	Ecolab Inc. M.E. Besse, R.O. Ruhr, G.K. Wichmann, T.A. Gutzmann	Thickened hard surface cleaner
U.S. 6,241,812, June 5, 2001	Pharmacia Corporation B.A. Smith, G.T. Colegrove, W.G. Rakitsky	Acid-stable and cationic-compatible cellulose compositions and methods of preparation
U.S. 6,221,827, April 24, 2001	Henkel Kommanditgesellschaft auf Aktien M. Mendoza Cruz, E. de Jorge	Viscoelastic bleaching and disinfecting compositions
EP1088545, April 4, 2001	Procter & Gamble Company G.N. McKelvey, K. Rigal	Hair care compositions

(continued)

TABLE 4.1 (Contd.)

Patent number and date	Assignee and inventors	Title
U.S. 6,187,221 B1, February 13, 2001	National Starch & Chemical Investment Holding Co. C.G. Gore, S.M. Steele	Controlled release bleach thickening composition having enhanced viscosity stability at elevated temperatures
U.S. 6,180,594 B1, January 30, 2001	Witco Surfactants GmbH M. Fender, K. Hans-Jurgen, S. Schussler	Low-concentration, high-viscosity aqueous fabric softeners
U.S. 6,177,396 B1, January 23, 2001	Albright & Wilson UK Limited R.M. Clapperton, J.R. Goulding, B.W.Grover, I.F. Guthrie, W.P. Haslop, E.T. Messenger, J.E. Newton, S.A. Warburton	Aqueous-based surfactant compositions
U.S. 6,150,320, November 21, 2000	3M Innovative Properties Company J. McDonell, J. Mlinar	Concentrated cleaner compositions capable of viscosity increase upon dilution
U.S. 6,150,445, November 21, 2000	Akzo Nobel AV P. Bostrom, A. Myrstrom	Aqueous concentrate of an associative thickening polymer, and use of a nonionic surfactant for reducing the viscosity of the concentrate
U.S. 6,140,413, October 31, 2000	Henkel Corporation L.N. Castles, S.C. James, J. Stewart	Silicone softener viscosity reducer
U.S. 6,126,922, October 3, 2000	3M Innovative Properties Company B. Wang, S.B. Mitra, S.M. Rozzi	Fluid-releasing compositions and compositions with improved rheology
WO0046331, August 10, 2000	Procter & Gamble J.M. Clarks, G.K. Embleton, H.D. Hutton, J.D. Sadler, M.L. Kacher, D.P. Wallace	Diols and polymeric glycols in dishwashing detergent compositions

U.S. 6,100,228, August 8, 2000	Clorox Company B.P. Argo, C.K. Choy, A. Garabedian, Jr.	Bleaching gel cleaner thickened with amine oxide, soap, and solvent
U.S. 6,087,320, July 11, 2000	Henkel Corporation A.D. Urfer, V. Lazarowitz, P.E. Bator, B.A. Salka, G. de Goederen, R.A. Alaksejczyk	Viscosity-adjusted surfactant concentrate compositions
U.S. 6,083,893, July 4, 2000	Procter & Gamble Company D.R. Zint, T. Pace, R. Owens, M.L. Kacher	Shaped semisolid or solid dishwashing detergent
U.S. 6,083,854, July 4, 2000	Procter & Gamble Company M.S. Bogdanski, U.C. Glaser	Wet wipes with low-viscosity silicone emulsion systems
WO0015180, March 23, 2000	Hercules Inc. J.E. Brady	Rheology-modified compositions and processes thereof
U.S. 6,028,043, February 22, 2000	Procter & Gamble Company R.W. Glenn, Jr., M.D. Evans, M.E. Carethers, S.C. Heilshorn	Liquid personal cleansing compositions which contain a complex coacervate for improved sensory perception
U.S. 6,008,261, December 8, 1999	Condea Augusta SpA C. Genova, F. Montesion, E. Bozzeda	Aqueous surfactant compositions with a high viscosity
U.S. 6,008,184, December 28, 1999	Procter & Gamble Company J.G.L. Pluyter, M.G. Eeckhout	Block copolymers for improved viscosity stability in concentrated fabric softeners
U.S. 5,997,764, December 7, 1999	B F Goodrich Co. S.V. Kotian, H. Ambuter	Thickened bleach compositions
U.S. 5,939,375, August 17, 1999	Th. Goldschmidt AG F. Muller, J. Peggau	Low-viscosity alkaline cleaning emulsion

(continued)

TABLE 4.1 (Contd.)

Patent number and date	Assignee and inventors	Title
U.S. 5,932,538, August 3, 1999	Procter & Gamble Company R.W. Glenn, Jr., M.D. Evans, M.E. Carethers, S.C. Heilshorn	Liquid personal cleansing compositions which contain an encapsulated lipophilic skin moisturizing agent comprised of relatively large droplets
U.S. 5,922,667, July 13, 1999	Diversey Lever, Inc. E.C. van Baggem, N.J. Pritchard, G. de Goederen, R. Jakobs	Cleaning gels
U.S. 5,922,664, July 13, 1999	Colgate-Palmolive Company H.C. Cao, P. Pagnoul	Pourable detergent concentrates which maintain or increase in viscosity after dilution with water
U.S. 5,851,979, December 22, 1998	Procter & Gamble Company S. Scialla, S. Dardola, G.O. Boamcjetto	Pseudoplastic and thixotropic cleaning compositions with specifically defined viscosity profile
U.S. 5,981,457, November 9, 1999	Kay Chemical Company F.U. Ahmed	Concentrated liquid gel warewash detergent
U.S. 5,965,502, October 12, 1999	Huels Aktiengesellschaft D. Balzer	Aqueous viscoelastic surfactant solutions for hair and skin cleaning
U.S. 5,962,392, October 5, 1999	Solvay Interox Limited	Thickened peracid compositions
U.S. 5,939,375, August 17, 1999	Th. Goldschmidt AG F. Fuller, J. Peggau	Low-viscosity alkaline cleaning emulsion
U.S. 5,922,664, July 13, 1999	Colgate-Palmolive Company H.C. Cao, P. Pagnoul	Pourable detergent concentrates which maintain or increase in viscosity after dilution with water

U.S. 5,916,859, June 29, 1999	Clorox Company C.K. Choy, P.F. Reboa	Hexadeylamine oxide/counterion composition and method for developing extensional viscosity in cleaning compositions
U.S. 5,912,220, June 15, 1999	S.C. Johnson & Son, Inc. J.A. Sramek, H.A. Doumaux, T. Tungsubutra, P.J. Schroeder	Surfactant complex with associative polymeric thickener
U.S. 5,888,487, March 30, 1999	Hankel Kommanditgesellschaft auf Aktien G. Baumoeller, A. Wadle, C. Ansmann, H. Tesmann, T. Foerster	Low-viscosity opacifier concentrates
U.S. 5,851,979, December 22, 1998	Procter & Gamble Company S. Scialla, S. Cardola, G.O. Bianchetti	Pseudoplastic and thixotropic cleaning compositions with specifically defined viscosity profile
SK279419B, November 4, 1998	Colgate-Palmolive Company G.A. Durga, M. Prencipe	Viscoelastic dentifrice composition
U.S. 5,804,540, September 8, 1998	Lever Brothers Company L.S. Tsaur, M. He, M. Massaro, M.P. Aronson	Personal wash liquid composition comprising low-viscosity oils prethickened by nonantifoaming hydrophobic polymers
U.S. 5,811,383, September 22, 1998	Dow Chemical Company J. Klier, C.J. Tucker, G.M. Strandburg	High water content, low-viscosity, oil continuous microemulsions and their use in cleaning applications
U.S. 5,798,324, August 25, 1998	S.C. Johnson & Son, Inc. G.J. Svoboda	Glass cleaner with adjustable rheology
U.S. 5,776,883. July 7, 1998	Lever Brothers Company T.V. Vasudevan	Structured liquid detergent compositions containing nonionic structuring polymers providing enhanced shear thinning behavior

(continued)

TABLE 4.1 (Contd.)

Patent number and date	Assignee and inventors	Title
U.S. 5,759,989, June 2, 1998	Procter & Gamble Company S. Scialla, S. Cardola, G.O. Bianchetti	Stable aqueous emulsions of nonionic surfactants with a viscosity controlling agent
U.S. 5,733,861, March 31, 1998	BASF Corporation S. Gopalkrishnan, K.M. Guiney, J.V. Sherman, D.T. Durocher, M.C. Welch	Hydrophilic copolymers for reducing the viscosity of detergent slurries
U.S. 5,728,665, March 17, 1998	Clorox Company C.K.-M. Choy, B.P. Argo	Composition and method for developing extensional viscosity in cleaning compositions
U.S. 5,688,435, November 18, 1997	Reckitt & Colman Inc. D.A. Chang, J.W. Cavanagh	Pigmented rheopectic cleaning compositions with thixotropic properties
U.S. 5,389,157, February 14, 1995	Clorox Company W.L. Smith	Viscoelastic cleaning compositions with long relaxation times
U.S. 5,409,630, April 25, 1995	Colgate-Palmolive Co. R. Lysy, M. Marchal	Thickened stable acidic microemulsion cleaning composition
U.S. 5,336,426, August 9, 1994	J.E. Rader, W.L. Smith	Phase stable viscoelastic cleaning compositions

a cyclic terpene/sesquiterpene compound, such as eucalyptol, added with cationic surfactants to yield the desired viscosity. An optimum rheology is claimed for vertical hard surface applications such as toilet bowl cleaners. Optimum viscosity is most preferably 250 or 900 cP at 20°C measured using a Brookfield viscometer at 60 r/min using Spindle no. 2 or with the Carri-Med viscometer at a shear stress of 50 dyn/cm^2. Thickened aqueous bleach cleaners containing hypohalite or peroxygen bleaches for hard surfaces are also the subject of U.S. Patent 5,997,764. Storage stability viscosity data at 20 r/min and 20°C are provided for example formulations containing viscosity stabilizers. A thickened bleach gel cleaner comprising hypochlorite-generating compounds, a ternary thickening system consisting of an alkali metal soap, hydrotrope, and bleach stable solvent, buffer/electrolyte stabilizer, and water is mentioned in U.S. Patent 6,100,228.

Viscoelastic non-Newtonian bleaching and disinfecting compositions are further cited in U.S. Patent 6,221,827. Brookfield RVT (Spindle no. 1, 60 r/min) viscosity data are included for several examples following storage for four weeks at 40°C. The compositions are noted to yield high stability in storage. A controlled release bleach thickening composition cited to have enhanced viscosity stability at higher temperatures is disclosed in U.S. Patent 6,187,221. The controlled release thickening composition contains halogen bleach, water, a crosslinked carboxylated polymer, and degradable crosslinking monomer. Brookfield viscosity of examples aged at 50°C is provided. Thickened peracid compositions are included in U.S. Patent 5,962,392 containing an aliphatic alcohol ethoxylate and an amine oxide cosurfactant. Brookfield viscosity data (Spindle no. 2, 50 r/min) are included in the patent text.

A rheopectic pigmented bleach (alkali metal hypochlorite) hard surface cleaner formulated with bentonite clay is disclosed in U.S. Patent 5,688,435. Examples of time-dependent shear effects determined from constant shear rate measurements at 1, 10, 50, and 100 sec^{-1} are provided in the patent and shown in Figure 4.2 and Figure 4.3. The viscosity data show evidence of shear thickening as a function of time at constant shear rates of 1 and 10 sec^{-1} and thixotropy occurs at 50 and 100 sec^{-1}. The formulation is rheopectic at 10 sec^{-1}. Dynamic mechanical data are also contained in the patent and the storage and loss modulus as a function of strain amplitude is shown in Figure 4.4, for one patent example.

Hypochlorite hard surface and drain cleaner compositions exhibiting enhanced extensional viscosity are mentioned in U.S. Patents 5,728,665 and 5,916,859. The viscoelastic compositions are intended for use with trigger sprayers and the hexadecyl amineoxide/organic counterion compositions provide low bleach odor and reduced spray misting. The patent contains extensional viscosity data in support of the claims. Viscosity as a function of shear rate at various C_{16} diphenyloxide disulfonate concentrations is shown in Figure 4.5. Examples of steady shear and extensional viscosity as a function of shear rate and extensional rate are shown in Figure 4.6 and Figure 4.7.

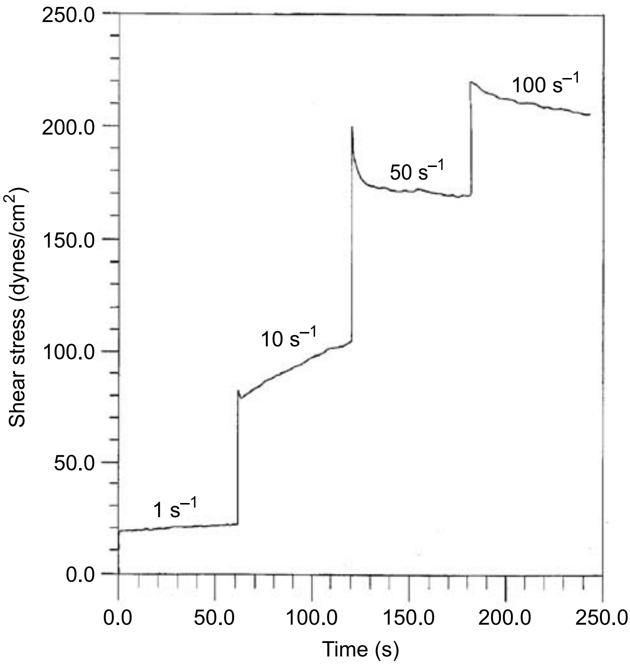


FIG. 4.2 Step shear rate measurements of a bleach hard surface cleaner containing bentonite clay. (Reprinted from U.S. Patent 5,688,435.)

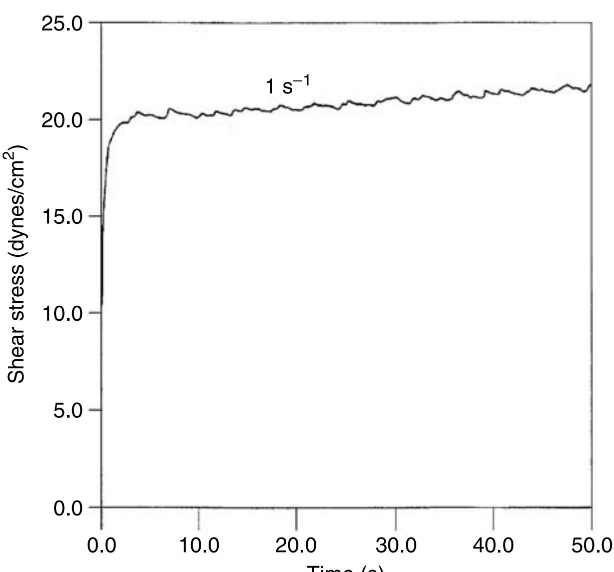


FIG. 4.3 Step shear rate measurement of a bleach hard surface cleaner containing bentonite clay. (Reprinted from U.S. Patent 5,688,435.)

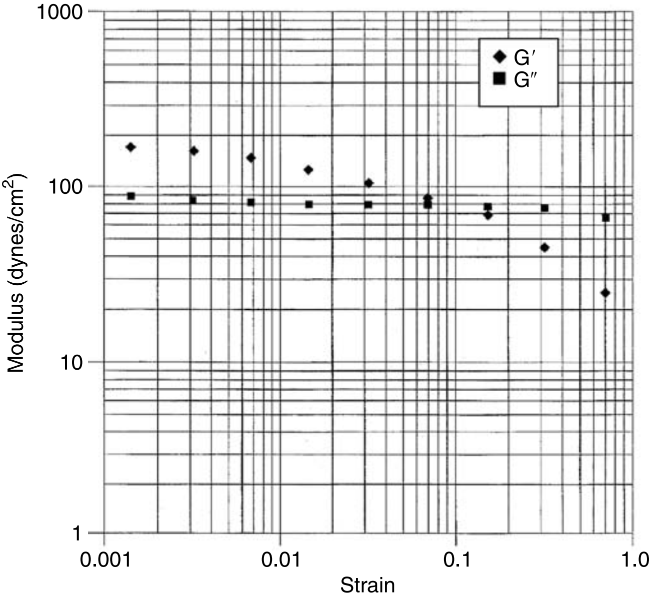


FIG. 4.4 Dynamic mechanical test results for bleach hard surface cleaner. (Reprinted from U.S. Patent 5,688,435.)

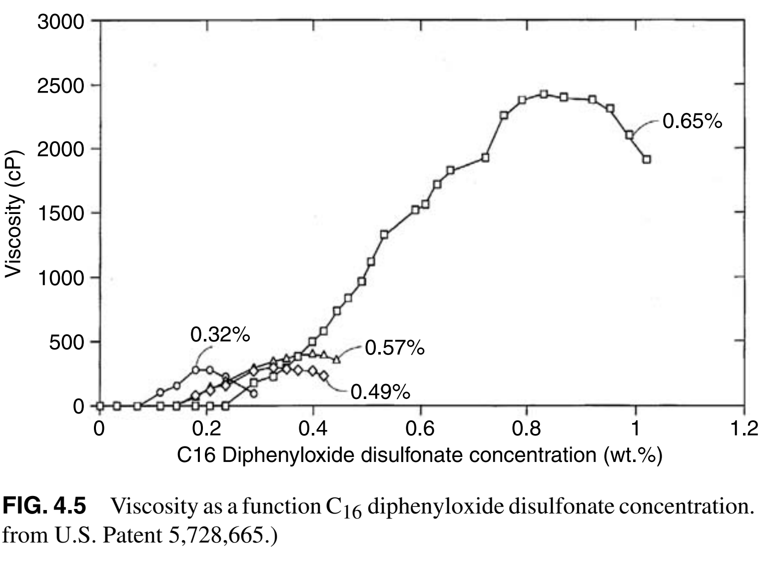


FIG. 4.5 Viscosity as a function C_{16} diphenyloxide disulfonate concentration. (Reprinted from U.S. Patent 5,728,665.)

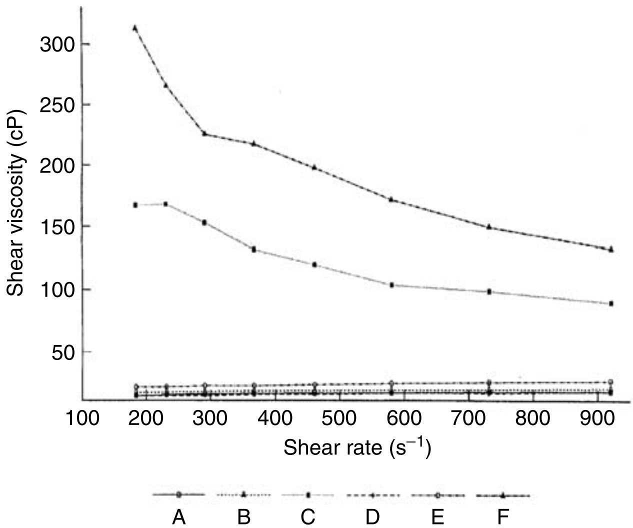


FIG. 4.6 Viscosity differences between state-of-the-art Newtonian systems and the extensional system of an invention cited in a patent. (Reprinted from U.S. Patent 5,918,665.)

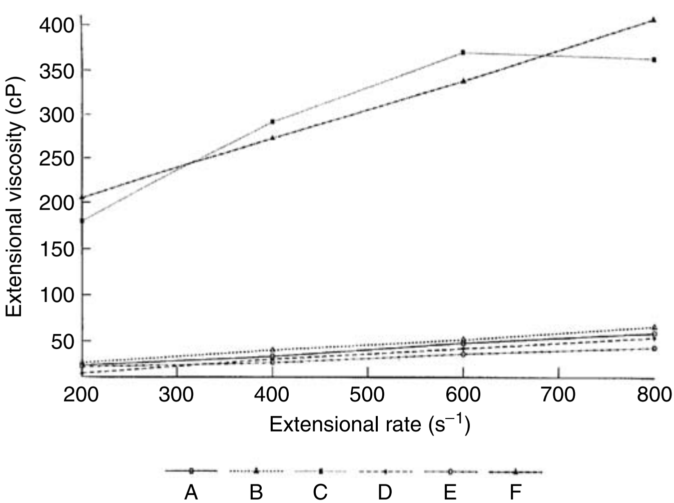


FIG. 4.7 Extensional viscosity differences between state-of-the-art Newtonian systems and the extensional system of an invention cited in a patent. (Reprinted from U.S. Patent 5,918,665.)

Structured surfactant systems are also cited in patents. One example is a stable, pourable, spherulitic surfactant composition containing up to 80% by weight surfactant in U.S. Patent 6,177,396. This patent also contains a list of prior art worldwide patents using "structured surfactant" systems. Structured viscoelastic surfactant systems developed for suspending particles are cited in U.S. Patent 6,258,859, comprised of amphoteric/zwitterionic surfactants and their mixtures. The systems are also cited to increase effectively the average droplet size of sprays. The patent contains steady shear and dynamic mechanical data for disodium tallowiminodipropionate with phthalic acid, as well as disodium oleomidopropyl betaine solutions containing potassium chloride and phthalic acid. An acidic microemulsion cleaning composition, a viscoelastic gel, is described in U.S. Patent 5,409,630. The composition contains a sodium paraffin sulfonate, nonionic detergent, one aliphatic carboxylic acid, water-insoluble perfume, water, and an associative polymeric thickener. The pH is preferably in the range of 1 to 5 and dynamic mechanical data are cited in the patent as a function of strain and frequency.

U.S. Patent 6,268,324 describes low-viscosity cleaning compositions that increase in viscosity upon dilution. Thickening is attributed to rod-like micellar structuring. A shear thinning heavy-duty liquid containing 30 to 80% surfactants as lamellar drops dispersed in an aqueous medium is disclosed in U.S. Patent 5,776,883. Shear thinning behavior is cited using the Sisko model constants, k and n, as well as pour viscosity (21 sec^{-1}) and it states that n should be less than 0.35, preferably less than 0.3. A nonaqueous liquid detergent composition containing a surfactant-structured continuous phase is disclosed in U.S. Patent 6,277,804. The "particulate containing detergent compositions" exhibit viscosity ranging from 300 to 5000 cP as measured with a Carrimed CSL2 rheometer at a shear rate of 20 sec^{-1}. Examples are cited in the patent for nonaqueous base systems giving yield values and pouring viscosity test results. The transformation of a detergent concentrate from micellar to lamellar phase in the presence of a water-soluble electrolyte produces an increase in viscosity upon dilution (U.S. Patent 5,922,664). The viscosity enhancement of an illustrative laundry detergent concentrate using potassium citrate as a function of concentration is provided in the patent. Enhancement is demonstrated with Brookfield viscosity measurements (Spindle nos. 1 and 2 at 25°C).

U.S. Patent 5,798,324 discloses a glass cleaner containing a synthetic polymer thickener in the presence of certain glycol ethers, nonionic surfactants, and linear alcohols that increases viscosity synergistically. Cited compositions exhibit optimal vertical cling and ease of use.

Light-duty or gel dishwashing compositions containing an alkyl ether sulfate-based anionic surfactant, polyhydroxy fatty acid amide nonionic surfactant, suds boosters/stabilizers, aqueous liquid carrier, pH control agent, and acrylic copolymer thickener are disclosed in U.S. Patent 6,274,539. Viscosity as determined using a Brookfield viscometer with RV no. 2 spindle at 1 r/min ranges from 800 to 1500 cP at 25°C.

A pseudoplastic and thixotropic cleaning composition is disclosed in U.S. Patent 5,851,979, which is suitable for both fabric and hard surface care. The viscosity values of the compositions range from 60 to 1500 cP at 12 r/min, 40 to 800 cP at 30 r/min, and 20 to 500 cP at 60 r/min (Spindle no. 2 and 20°C).

Concentrated compositions that increase in viscosity when diluted are described in U.S. Patent 6,150,320. A Bostwick consistometer is used for all viscosity measurements and equivalence is offered to Brookfield measurements using Spindle no. 1, at 60 r/min, and the Zahn viscometer, no. 1 cup. A low-viscosity hard surface cleaning emulsion, approximately 12 mPa s, is described in U.S. Patent 5,934,375 that increases in viscosity upon dilution with water to 800 to 1200 mPa s.

Pseudoplastic and thixotropic liquid detergents as emulsions are the subjects of U.S. Patent 5,851,979. Equilibrium viscosity values measured using a Brookfield viscometer with Spindle no. 2 at 20°C are cited at 12, 30, and 60 r/min. For one example containing hydrogen peroxide, the viscosity is 1020, 400, and 220 cP at 12, 30, and 60 r/min, respectively. Pseudoplasticity is clearly evident, as the viscosity decreases with increasing rotational speed.

B. Personal Care Products

Rheology is a product attribute frequently exploited in personal care products to create visual appeal to prospective consumers. Liquid products in transparent packaging may highlight the gel strength of the continuous phase with obvious suspension of the particulate phases. In certain instances, aeration may be introduced to emphasize the gel-like consistency of the product. Premium brand products may include stable suspensions captured within the gel matrix of encapsulated fragrances, moisturizers, exfoliating compounds, etc.

Because of the frequent use of personal care products by the consumer for hair, body, and skin care, rheological properties are designed to achieve product differentiation. Products are formulated to achieve efficacy within a definite matrix of rheological properties. Certain manufacturers lean toward lower viscosity systems, while others focus on a thicker, “richer” composition. Regardless of the rheology preference, formulators need to overcome obstacles to achieve robust product design, including variables such as pH and electrolyte concentration.

Aqueous viscoelastic surfactant solutions for hair and skin care are disclosed in U.S. Patent 5,965,502. Rheology conditions are specified for optimum flow behavior, in terms of the shear modulus as a function of temperature and pH. A representative graph of the storage and loss modulus as a function of angular frequency is presented in the patent and this is shown in Figure 4.8. Cited compositions contain anionic, betainic, and nonionic surfactants, electrolytes, and a water-soluble polymer. A nonionic gel personal cleanser is specified in U.S. Patent

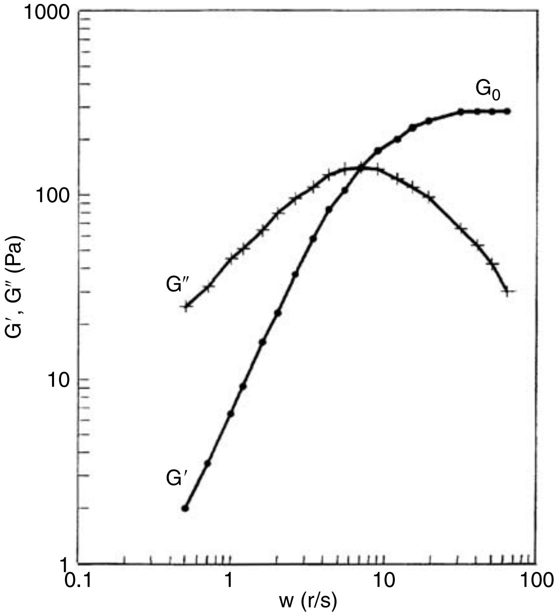


FIG. 4.8 Dynamic mechanical test results for a personal care product. (Reprinted from U.S. Patent 5,965,502.)

6,277,798. The high-viscosity composition has a viscosity (Helipath, Spindle A, 10 r/min and 25°C) ranging from 500 to 10,000 cP. Emulsion, moisturizing personal cleansing compositions containing a complex coacervate are disclosed in U.S. Patent 6,028,043 having a viscosity ranging from 2,000 to 100,000 cP and a yield point from about 5 to 50 dyn/cm^2. Patent rheology data cited are determined using the Carrimed CSL 100 controlled stress rheometer and the Wells-Brookfield cone/plate viscometer (2.4 cm cone). The instruments are used to determine the consistency and shear index, *k* and *n*. The complex coacervate is characterized using the Stable MicroSystems Universal TA.XT2 texture analyzer. U.S. Patent 5,932,528 cites encapsulated lipophilic skin moisturizing agents. The Carrimed CSL 100 controlled stress rheometer is using to determine yield stress, as the amount of stress required to produce a strain of 1%.

Viscoelastic dentifrice compositions are disclosed in patents SK279419B and PL169998B. Hair care compositions comprising at least one associative polymer are disclosed in patent EP1088545. They are said to be easy to dispense and apply to the hair, having an excellent rheology profile.

A skin cleansing and moisturizing composition is disclosed in U.S. Patent 5,804,504. Low-viscosity oils having a viscosity less than 1000 cP prethickened with hydrophobic polymers having a low degree of crystallinity are used to deliver skin benefits without compromising foaming. A hand soap concentrate having a viscosity of 200 cP is disclosed in U.S. Patent 6,271,187 that increases in viscosity when mixed with an aqueous solution. Preferred thickeners for this application are polyalkylene ether diesters.

A nonaqueous dentifrice gel and/or paste composition is disclosed in U.S. Patent 6,331,291 B1, cited as a thixotropic and smooth-flowing substance. Brookfield viscosity values are reported in the patent for illustrative examples of the invention using Spindle no. 6 at 10 r/min and 23.5°C. The preferred viscosity range is 75,000 to 150,000 cP.

C. Actives

Modifying the rheological behavior of high-concentration surfactants is desirable for various reasons and this is also reflected in the patent literature. One example is U.S. Patent 6,313,085 involving high-concentration anionic surfactant mixtures of alkyl ether sulfate (60 to 90%) and alkyl sulfates (10 to 40% alkyl sulfate). This patent defines "flowable" by means of a Brookfield viscosity, as measured with an RVT instrument, 20°C, 10 r/min, Spindle no. 1. To be flowable, the patent states that the viscosity is less than 50,000 mPa s, preferably less than 10,000 mPa s. A pumpable, flowable, and pourable surfactant concentration is disclosed in U.S. Patent 6,087,320 for an aqueous blend of alkylpolyglycoside (70%) and anionic or amphoteric surfactants (30%) in the presence of inorganic and/or organic electrolytes. Viscosity determinations are included obtained using a viscometer at 25°C with Spindle no. 4, at 10 r/min.

Hydrophilic copolymers that reduce the viscosity of detergent slurries are disclosed in U.S. Patent 5,733,861. Viscosity-reducing properties are illustrated using data obtained from a Brookfield viscometer, Spindle no. 4, 20 r/min, at 25°C. The copolymer comprises an unsaturated hydrophilic monomer copolymerized with an oxyethylated monomer.

The process for producing detergent agglomerates from high active surfactant pastes is discussed in U.S. Patent 5,574,005. The surfactant paste is identified as having nonlinear viscoelastic properties, described as a power law fluid. An example of paste characterization is provided using a stress-controlled rheometer with truncated 2° cone (4 cm in diameter) and solvent vapor trap. A schematic of the rheometer tooling is shown in the patent with a shear stress–shear rate diagram for the paste where "shear fracture" is evidenced. Using a Carri-Med rheometer, a stress ramp from 5 to 5000 dyn/cm^2 is applied over a three-minute period.

It is very apparent that a great deal of effort is put in by research groups in defining the relevant mechanical properties of personal and home care liquid detergent formulations. Throughout the industry it is apparent that more rigorous characterization methods are being applied and included in product definitions comprising corporate patent portfolios.

III. RHEOLOGY MEASUREMENTS

A. Measurement Technology

During the past decade there has been a surge of technical developments in the rheometer industry and this is reflected in worldwide patents. Several examples are provided below:

WO0169231, Method of Fluid Rheology Characterization and Apparatus
U.S. 6,378,357, Method of Fluid Rheology Characterization and Apparatus
U.S. 5,456,105, Rheometer for Determining Extensional Elasticity
U.S. 5,532,289, Apparatus and Method for the Study of Liquid–Liquid Interfacial Rheology
U.S. 6,200,022, Method and Apparatus for Localized Dynamic Mechano-Thermal Analysis with Scanning Probe Microscopy
U.S. 5,543,594, Nuclear Magnetic Resonance Imaging Rheometer
U.S. 6,220,083, Elongational Rheometer and On-Line Process Controller
U.S. 5,520,042, Apparatus and Method for the Simultaneous Measurements of Rheological and Thermal Characteristics of Materials and Measuring Cell

Rheology is increasingly being coupled to other analytical test methods for more comprehensive material characterizations. Many of these developments are driven by research needs for broadened characterization capability. For fundamental studies of detergent systems this offers a broad suite of methods to probe surfactant mesophases and internal microstructure.

An overview of the viscometer and rheometer market from 1969 to 1999 is given by Barnes *et al.* [2] and examples of other advances are addressed in the technical literature [3–16]. Concurrent with new developments in rheology instrumentation are both introductory and advanced texts on rheology for industrial scientists [17–22].

Flow visualization, conductivity, turbidity, and light scattering can be simultaneously conducted with rheology measurements. Small-angle light scattering (SALS) coupled to rheology measurements is provided by Paar Physica (Rheo-SALS). Using a modular design concept, the SALS system is an add-on accessory to the research rheometer using concentric cylinder, parallel plate geometries. The laser wavelength is 658 nm and the maximum scattering angle for the concentric cylinder geometry is 11.3°.

GBC Scientific Equipment offers a Micro Fourier Rheometer, MFR 2100. The rheometer applies a squeezing motion to the sample, performing analyses on sample volumes less than 100 μl. An automated sample injection system is included in the instrument design. The rheometer is capable of handling low-viscosity fluids, 1 mPa s, with storage modulus measurement down to 10^{-4} Pa. Using a different measurement technique, both benchtop and in-line, the real-time ultrasonic rheometer and fluid characterization device uses spatially resolved ultrasonic

Doppler velocimetry techniques to monitor rheology of fluids and slurries (Pacific Northwest National Laboratory, Richland, WA).

Brookfield Engineering Laboratories has recently introduced a stress-controlled and yield stress viscometer, and the Thermo Haake RheoScope1 includes optical microscopy with video accessory for the cone and plate rheometer. With the RheoScope1, rheology measurements are integrated with image/video acquisition. This accessory permits flow visualization during rheology measurements to observe and document shear-induced microstructural changes.

Although there have been steady advances in rheology measurement technology, not all areas have been equally addressed. One of the most difficult is the facile transition of characterization tools from R&D laboratories to the factory floor. For viscoelastic compositions, frequently encountered in personal and household care products, this presents a challenge to both R&D and production facilities. Further, rotational devices are limited in the shear rate and shear stress operating range. For process simulations, high-shear measurement tools are not readily available in the appropriate viscosity range. Several additional needs are discussed in the following sections.

B. Quality Control Metrics

"Simple" rheology measurements appear to be the measurements of choice in many industrial settings. Relative consistency indices are used routinely in both product development and manufacturing facilities as benchmarks, regardless of the complex nature of the fluids under consideration, obtained using analog or digital rotational devices. For structured detergents with yield stresses, the vane tool is more widely accepted and other characterization methods are frequently applied [23–26]. For many R&D and quality control (QC) applications, viscometry is still the principal characterization tool and several review articles discuss the use of rotational instruments in QC applications [27,28].

Texture analyzers are also used to assess deformability of a fluid, using penetration force vs. depth profiles, etc. These instruments in addition to Brookfield and Haake viscometers are common QC metrics. Other methods include viscosity flow cups and bubble or falling ball viscometers, and several relevant standard test methods include ASTM D1200, DIN/ISO 2431, ASTM D5125, BS3900:Part A6, ASTM D1545, and ASTM D1725.

For viscoelastic liquid detergent systems, oscillatory measurements may be more appropriate for QC applications. A benchtop, portable QC oscillatory instrument providing storage and loss modulus, complex viscosity values as a function of time and/or temperature, known as the T2SR® (Fluid Dynamics, Inc.) time/temperature scanning rheometer, has recently been introduced. The instrument uses a simple testing geometry in the shape of a flattened blade that is relatively noninvasive. The instrument, operating at 110 to 120 or 220 to 240 V

FIG. 4.9 T2SR rheometer with temperature controller and high-temperature heating cell. (Courtesy of Fluid Dynamics, Inc.)

(50 to 60 Hz), is shown in Figure 4.9 [29]. A schematic of the instrument is shown in Figure 4.10. Originally designed at the University of Strathclyde as a rheometer for cure studies [30], the rheometer has been redesigned and electronically upgraded with modifications producing an oscillatory rheometer for general R&D and QC use for structured fluid systems.

Examples of time sweep test results at 2 Hz for an antibacterial hand soap are shown in Figure 4.11 and Figure 4.12. Figure 4.11 summarizes the complex modulus components, G' and G'', and the complex viscosity, n^*, while Figure 4.12 shows the experimental variables of phase angle and amplitude obtained at 23 to 24°C.

For high-consistency viscoelastic personal and home care products, the T2SR provides a means of obtaining complex rheology information under constant frequency conditions in time sweeps, isothermally, or with temperature control in temperature sweeps. The viscosity range is listed as 10 to 10,000 Pa s, in the frequency range 0.5 to 5 Hz, and in the temperature range −20 to 400°C.

C. High-Shear Viscometry

Most capillary rheometers are designed for high-viscosity materials such as polymer melts and have limited application to lower viscosity liquid detergent systems.

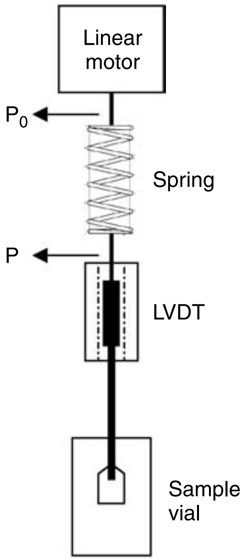


FIG. 4.10 Design elements of the T2SR (time/temperature scanning rheometer). (Courtesy of Fluid Dynamics, Inc.)

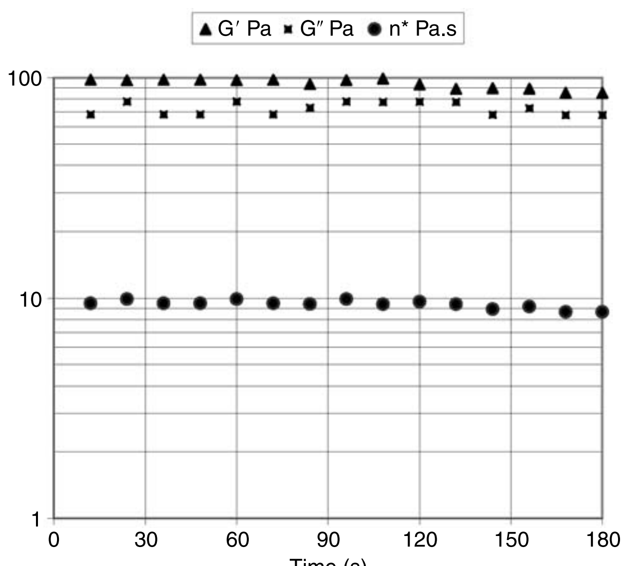


FIG. 4.11 Measurement results for an antibacterial hand soap determined at 2 Hz using the T2SR rheometer at room temperature.

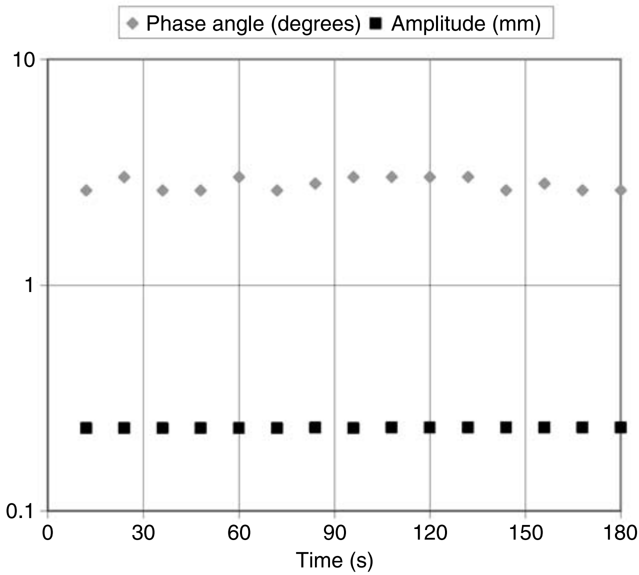


FIG. 4.12 Phase angle and amplitude measurement results for an antibacterial hand soap at 2 Hz using the T2SR rheometer.

There are notable exceptions, however, such as the CEP Lodge Stressmeter®. This rheometer is unique in that it measures both viscosity and first normal stress difference, N1. Both laboratory and in-line configurations are available. The instrument is shown in Figure 4.13. The Lodge Stressmeter is applicable to low-viscosity systems and available commercially from Chemical ElectroPhysics Corp. (Delaware, NJ).

The ACAV A4 (ACA Systems Oy, Finland), a pneumatic instrument, can also handle lower viscosity fluids, $<$50 mPa s. The ACAV A4, designed for coating applications, covers a broad shear rate range of 1×10^3 to 4×10^6 sec^{-1} [31]. The benchtop instrument is shown in Figure 4.14. To demonstrate the low-viscosity range, Figure 4.15 provides viscosity vs. shear rate data for simple sugar/water solutions [32].

With design modifications, rotational rheometers can be used for high-shear-rate measurements. A high-shear rotational rheometer constructed with optically transparent parallel plates set up for simultaneous birefringence measurements on thin films is reported by Mriziq *et al.* [33]. Rheology and birefringence measurements for a perfluoropolyether lubricant are reported over a range of strain rates from 10^3 to greater than 10^6 sec^{-1}.

FIG. 4.13 CEP Lodge Stressmeter. (Courtesy of Chemical ElectroPhysics Corp.)

D. Extensional Viscosity Measurements

While dynamic mechanical and steady shear measurements are frequently used in rheology studies of surfactant systems, extensional viscosity measurements are lacking. This can be attributed to the difficulties associated with such measurements and the lack of commercial laboratory instrumentation since the discontinuance of the Rheometric Scientific RFX rheometer. For many detergent compositions, the relatively low viscosity further complicates such measurements. There appear to be very few data on extensional or elongation viscosity for detergent consumer products and actives in the technical literature at this time.

Filament stretching and capillary breakup rheometers are two experimental instruments used to impose uniaxial extension to fluids [34–39]. In both of these devices a fluid is placed between two surfaces or platens, and the spacing between the platens holding the sample is increased, as shown in Figure 4.16.

There are many practical situations in which extensional flow properties are important, both in processing detergent compositions and during consumer use. One of the most problematic can be the filling operation where a clean separation of the fluid and the filling nozzle does not occur. When extensional viscosity is

FIG. 4.14 ACAV A4 capillary rheometer. (Courtesy of ACA Systems, Oy, Finland.)

high, a consumer will experience problems with "stringiness" in dispensing fluid from a pump or tube. This has been observed with various commercial personal care products. An example of one hair care product is shown in Figure 4.17, where the dispersion is quite stringy. This property is readily perceivable by the consumer and might not be an acceptable characteristic, since a clean break of the fluid from the dispensing orifice is generally desirable. Certainly this is true of fluids that are processed in high-throughput filling lines.

A commercial instrument for extensional viscosity measurements is currently offered by the Thermo Electron Corporation [40]. The device uses capillary breakup techniques and is called the Haake CaBER™. Vilastic Scientific, Inc. also offers an orifice attachment to their oscillatory rheometer for extensional viscosity determinations [41,42]. The principle of operation of the rheometer is oscillatory tube flow [43,44]. Dynamic mechanical properties can be determined

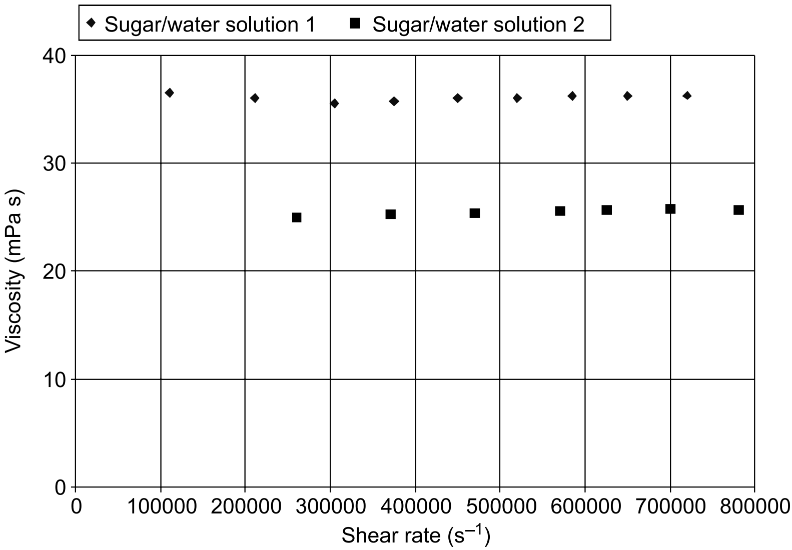


FIG. 4.15 Example test results using the ACAV capillary rheometer. (Courtesy of ACA Systems, Oy, Finland.)

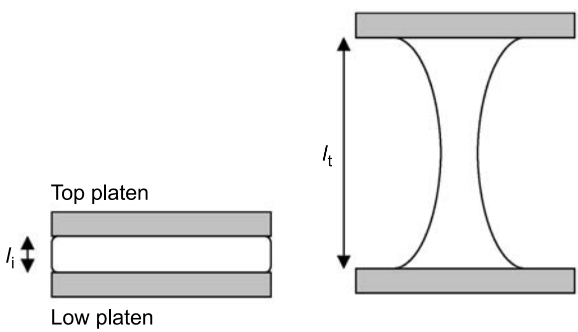


FIG. 4.16 Example of an extensional viscosity measurement configuration using parallel plates.

as a function of frequency in the range 0.01 to 40 Hz. Shear stress and shear rates are 0.01 to 1000 dyn/cm^2 and 0.1 to 1000 sec^{-1}, respectively, for 0.4 to 90°C. This tube flow rheometer uses water as a calibration fluid and can handle very low-viscosity fluids for testing. With the orifice attachment, measurement of oscillatory pressure and flow through the converging channel allows extensional viscosity and elasticity to be calculated. The rheometer operates with small sample volumes (3 ml).

FIG. 4.17 Liquid soap solution in extension.

E. Interfacial Rheology

The properties of liquid/surface and liquid/liquid interfaces are fundamental to surfactant science. Surface tension measurements are quite common but interfacial rheology measurements are not and the rheology of these interfaces determines emulsion and foam stability, for example. Various experimental methods have been developed to determine interfacial rheology, including Gibbs elasticity and surface dilatational viscosity [45–52]. Common testing geometries for interfacial rheology measurements are shown in Figure 4.18.

A commercial stress-controlled interfacial rheometer is available from Camtel Ltd, CIR-100, equipped for use with a Langmuir trough accessory, CIR-LT. A schematic diagram of the CIR-100 drive mechanism and test sensor is shown in Figure 4.19 [53]. For the Camtel CIR-100, the platinum Du Nouy ring is the standard geometry. This rheometer applies an oscillating stress to a test sample and interfacial viscosity and elasticity are calculated from strain amplitude (γ) and phase angle (δ), as shown in Figure 4.20. Measurement capabilities include time, strain, frequency, and temperature sweeps in simple shear and under changing surface pressure. Interfacial dilatational complex modulus can be determined at

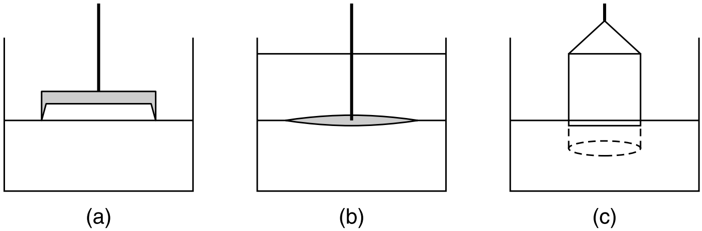


FIG. 4.18 Typical geometries for use in interfacial rheometers.

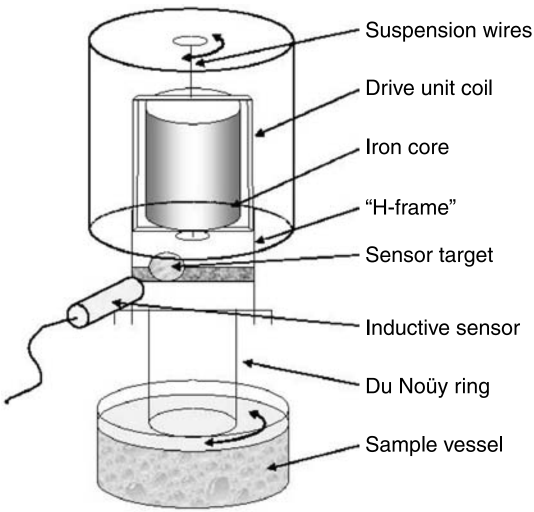


FIG. 4.19 Schematic diagram of drive mechanism and sensor of CIR-100. (Courtesy of Camtel Ltd, U.K.)

the liquid/gas and liquid/liquid interfaces as a function of surface area and pressure, using the Langmuir trough. Application notes describing the operation of the CIR-100 are available from Camtel Ltd [54] and there are publications reviewing the principles and applications of surface/interfacial rheology [55–57].

Sinterface Technologies Profile Analysis Tensiometer (PAT1) can also be used for dynamic dilatational rheology measurements using a different testing method from the Camtel instrument [58]. The PAT1 is a sessile or pendant drop and drop/bubble oscillation instrument consisting of an automatic dosing system and video camera with framegrabber (Figure 4.21). Oscillations can be programmed to determine surface elasticity with temperature control in the range 10 to 350°C.

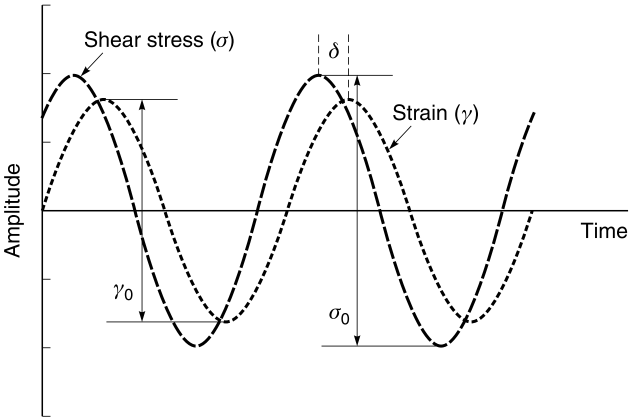


FIG. 4.20 Stress/strain relationship for oscillatory shear viscoelastic measurements.

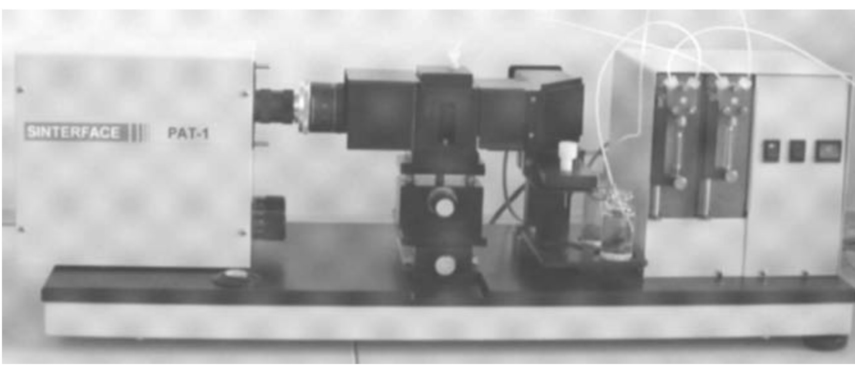


FIG. 4.21 PAT1 instrument. (Courtesy of Sinterface Technologies.)

There is an extra oscillation module, based on direct measurements of the capillary pressure, which operates from 1 to 150 Hz. There is also an additional accessory for the PAT1 for low-frequency oscillations. The range of surface and interfacial tension is 1 to 1000 mN/m with a resolution of ±0.1 mN/m. The instrument allows for transient relaxation measurements, using perturbations such as ramp, square pulse, or trapezoidal area changes.

An Interfacial Shear Rheometer (ISR-1) is also offered by Sinterface Technologies for measuring interfacial shear properties, in the frequency range 0.02 to 0.2 Hz, dependent on the measurement system, in the temperature range 10 to 50°C. The measurement ranges of the rheometer include surface shear viscosity

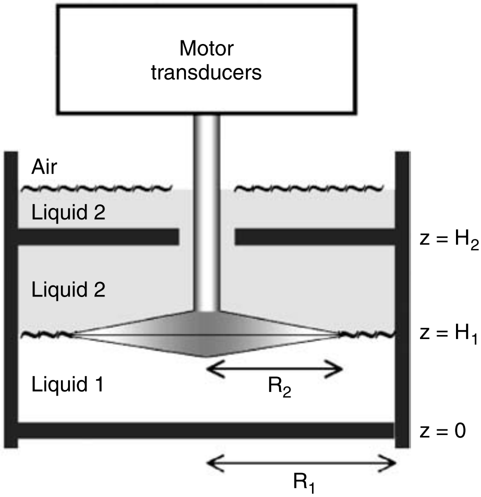


FIG. 4.22 Schematic of biconical tool for surface rheology measurements using the Paar Physica interfacial rheometer. (Courtesy of American Institute of Physics.)

range of 1 μNs/m to 100 mNs/m and surface shear elasticity range of 1 μPa s to 100 mPa s.

A biconical disk interfacial rheometer is available from Anton Paar, known as the Physica Interfacial Rheology System (IRS). A schematic of the rheometer tool is shown in Figure 4.22. Current specifications of the instrument include a torque range of 0.02 μNm to 150 mNm with temperature control from 5 to 70°C. All rheological test modes are available for the interfacial rheometer including oscillatory testing [59].

IV. PRODUCT AND RAW MATERIAL CHARACTERIZATIONS

U.S. commercial products were selected for rheological characterization, demonstrating the breadth of rheology exhibited by current household and personal care products. Products include fabric softeners, dishwashing liquids, laundry detergents, shampoos, and dentifrices.

For dynamic mechanical and steady shear measurements, the Rheometric Scientific RFSII rheometer was used equipped with the sensitive range force rebalance transducer and couette geometry or parallel plate tooling.

Liquid detergent formulations covering the personal care and household care product categories exhibit a very wide range of rheological properties as shown in

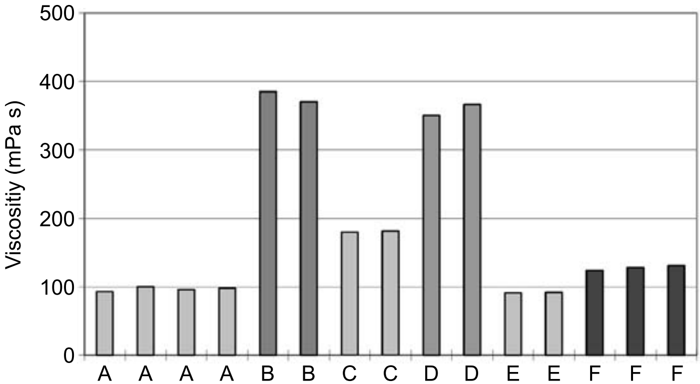


FIG. 4.23 Newtonian viscosity of U.S. liquid laundry detergent products.

Figure 4.1. Within a single product category such as hair care one finds simple low-viscosity Newtonian fluids, non-Newtonian viscoelastic dispersions with time-dependent shear effects, and transparent highly elastic gels.

A. Fabric Care Products

U.S. laundry detergents are typically Newtonian fluids and the viscosity of six commercial products is summarized in Figure 4.23. Several lots of each product, labeled A to F, were obtained and measurements completed at room temperature, 20 to 25°C, as a function of shear rate from 0 to 500 sec^{-1}. A typical shear stress–shear rate diagram is shown in Figure 4.24 for a product sampled from a 50 fl oz container. All six products tested are Newtonian with a viscosity less than 0.5 Pa s at room temperature, 21 to 23°C, with the shear rate ramped from 0 to 500 sec^{-1} at an acceleration rate of 0.83 sec^{-2}. Newtonian behavior was confirmed through additional step shear rate measurements within the selected shear rate range.

Liquid fabric softeners are generally non-Newtonian and examples of the shear stress–shear rate relationship for two commercial products (A and B) is shown in Figure 4.25, determined at 22.5°C. In the shear rate range 0 to 250 sec^{-1}, we note non-Newtonian pseudoplastic behavior.

Dynamic mechanical strain-controlled measurements for both concentrated fabric softeners are shown in Figure 4.26. There are significant differences between the two products as regards the magnitude of the complex viscosity and complex modulus components and their strain dependence. Product B exhibits a higher viscosity and markedly longer linear region. The zero shear viscosity of product B is approximately 95 mPa s whereas that of product A is approximately half of this value at 50 mPa s.

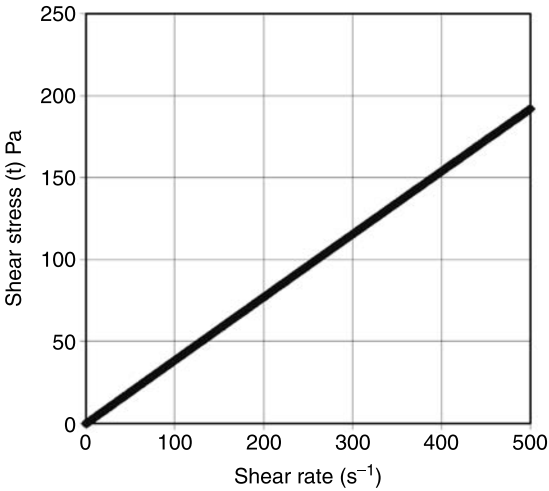


FIG. 4.24 Typical shear stress–shear rate relationship for Newtonian laundry detergent.

Both liquid fabric softeners exhibit time-dependent shear effects as shown in step shear rate measurements at room temperature. Figure 4.27 summarizes the steady shear viscosity as a function of time at shear rates of 0.1, 0.5, 1, and 5 sec^{-1}. Each shear rate is held for a period of 30 sec.

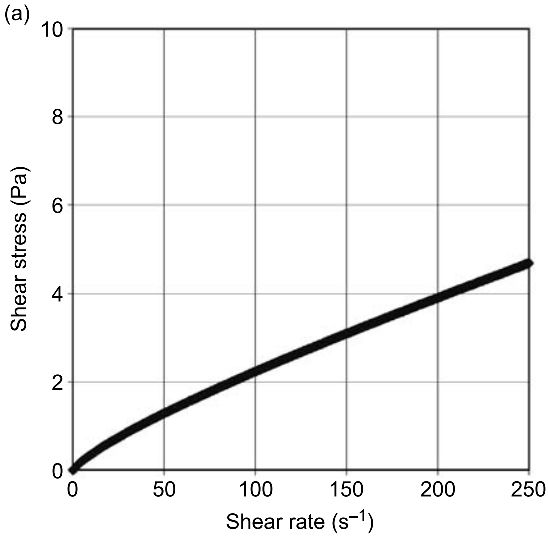
Fabric softeners, as demonstrated by these two commercial concentrated products, are more complex compositions due to their dispersion characteristics. The systems studied are non-Newtonian with time-dependent shear effects.

B. Personal Care Products

Shampoos, conditioning shampoos, body washes, and dentifrices cover a broad range of the rheology spectrum. This is a creative category where there are as many types of rheological fluids as there are containers. Examples of shear stress–shear rate profiles of randomly selected premium and value brand products obtained during thixotropic loop measurements, 0 to 25 sec^{-1}/60 sec, are shown in Figure 4.28. These products include clarifying and conditioning shampoos.

Several conditioning shampoos exhibit rheopectic behavior at low shear rates and examples for two commercial products are provided in Figure 4.29 at 0.05 and 0.1 sec^{-1}. The shear rates are applied sequentially for a time interval of 120 sec. Within this timeframe an equilibrium steady state shear stress is not reached. For product A, the shear rate is extended to 5 sec^{-1} with similar results.

The oral care category has become a more complex product category, with the introduction of many products tailored to the youthful and senior consumer.



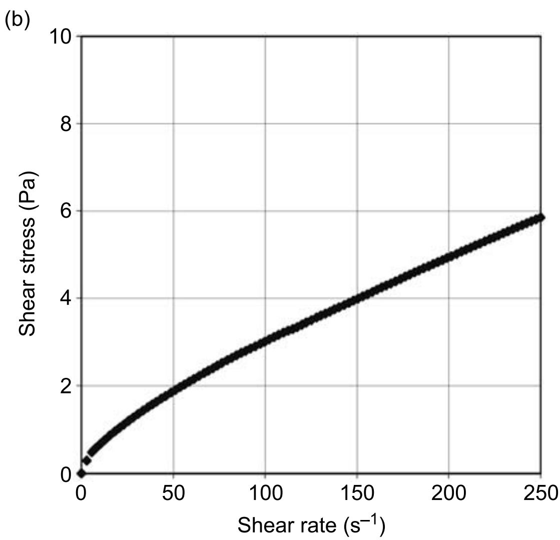


FIG. 4.25 (a) Pseudoplasticity of product A (concentrated fabric softener). (b) Psuedoplasticity of product B (concentrated fabric softener).

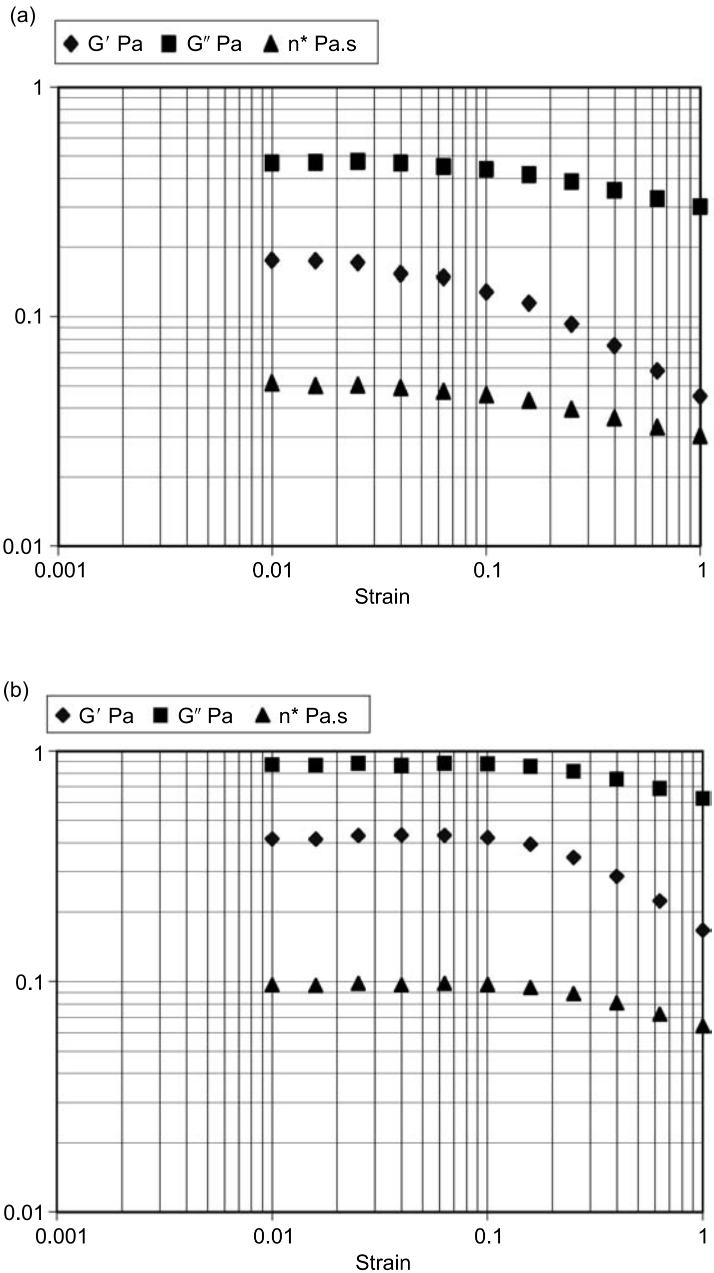


FIG. 4.26 Strain sweep measurements at 10 rad/sec: (a) product A (concentrated fabric softener); (b) product B (concentrated fabric softener).

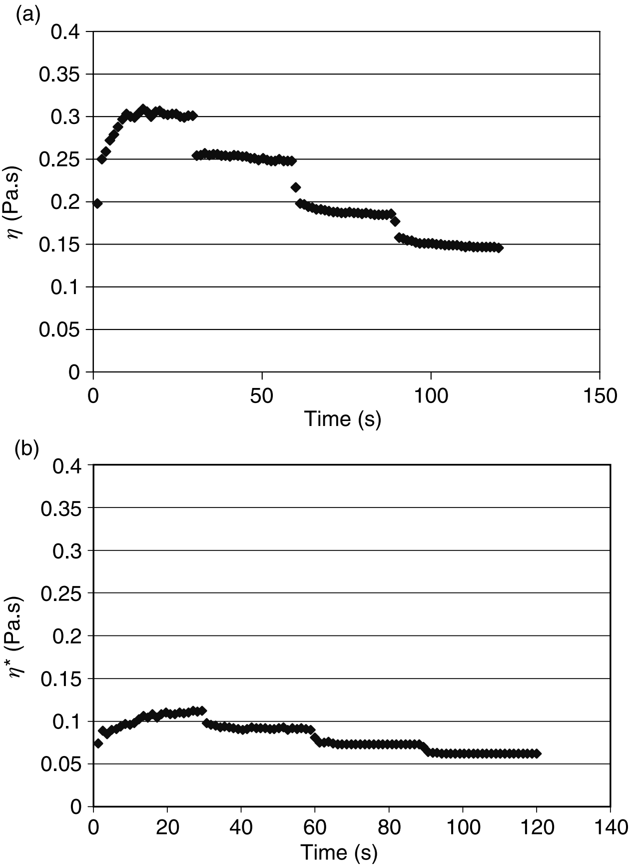


FIG. 4.27 Viscosity during consecutive step shear rates of 0.1, 0.5, 1, and 5 sec^{-1}: (a) product A (concentrated fabric softener); (b) product B (concentrated fabric softener).

Different flavors, colorants, and "sparkling" additives, as well as packaging, are clearly adding complexity to the R&D product development venue for the junior market. In addition, the dentifrice product category has seen the recent introduction of many bleaching or "tooth whitening" compositions from many manufacturers. Some of these products are in the form of films for direct placement on the teeth, and others are in the conventional dentifrice form of pastes or gels. Rheology measurements show that the properties of these "whitening" compositions have broadened the spectrum of the rheology matrix, since some of these products appear markedly lower in consistency.

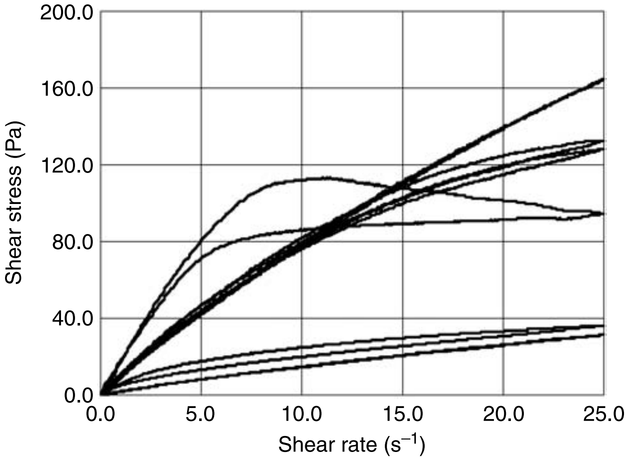


FIG. 4.28 Thixotropic loop measurement results for six commercial U.S. shampoos products.

V. FUNDAMENTAL RHEOLOGY STUDIES

Over the past few decades there has been an increase in the research tools for fundamental rheology studies of surfactant solutions and commercial detergent formulations. The coupling of rheometers with other methods has broadened the range of studies that can be completed, leading to a better understanding of solution properties, self-assembled mesophases, multiple-component dispersions, and gels.

An x-ray shear cell for studying the complex fluid of nematic surfactants in time-dependent shearing flows has been developed by Caputo *et al.* [60]. Shear aligning and director tumbling are cited for two surfactant systems, SDS/decanol and CPyCl/hexanol. A microscopic particle imaging velocimeter with a torsional shearing-flow cell has also been used to study the shear thickening of worm-like micelle solutions [61]. The effect of wall slip on the rheology of the micellar solutions as a function of shear rate is deduced from coupled flow visualization and rheology measurements. Particle image velocimetry of micellar solutions in unstable capillary flow has also been carried out [62]. At a critical stress found to be independent of strain rate, the worm-like micelle filaments rupture near the axial midplane. Filament failure is thought to occur from local scission of individual micellar chains.

Coupled controlled velocity, magnetic resonance imaging (MRI)/rheology measurements of thixotropic and yielding colloidal suspensions further demonstrate the importance of paired measurements [63]. Shear rate profiles obtained in laminar tube flow for both Newtonian and non-Newtonian fluids from MRI

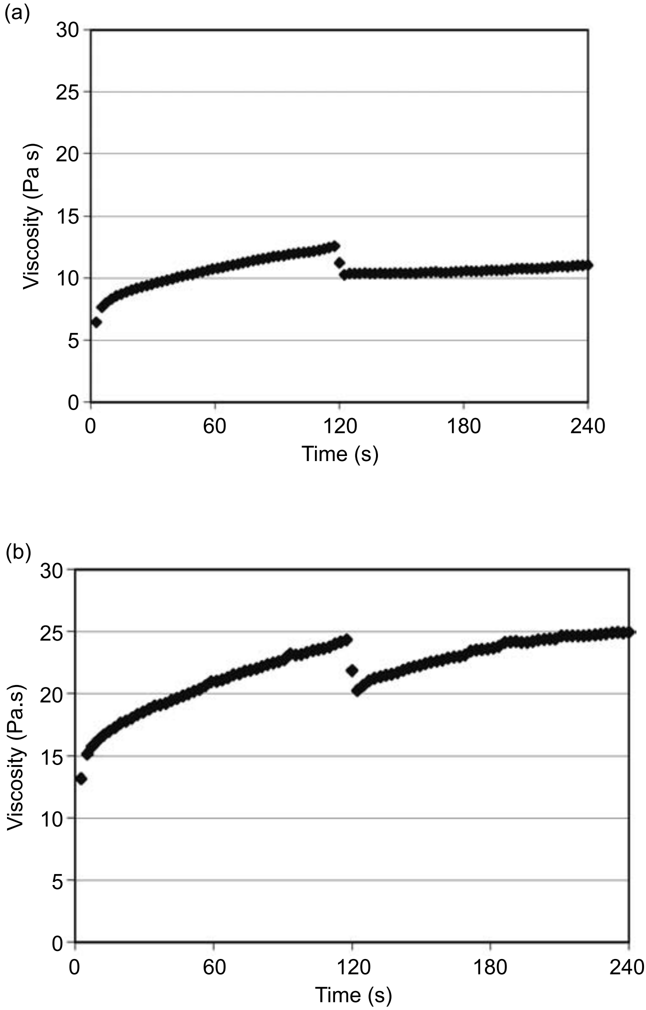


FIG. 4.29 Time-dependent shear effects at step shear rates of 0.05 and 0.1 sec^{-1}: (a) conditioning shampoo A; (b) conditioning shampoo B.

and laser Doppler velocimetry data using Tikhonoz regularization is discussed by Yeow and Taylor [64]. NMR investigations during rheology measurement at rest and under shear for a nematic surfactant system (sodium dodecylsulfate, decanol, water) have been carried out. These measurements are used to determine the director orientations of the surfactant [65]. Shear-thickening self-assembling fluids have been studied using rheooptics, revealing unusual flow behavior at various flow conditions [66]. Measurements included stress growth, steady state viscosity, and stress relaxation for aqueous CTSAB/sodium salicylate solutions.

An overview of rheological measurements coupled with magnetic resonance is provided by Callaghan [67]. Rheo-NMR of emulsified systems has been studied, the systems including formulations with yield stress exhibiting wall slip [68]. Comparisons are provided between conventional rheological techniques and Rheo-NMR characterization.

VI. CONCLUSIONS

The past decade has seen many advances in the science of rheology with applications to liquid detergent systems. This is in keeping with the progressive developments in detergent systems for personal, household, and industrial use. Very common household products exhibit remarkably rich rheology profiles and significant effort is being directed toward understanding how to expand, manipulate, and control these properties to generate high-performance products for consumer use. With new generations of raw materials, this continues to be a difficult field of rheology research.

Coupling of rheology measurements to other analytical techniques such as light scattering and NMR facilitates the study of micellar solutions and liquid crystalline phases, microemulsions, vesicles, etc., leading to the development of new surfactant systems. We anticipate continuing advances in rheology measurement technology with direct applications to the study of liquid detergent systems.

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