

Linear Viscoelasticity of Emulsions

I. The Effect of an Interfacial Film on the Dynamic Viscosity of Nondilute Emulsions

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The dynamic viscosity of nondilute monodisperse emulsions is calculated by using a cell model. Two possibilities for describing the mechanical properties of the interfacial film between the internal and the external phase are considered: (A) the film is assigned a two-dimensional linear viscoelastic behavior and (B) the film is treated as a shell with finite thickness containing a Newtonian liquid. The resulting expressions for the dynamic viscosity show that model B has two relaxation times and model A has at least two or more. If a Voigt-Kelvin model is used to describe the interfacial rheology, model A will also have just two relaxation times. The results obtained may be used to interpret measurements on emulsions in terms of microscopic parameters of these emulsions.

INTRODUCTION

The first predictions on the linear viscoelasticity of emulsions, caused by droplet deformations, were made by Oldroyd (1). His model of an emulsion is that of monodisperse spherical droplets of a Newtonian fluid immersed in another Newtonian fluid. At the infinitesimally thin interface between the two liquids a constant interfacial tension is active. The model has one relaxation and one retardation mechanism and is correct to the first order in the concentration. In Oldroyd's second paper (2) on this subject, the interfacial film is assigned an interfacial tension and a two-dimensional linear viscoelasticity. The interfacial viscoelasticity is described by four parameters which are independent of frequency. This model gives rise to two relaxation and two retardation mechanisms. An alternative method to account for an interfacial film was proposed by Sakanishi and Takano (3).

They described the interfacial film as a shell with finite thickness. This model for a dilute emulsion with incompressible shear-elastic shells between Newtonian droplets and a Newtonian continuous phase already leads to four relaxation and four retardation mechanisms. Due to the limited accuracy of the instruments for measuring linear viscoelasticity the effects predicted by these models are difficult to demonstrate in the concentration range for which they have a chance of validity.

Using a cell model Choi and Schowalter (4) derived a nonlinear constitutive equation for "non-dilute" monodisperse emulsions. The meaning of "non-dilute" implies that, as a result of the use of a cell model, the hydrodynamic interaction between particles is to some extent accounted for. The linear viscoelastic behavior of the basic Oldroyd model (1) is included in this result as a special case.

Analogously to an approach given by Simha (5) the cell model of Choi and Schowalter can be modified in such a way that

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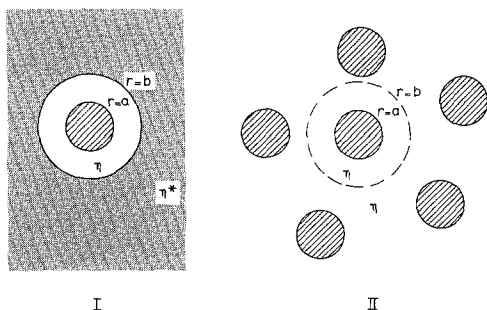


FIG. 1. Self-consistent cell model (I); statistical cell model (II).

the steady-state viscosity data of suspensions of rigid spheres can be predicted. This modified model is elucidated in the next section. In the present paper it is used to calculate the dynamic viscosities of moderately concentrated emulsions with more complex mechanical properties of the interfacial film than those of (4).

As for the description of the mechanical properties of the interfacial film we start with two relatively simple models of interfaces. Obviously these simple models can only partly describe the interfaces of real systems, but more sophisticated models are difficult to handle mathematically and they involve a large number of parameters. At this moment even the relative importance of the parameters is unknown due to a lack of data from viscoelastic experiments involving curved interfaces. The two models are:

Model A: the interfacial film is infinitesimally thin and possesses an interfacial tension and a two-dimensional viscoelasticity, as in (2);

Model B: the interfacial film consists of a Newtonian liquid and has a finite thickness. It may display different interfacial tensions at its contact surfaces with the inner and outer liquids.

CELL MODELS

The problem of how to predict the rheological characteristics of nondilute dispersions on the basis of sound statistical principles has as yet not been completely

solved (6). Progress has been made with dispersions of rigid spherical particles in extensional flow (7), where an expression, correct to the second order of concentration, was derived after an analysis of the hydrodynamic interaction between two particles. A promising line of research (8) uses an a priori assumption about the interparticle radial distribution function and leads to a relation between viscosity and particle concentration which displays qualitative agreement with experimental data, i.e., the value of the concentration where the viscosity of the suspension diverges is below that at the closest packing.

A rigorous treatment of a nondilute emulsion of deformable spheres is even more difficult to achieve. A simplification of the hydrodynamic particle interactions by means of a cell model is then interesting. These models are "engineering approximations" in which exact results on dilute dispersions are included in the results on nondilute ones. A comparison of the influences of various interfacial properties of particles is possible, as the hydrodynamic interaction is approximated in a standard algorithm.

A cell consists of a particle and a certain volume of fluid around it. At the boundary of the cell, conditions are applied which are chosen to model the effect of the rest of the suspension. Two cell models from the literature are described briefly: (I) the "self-consistent cell model" and (II) the "statistical cell model" (Fig. 1).

(I) In the self-consistent cell model (9) a requirement is that the disturbances caused by the insertion of a "unit cell of emulsion" in a homogeneous fluid with viscosity η^* are negligible on a macroscopic scale. The radius of the unit cell is chosen so that $b = a\phi^{-1/3}$. Oldroyd (1) made plausible that this model "cannot be relied upon to give more than first-order terms in ϕ ."

(II) In the statistical cell model it is assumed that the average hydrodynamic effect of neighboring particles may be expressed in boundary conditions that apply

at a certain distance b from each particle. This distance can be regarded as the hydrodynamic interaction radius. The concentration dependence of properties calculated using this model is governed by an adopted relation between b and the concentration. This relation depends on many factors, such as concentration, particle interaction, Brownian motion, and type of flow. In the cell model of Choi and Schowalter the relation between b and ϕ is $b = a\phi^{-1/3}$. Another relation was proposed by Simha (5) for the low-concentration region:

$$b = fa\phi^{-1/3}. \quad [1]$$

Thomas (10) compared the results of Simha's calculations with high-shear steady-state viscosity data on suspensions of rigid spheres. He found a good agreement with experiments if $f = 1.111$ for $\phi \leq 0.1$. We will therefore use the latter relation between b and ϕ in the cell model of Choi and Schowalter as the basis of our calculation.

FORMAL CALCULATION OF η^*

For the calculation of η^* we will use the general definition:

$$\langle \mathbf{T} \rangle \equiv 2\eta^* \langle \mathbf{D} \rangle. \quad [2]$$

The deviatoric part of the volume-averaged stress $\langle \mathbf{T} \rangle$ may be evaluated by surface integrals over the particles (11):

$$\langle \mathbf{T} \rangle = 2\eta \langle \mathbf{D} \rangle + \Sigma^p, \quad [3]$$

with

$$\Sigma^p = \frac{1}{V} \sum_k \int_{\partial V_p} \{ \mathbf{T} \cdot \mathbf{n}r - \eta(\mathbf{v}\mathbf{n} + \mathbf{n}\mathbf{v}) - \frac{1}{3}(\mathbf{r} \cdot \mathbf{T} \cdot \mathbf{n})\mathbf{1} \} dS \quad [4]$$

and the volume-averaged rate of strain tensor $\langle \mathbf{D} \rangle$ may be related to the macroscopic velocity at the sample boundaries:

$$\langle \mathbf{D} \rangle = \frac{1}{2V} \int_{\partial V_s} (\mathbf{v}^0 \mathbf{n} + \mathbf{n} \mathbf{v}^0) dS. \quad [5]$$

In principle this method gives a complete constitutive equation, but for spherical

particles η^* turns out to be just a scalar function (12). At $r = b$ we shall use Simha's boundary conditions (5); i.e., the velocity at $r = b$ is equal to the velocity of a homogeneous sample at that place.

Since almost spherical particles are the only ones we will consider, the rotational part of the flow may be neglected (13) and only the pure straining contribution of the flow needs to be considered. For convenience we will take the harmonically oscillating flow at the boundaries of the sample and the cell to be identical with Oldroyd's (1), (2) flow field. Complex notation will be used.

$$\mathbf{v}^0 = G \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \mathbf{r} \exp(i\omega t)$$

$$\text{for } \begin{cases} \mathbf{r} \text{ at } \partial V_c, & [6a] \\ \mathbf{r} \text{ at } \partial V_s. & [6b] \end{cases}$$

The fluid in each phase is treated as incompressible and Newtonian:

$$\nabla \cdot \mathbf{v} = 0, \quad [7]$$

$$\mathbf{T} = -p\mathbf{1} + 2\eta\mathbf{D}. \quad [8]$$

The Reynolds number is taken to be sufficiently small for the creeping-motion equation to be valid:

$$\eta\Delta\mathbf{v} = \nabla p. \quad [9]$$

The complete solution of [9] with condition [7] is given by Lamb (14). The formulae with symmetry of [6] are most conveniently expressed in spherical coordinates and given in (9):

$$u = u(r)P_2(\cos \theta) \exp(i\omega t), \quad [10]$$

with

$$u(r) = \frac{1}{7}Ar^3 + \frac{1}{2}Br^{-2} + 2Cr - 3Dr^{-4}, \quad [11]$$

$$v = v(r)P_2'(\cos \theta) \exp(i\omega t), \quad [12]$$

with

$$v(r) = \frac{5}{42}Ar^3 + Cr + Dr^{-4}, \quad [13]$$

$$p = \eta\{Ar^2 + Br^{-3}\}P_2(\cos \theta) \times \exp(i\omega t) + p_0, \quad [14]$$

where

$$P_2(\cos \theta) = \frac{1}{2}\{3 \cos^2 \theta - 1\} \quad [15]$$

and

$$P_2'(\cos \theta) = \frac{dP_2(\cos \theta)}{d\theta} = -3 \cos \theta \sin \theta. \quad [16]$$

The components of the stress tensor that are relevant for the calculation of η^* are given by:

$$T\langle rr \rangle = T\langle rr \rangle(r)P_2(\cos \theta) \times \exp(i\omega t) - p_0, \quad [17]$$

with

$$T\langle rr \rangle(r) = \eta\{-\frac{1}{7}Ar^2 - 3Br^{-3} + 4C + 24Dr^{-5}\}, \quad [18]$$

$$T\langle r\theta \rangle = T\langle r\theta \rangle(r)P_2'(\cos \theta) \exp(i\omega t), \quad [19]$$

with

$$T\langle r\theta \rangle(r) = \eta\{\frac{8}{21}Ar^2 + \frac{1}{2}Br^{-3} + 2C - 8Dr^{-5}\}. \quad [20]$$

It is now possible to express η^* formally in terms of the constants, A, B, C, and D of the flow field in the outer region of the cell. If there are no net forces acting on the particles and inertia effects are neglected, the choice of the origin has no effect on the evaluation of the integral in [4]. It is thus permissible to choose a different origin for each particle.

If Σ^p is calculated, one finds:

$$\Sigma^p = \frac{1}{V} \sum_k T^p \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad [21]$$

with

$$T^p = \frac{1}{5} \cdot \frac{4}{3}\pi a^3 \{T\langle rr \rangle(a) + 3T\langle r\theta \rangle(a) - 2\eta u(a) + 6\eta v(a)\}. \quad [22]$$

Using [11], [13], [18], and [20], we find:

$$T^p = -\frac{2}{3}\pi\eta B \quad [23]$$

so

$$\langle \overline{\mathbf{T}} \rangle = 2\eta \langle \mathbf{D} \rangle - \frac{1}{V} \sum_k \frac{2\pi\eta B}{3} \times \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \exp(i\omega t). \quad [24]$$

Applying [6b] in the calculation of $\langle \mathbf{D} \rangle$ in [5] gives:

$$\langle \mathbf{D} \rangle = G \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \exp(i\omega t). \quad [25]$$

Consequently with definition [2] it follows:

$$\eta_{\text{spec}}^* = \eta^*/\eta - 1 = -\frac{1}{4}\phi a^{-3}B/G. \quad [26]$$

The explicit dependence of η_{spec}^* on A, C, and D has disappeared in [24] and [26] as an incidental consequence of our choice of boundary conditions at $r = b$. Different boundary conditions (see Safrai (15)) result in more complicated expressions than [24] and [26].

EXPLICIT EXPRESSION FOR THE DYNAMIC VISCOSITY OBTAINED WITH MODEL A (INFINITESIMALLY THIN INTERFACIAL FILM)

We will closely follow the method given by Oldroyd (1), (2). All quantities and constants pertinent to the inner region of the droplet ($r < a$) are denoted by a prime. The requirement of finite velocity at $r = 0$ gives:

$$B' = 0, \quad D' = 0. \quad [27]$$

At the cell boundary ($r = b$) the condition [6a] is applied. By using [10] and [12] it follows that

$$\frac{1}{7}b^2A + \frac{1}{2}b^{-3}B + 2C - 3b^{-5}D = 2G, \quad [28]$$

$$\frac{5}{14}b^2A + 3C + 3b^{-5}D = 3G. \quad [29]$$

At the droplet surface ($r = a$) continuity

of motion and force equilibrium are required. The former condition leads to:

$$\begin{aligned} \frac{1}{7}a^2A + \frac{1}{2}a^{-3}B + 2C - 3a^{-5}D \\ = \frac{1}{7}a^2A' + 2C', \quad [30] \end{aligned}$$

$$\begin{aligned} \frac{5}{14}a^2A + 3C + 3a^{-5}D \\ = \frac{5}{14}a^2A' + 3C'. \quad [31] \end{aligned}$$

In the calculation of the force equilibrium at $r = a$ the interfacial tension and the surface-rheological behavior of the interfacial film are important. For infinitesimally small harmonic deformations of the film its mechanical behavior may be described as that of a linear viscoelastic two-dimensional body. In this case it is advantageous to separate the interfacial deformation into area deformation and shear deformation at constant area. In Cartesian coordinates the relation between the surface-stress tensor \mathbf{P} and the surface-strain tensor \mathbf{E} for a flat film is then given by:

$$\begin{aligned} \mathbf{P} = \{\gamma + (\kappa + i\omega\sigma)(tr\mathbf{E})\mathbf{1} \\ + 2(\mu + i\omega\zeta)\bar{\mathbf{E}}. \quad [32] \end{aligned}$$

In this expression γ is the interfacial tension. The surface rheology is expressed in four parameters: the dynamic area elasticity κ , with corresponding viscosity σ , and the dynamic shear elasticity μ , with corresponding viscosity ζ . In general, κ , σ , μ , and ζ are functions of frequency. The calculations of the force equilibrium at the deformed interface $r \approx a$ in curvilinear coordinates (2) result in:

$$p_0 = p'_0 - 2\gamma/a, \quad [33]$$

$$\begin{aligned} i\omega\eta\{-\frac{1}{7}a^2A - 3a^{-3}B + 4C + 24a^{-5}D\} \\ = \frac{1}{7}a\{4\gamma - 6(\kappa + i\omega\sigma) - i\omega\eta'\}A' \\ + 4\{2a^{-1}\gamma - a^{-1}(\kappa + i\omega\sigma) \\ + i\omega\eta'\}C', \quad [34] \end{aligned}$$

$$\begin{aligned} i\omega\eta\{\frac{5}{14}a^2A + \frac{3}{2}a^{-3}B + 6C - 24a^{-5}D\} \\ = \frac{1}{7}a\{10(\mu + i\omega\zeta) + 9(\kappa + i\omega\sigma) \\ + 8i\omega\eta'\}A' + 6\{2a^{-1}(\mu + i\omega\zeta) \\ + a^{-1}(\kappa + i\omega\sigma) + i\omega\eta'\}C'. \quad [35] \end{aligned}$$

The set of six linear homogeneous equations [28], [29], [30], [31], [34], and [35] in the seven unknowns A' , C' , A , B , C , D , and G provide sufficient information to calculate B/G . Then η^* is found from [26]. An analytic expression for η^* is most easily obtained by using a symbolic computer language (16). The complete expression, obtained with REDUCE 2, is given in Appendix I. It can be written in the following form:

$$\eta^* = \bar{\eta} \cdot \frac{\{1 + i\omega\tau_1(\omega)\}\{1 + i\omega\tau_2(\omega)\}}{\{1 + i\omega\lambda_1(\omega)\}\{1 + i\omega\lambda_2(\omega)\}}. \quad [36]$$

The relationship between the rheology of the droplet-surface film and the dynamic viscosity of an emulsion will be further analyzed by assuming that the surface rheological parameters κ , σ , μ , and ζ are constants (the two-dimensional analog of a Voigt-Kelvin model). In this case τ_1 , τ_2 , λ_1 , and λ_2 are no longer functions of frequency and Eq. [36] reduces to an expression for η^* in terms of two relaxation times, λ_1 and λ_2 , and two retardation times, τ_1 and τ_2 .

In the low-frequency limit the steady-state viscosity coincides with the expression for the viscosity of a suspension of rigid spheres given by Simha (5), if at least two of the parameters γ , κ , and μ are nonzero:

$$\lim_{\omega \rightarrow 0} \eta_{\text{spec}}^* = 10\phi R^3(R^7 - 1)/g(R), \quad [37]$$

with

$$\begin{aligned} g(R) = 4(R^{10} + 1) \\ - 25(R^7 + R^3) + 42R^5. \quad [38] \end{aligned}$$

In the high-frequency limit η_{spec}^* depends on ϕ , η'/η , $\sigma/(a\eta)$, and $\zeta/(a\eta)$.

In the intermediate frequency range the relation between η^* and the model parameters is complicated and interpretation of experimental data is facilitated if λ_1 and λ_2 are some order of magnitude apart, whereby three relatively simple cases can be dis-

cerned. In each case $\text{Re}\{\eta^*\}$ reaches a plateau value for $\lambda_1^{-1} < \omega < \lambda_2^{-1}$ and $\text{Im}\{-\eta^*\}$ has distinct maxima for $\omega = \lambda_1^{-1}$ and $\omega = \lambda_2^{-1}$. The three cases are:

(a) No area changes in the film for $\omega \ll \lambda_2^{-1}$ if $\kappa \gg \mu, \gamma$. The concentration-independent parts of the relaxation times are:

$$\lambda_1 = \frac{4a\eta}{3\gamma + 2\mu} f_{1\kappa} \left(\frac{\eta'}{\eta}, \frac{\zeta}{a\eta} \right),$$

$$\lambda_2 = \frac{3a\eta}{4\kappa} f_{2\kappa} \left(\frac{\eta'}{\eta}, \frac{\zeta}{a\eta}, \frac{\sigma}{a\eta} \right), \quad [39]$$

where $f_{1\kappa}$ and $f_{2\kappa}$ are dimensionless functions on the order of unity. The plateau value of $\text{Re}\{\eta_{\text{spec}}^*\}$ is:

$$\text{Re}\{\eta_{\text{spec}}^*\}_{\kappa} = \frac{10\phi R^3 \{(23\eta' + 16a^{-1}\zeta)(R^7 - 1) - \eta(16R^7 - 23)\}}{(23\eta' + 16a^{-1}\zeta)g(R) + \eta g_{\kappa}(R)}, \quad [40]$$

with

$$g_{\kappa}(R) = 128R^{10} + 400R^7 - 336R^5 - 100R^3 - 92. \quad [41]$$

This result was also obtained by Brennen (17) for the steady-state viscosity of a suspension of blood cells with a "shear viscous membrane". The properties of this membrane were described by the theory of a linear viscoelastic shell (18), neglecting interfacial tensions. In the calculations an approximation to the first order in the shell thickness was used.

(b) No shear deformations in the film for $\omega \ll \lambda_2^{-1}$ if $\mu \gg \kappa, \gamma$. Relaxation times:

$$\lambda_1 = \frac{3a\eta}{2(\gamma + \kappa)} f_{1\mu} \left(\frac{\eta'}{\eta}, \frac{\sigma}{a\eta} \right),$$

$$\lambda_2 = \frac{a\eta}{\mu} f_{2\mu} \left(\frac{\eta'}{\eta}, \frac{\sigma}{a\eta}, \frac{\zeta}{a\eta} \right). \quad [42]$$

The plateau value is:

$$\text{Re}\{\eta_{\text{spec}}^*\}_{\mu} = \frac{10\phi R^3 \{(13\eta' + 8a^{-1}\sigma)(R^7 - 1) + \eta(8R^7 + 14)\}}{(13\eta' + 8a^{-1}\sigma)g(R) + \eta g_{\mu}(R)}, \quad [43]$$

with

$$g_{\mu}(R) = 48R^{10} - 200R^7 + 504R^5 - 200R^3 - 52. \quad [44]$$

(c) The droplets remain completely spherical for $\omega \ll \lambda_2^{-1}$, if $\gamma \gg \mu, \kappa$. Relaxation times:

$$\lambda_1 = \frac{5a\eta}{(3\kappa + 2\mu)} f_{1\gamma} \left(\frac{\eta'}{\eta}, \frac{\sigma}{a\eta}, \frac{\zeta}{a\eta} \right),$$

$$\lambda_2 = \frac{6a\eta}{5\gamma} f_{2\gamma} \left(\frac{\eta'}{\eta}, \frac{\sigma}{a\eta}, \frac{\zeta}{a\eta} \right), \quad [45]$$

and plateau value:

$$\text{Re}\{\eta_{\text{spec}}^*\}_{\gamma} = \frac{10\phi R^3 \{(5\eta' + 6a^{-1}\sigma + 4a^{-1}\zeta)(R^7 - 1) + \eta(2R^7 + 5)\}}{(5\eta' + 6a^{-1}\sigma + 4a^{-1}\zeta)g(R) + \eta g_{\gamma}(R)}, \quad [46]$$

with

$$g_{\gamma}(R) = 20R^{10} - 50R^7 + 50R^3 - 20. \quad [47]$$

In Fig. 2 examples of $[\eta^*]$ for the three cases described above are shown. The intrinsic viscosities were calculated with neglect of the influence of possible surface

shear and surface area viscosities. The combination of elastic moduli which determine the viscoelastic transitions are indicated for $[\eta_1]$. The vibration modes of the interface at the plateaus A, B, C, D, and E of $[\eta_1]$ are given in Table I.

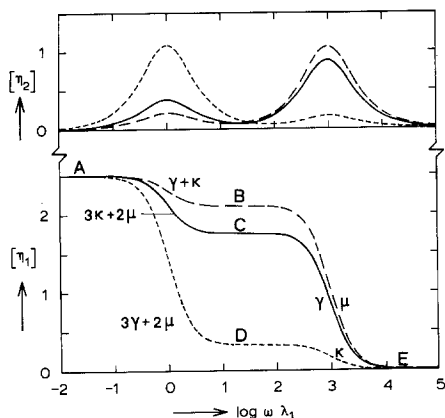


FIG. 2. Intrinsic dynamic viscosity of an emulsion according to model A. $\eta'/\eta = 1$ and $\sigma = \zeta = 0$, κ , μ , and γ are chosen so that $\lambda_1/\lambda_2 = 1000$. Line: $\gamma \gg \mu, \kappa$; short dashes: $\kappa \gg \gamma, \mu$; long dashes: $\mu \gg \gamma, \kappa$. See Table I for the vibration modes of the interface at the plateaus A, B, C, D, and E of $[\eta_1]$.

THE DYNAMIC VISCOSITY OF MODEL B (INTERFACIAL FILM WITH FINITE THICKNESS)

In this model the cell has three regions. In the inner region ($r < l$) all quantities and constants are denoted by primes and in the middle region ($l < r < a$) by double primes. All regions contain Newtonian fluids. At the interfaces $r = a$ and $r = l$ the interfacial tensions are γ and γ' respectively (see Fig. 3).

The boundary conditions [27] at $r = 0$ and [28], [29] at $r = b$ are identical to those of model A. At $r = l$ and $r = a$ continuity of motion and force equilibrium are required. At $r = l$ it is found:

$$\begin{aligned} \frac{1}{7}l^2A'' + \frac{1}{2}l^{-3}B'' + 2C'' - 3l^{-5}D'' &= \frac{1}{7}l^2A' + 2C', \\ \frac{5}{14}l^2A'' + 3C'' + 3l^{-5}D'' &= \frac{5}{14}l^2A' + 3C', \\ i\omega\eta''\{-\frac{1}{7}l^2A'' - 3l^{-3}B'' + 4C'' + 24l^{-5}D''\} &= \frac{1}{7}\{4\gamma l^{-1} - i\omega\eta'\}l^2A' \\ &\quad + 4\{2\gamma l^{-1} + i\omega\eta'\}C', \\ \eta''\{\frac{8}{7}l^2A'' + \frac{3}{2}l^{-3}B'' + 6C'' - 24l^{-5}D''\} &= \eta'\{\frac{8}{7}l^2A' + 6C'\}, \quad [48] \end{aligned}$$

and at $r = a$ it is found:

$$\begin{aligned} \frac{1}{7}a^2(A'' - A) + \frac{1}{2}a^{-3}(B'' - B) + 2(C'' - C) &- 3a^{-5}(D'' - D) = 0, \\ \frac{5}{14}a^2(A'' - A) + 3(C'' - C) &+ 3a^{-5}(D'' - D) = 0, \\ i\omega\{-\frac{1}{7}a^2(\eta''A'' - \eta A) + 3a^{-3}(\eta''B'' - \eta B) &+ 4(\eta''C'' - \eta C) + 24a^{-5}(\eta''D'' - \eta D)\} \\ = \frac{4}{7}\gamma a A + 2\gamma a^{-4}B + 8\gamma a^{-1}C - 12\gamma a^{-6}D, & \\ \frac{8}{7}a^2(\eta''A'' - \eta A) + \frac{3}{2}a^{-3}(\eta''B'' - \eta B) &+ 6(\eta''C'' - \eta C) - 24a^{-5} \\ \times (\eta''D'' - \eta D) = 0. \quad [49] \end{aligned}$$

The homogeneous set of the 10 boundary conditions [28], [29], [48], and [49] in the 11 constants $A', C', A'', B'', C'', D'', A, B, C, D$, and G allow calculation of B/G . By using [26], η^* is again obtained. The expression for η^* contains two relaxation times. The DEC system 10 computer at our university is too small to provide the complete analytical solution. Even the expression for the intrinsic viscosity, although in principle available, is too large to be manageable. Therefore only the expression for the intrinsic viscosity in the first order of the shell thickness d is given in Appendix II. It should be noted here that the validity of Appendix II is limited to very small values of d/a and η''/η , since higher-order terms of d are omitted. For an infinitesimally thin

TABLE I

Interface Shape and Deformation Modes at the Plateaus A, B, C, D, and E of $[\eta_1]$ in Fig. 2

Plateau	Spherical shape	Shear deformation	Compression-extension deformation
A	Yes	No	No
B	No	No	Yes
C	Yes	Yes	Yes
D	No	Yes	No
E	No	Yes	Yes

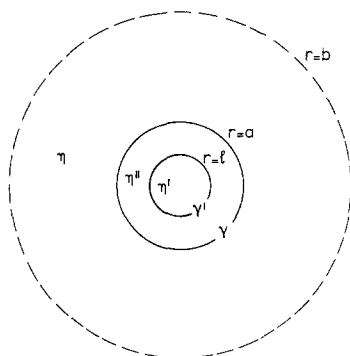


FIG. 3. The finite film cell model (model B).

shell the result at nonzero frequencies is identical to that of Oldroyd's (1) with an interfacial tension $\gamma + \gamma'$, but the steady-state intrinsic viscosity has a value $^{5/2}$, equal to the Einstein value for a suspension of rigid spheres (19). For a finite but thin shell ($d/a < 0.2$) the relaxation times are fairly separated from each other:

$$\lambda_1 = O\left\{\left(\frac{a}{d}\right)^2 a\eta\left(\frac{1}{\gamma} + \frac{1}{\gamma'}\right)\right\}, \quad [50]$$

$$\lambda_2 = O\left\{\frac{a\eta}{\gamma + \gamma'}\right\}. \quad [51]$$

In Fig. 4 it is demonstrated, with numerical results, that the larger relaxation time is influenced by the square of the shell thickness and the smaller of the two interfacial tensions. The smaller relaxation time is influenced by the sum of the two interfacial tensions. An analysis based on Appendix II fails when the film viscosity is high. Numerical results (Fig. 5) show that for high values of η^* the influence of the lower relaxation time on η^* is negligible. In this case, η^* can be approximated by an expression with one relaxation time.

Extremely thick films might be interesting as a model for a swollen micellar solution. As the film thickness d decreases, the influence of the properties of the inner phase, η' , l and γ' , on η^* become negligible (see

Fig. 6). The system can be fully described as a monodisperse emulsion with droplet radius a , interfacial tension γ , internal viscosity η'' , and external viscosity η .

INFLUENCE OF THE PARTICLE CONCENTRATION ON THE VISCOSITIES CALCULATED WITH BOTH MODELS

The influence of the particle concentration on the dynamic viscosity of model A is not easily recognized in the formulae in Appendix I, but on expanding η^* to second order in the concentration, and rewriting the result as

$$(\eta^* - \eta)/\eta\phi = [\eta^*]\{1 + k_H[\eta^*]\phi + \dots\} \quad [52]$$

the following surprisingly simple result for the Huggins coefficient is found:

$$k_H = 2.5/f^3. \quad [53]$$

If the characteristic times are again fairly distinct, the corresponding expressions for the relaxation times λ_n appear to be:

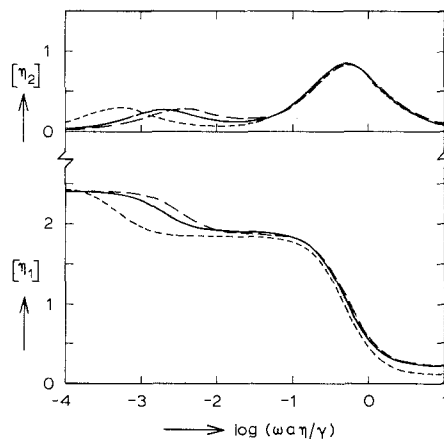


FIG. 4. Intrinsic dynamic viscosity of an emulsion according to model B. Influence of interfacial tensions and film thickness for a thin film. $\eta''/\eta = 2$ and $\eta'/\eta = 1$. Line: $\gamma'/\gamma = 0.1$, $d/a = 0.1$; long dashes: $\gamma'/\gamma = 0.2$, $d/a = 0.1$; short dashes: $\gamma'/\gamma = 0.1$, $d/a = 0.05$.

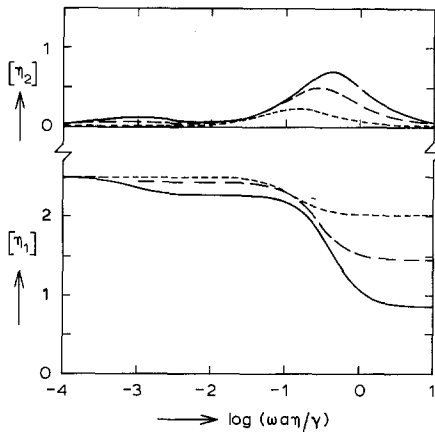


FIG. 5. Influence of a highly viscous thin film on the intrinsic dynamic viscosity of an emulsion according to model B. $\eta'/\eta = 1$, $\gamma'/\gamma = 0.1$, and $d/a = 0.1$. Line: $\eta''/\eta = 10$; long dashes: $\eta''/\eta = 30$; short dashes: $\eta''/\eta = 100$.

$$\lambda_n \approx \lambda_{n,0} \{1 + 2\phi k_H [\eta_2]_{(\omega = \lambda_{n,0}^{-1})}\},$$

$$n = 1, 2. \quad [54]$$

For model B exact results for higher concentrations are not available. The validity of [53] was therefore checked numerically. Within the wide ranges of parameter values that were investigated, no deviations from [53], beyond rounding-off errors, were observed.

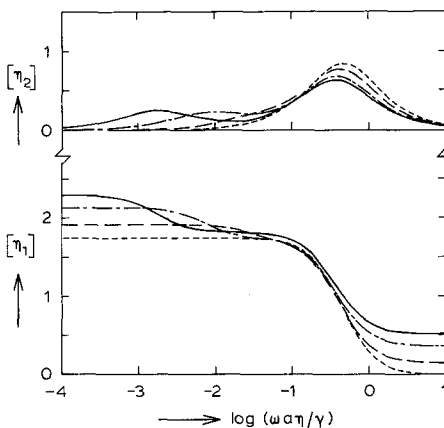


FIG. 6. Influence of increasing the film thickness on the intrinsic dynamic viscosity of an emulsion according to model B. $\eta''/\eta = 2$, $\eta'/\eta = 1$, $\gamma'/\gamma = 0.1$. (—) $d/a = 0.1$; (---) $d/a = 0.2$; (- - -) $d/a = 0.4$; (- · -) $d/a = 0.8$.

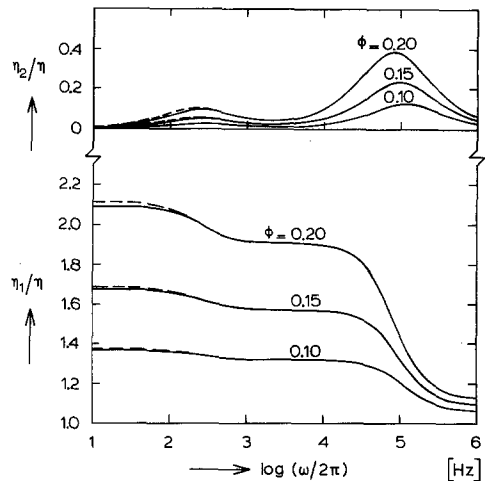


FIG. 7. Comparison of the dynamic viscosities of two emulsions according to model A and model B, for $\phi = 0.10$, $\phi = 0.15$, and $\phi = 0.20$. Both models use $a = 0.5 \times 10^{-7}$ m, $\eta = 10^{-3}$ N sec m^{-2} , $\eta' = 0.5 \times 10^{-3}$ N sec m^{-2} , and $f = 1.111$. Long dashes (model A): $\gamma = 1.1 \times 10^{-4}$ N m^{-1} , $2\mu + 3\kappa = 1.02 \times 10^{-6}$ N m^{-1} , $\zeta = 0.59 \times 10^{-10}$ N sec m^{-1} , and $\sigma = 0.12 \times 10^{-9}$ N sec m^{-1} . Line (model B): $\gamma = 10^{-4}$ N m^{-1} , $\gamma' = 10^{-5}$ N m^{-1} , $\eta'' = 10^{-2}$ N sec m^{-2} , and $d = 0.5 \times 10^{-8}$ m.

Both model A and model B contain many interfacial parameters, the values of which may not be determined from other experiments. Moreover it is possible to adjust the parameters of model B in such a way that the intrinsic viscosity of this model almost coincides with those of the three modes of model A over the complete frequency range. In our models second-order effects in the particle concentration are completely determined by the intrinsic viscosity and the correction factor f . It is thus improbable that experiments with varying concentration are conclusive for the choice between different sets of interfacial parameters (see Fig. 7).

DISCUSSION

The two models considered lead to a relation between a set of parameters used to describe the interfacial mechanics and the dynamic viscosity of an emulsion. As shown

in the previous section, experimental data on the dynamic viscosity of an emulsion allow interpretations in terms of both sets of interfacial parameters.

The two-dimensional viscoelasticity of model A is compatible with the concept of a transversely rigid shell (20). In this concept the film thickness remains constant and upon deformation all film elements orientated normal to the interface maintain their orientation due to the anisotropy of the interfacial layer. According to Maru *et al.* (21), two mechanisms giving rise to an interfacial viscoelasticity can be discerned. The "apparent" dilatational viscoelasticity is brought about by compositional changes, and the "intrinsic" viscoelasticity is related to the forces between the molecules in the interfacial layer. As specific interactions between the molecules in the interfacial layer are likely to play a role in the formation of emulsions, we may expect that the elastic parts of the intrinsic viscoelasticity are not always negligible. Apparent dilatational viscoelasticity is determined by the surface elasticity:

$$E_0 = - \frac{d\gamma}{d \ln \Gamma}, \quad [55]$$

and by two relaxation mechanisms which are the exchange of surface active materials between bulk liquid(s) and the interfaces,

and reorientation processes of adsorbed molecules (22). If the deformation rate is so fast that these relaxation processes no longer take place, only the Gibbs elasticity remains. In our opinion the distinction between intrinsic and apparent viscoelasticity is somewhat artificial, because molecular interaction processes, causing intrinsic viscoelasticity, are partly coupled to processes causing apparent viscoelasticity. Obviously model A is to some extent appropriate in the case of a monomolecular interfacial film. Model B was inspired by the concept of curvature of a microemulsion film as reviewed by Prince (23). In his concept the curvature of microemulsion droplets is caused by the difference in surface pressure between the hydrophobic and hydrophilic sides of the interfacial film. Model B does not allow for compositional changes of the interfacial film. Furthermore, the shell being treated as a continuum, it can only be realistic if the molecules in the film are small with respect to the film thickness.

As the formal predictions of the two models, i.e., two relaxation and two retardation times, are the same, a choice between these models can only be made on the basis of physical arguments, like those indicated above. In a following paper we shall use the present models for the interpretation of the viscoelastic behavior of (micro)emulsions in the kHz region.

APPENDIX I: SOLUTION FOR η^* IN MODEL A

Define:

$$\begin{aligned} E &= \eta'/\eta; & R &= b/a; & M &= \mu/\gamma; & K &= \kappa/\gamma; \\ Z &= \zeta/(a\eta); & S &= \sigma/(a\eta); & H &= ia\eta\omega/\gamma. \end{aligned} \quad [A1.1]$$

Then

$$\frac{\eta^* - \eta}{\eta} = \phi \frac{\alpha_0 + \beta_0 H + \gamma_0 H^2}{\alpha'_0 + \beta'_0 H + \gamma'_0 H^2}, \quad [A1.2]$$

where

$$\begin{aligned} \alpha_0 &= A_{10}R^{10} + A_3R^3; & \alpha'_0 &= A'_{10}R^{10} + A'_7R^7 + A'_5R^5 + A'_3R^3 + A'_0; \\ \beta_0 &= B_{10}R^{10} + B_3R^3; & \beta'_0 &= B'_{10}R^{10} + B'_7R^7 + B'_5R^5 + B'_3R^3 + B'_0; \\ \gamma_0 &= C_{10}R^{10} + C_3R^3; & \gamma'_0 &= C'_{10}R^{10} + C'_7R^7 + C'_5R^5 + C'_3R^3 + C'_0. \end{aligned} \quad [A1.3]$$

By using

$$\begin{aligned}\bar{A} &= 3K + 2M + 2KM, \\ \bar{B} &= 24S + 20E + 16Z + 23KE + 16KZ + 16SM + 26EM, \\ \bar{C} &= 23SE + 16SZ + 19E^2 + 26EZ,\end{aligned}\quad [\text{A1.4}]$$

it is found:

$$\begin{aligned}A_3 &= -80\bar{A}; & A_{10} &= 80\bar{A}; & A'_0 &= 32\bar{A}; & A'_3 &= -200\bar{A}; \\ A'_5 &= 336\bar{A}; & A'_7 &= -200\bar{A}; & A'_{10} &= 32\bar{A};\end{aligned}\quad [\text{A1.5}]$$

and

$$\begin{aligned}B_3 &= -10(\bar{B} - 20 - 23K - 26M); & B_{10} &= 10(\bar{B} + 8 - 16K + 16M); \\ B'_0 &= 4(\bar{B} - 20 - 23K - 26M); & B'_3 &= -25(\bar{B} - 8 + 4K + 25M); \\ B'_5 &= 42(\bar{B} - 8K + 24M); & B'_7 &= -25(\bar{B} + 8 - 16K + 16M); \\ B'_{10} &= 4(\bar{B} + 20 + 32K + M);\end{aligned}\quad [\text{A1.6}]$$

and

$$\begin{aligned}C_3 &= -10(\bar{C} - 23S - 38E - 26Z + 19); & C_{10} &= 10(\bar{C} - 16S - 3E + 16Z - 16); \\ C'_0 &= 4(\bar{C} - 23S - 38E - 26Z + 19); & C'_3 &= -25(\bar{C} + 4S - E + 24Z - 18); \\ C'_5 &= 42(\bar{C} - 8S - 3E + 24Z - 16); & C'_7 &= -25(\bar{C} - 16S - 3E + 16Z - 16); \\ C'_{10} &= 2(2\bar{C} + 64S + 89E + 48Z + 48).\end{aligned}\quad [\text{A1.7}]$$

APPENDIX II: APPROXIMATE SOLUTION OF $[\eta^*]$ IN MODEL B

Define:

$$\begin{aligned}E &= \eta'/\eta; & V &= \eta''/\eta; & H &= ia\eta\omega/\gamma; \\ F &= \gamma'/\gamma; & D &= d/a.\end{aligned}\quad [\text{A2.1}]$$

Then:

$$[\eta^*] = \frac{\alpha_0 + \beta_0 H + \gamma_0 H^2}{\alpha'_0 + \beta'_0 H + \gamma'_0 H^2}, \quad [\text{A2.2}]$$

where

$$\begin{aligned}\alpha_0 &= 5FD^2\{96V + (160E - 17856V + 64)D\}; \\ \alpha'_0 &= 2FD^2\{96V + (160E - 17856V + 169)D\}; \\ \beta_0 &= 40(F + 1)(\frac{3}{2}E + 1)V + 5\{-(3748 + 3740F)EV + 40(F + 1)E \\ &\quad + 88(F + 1)V^2 - (1504 + 1568F)\}D; \\ \beta'_0 &= 40(F + 1)(E + 1)V + 2\{-(3748 + 3740F)EV + 100(F + 1)E \\ &\quad + 88(F + 1)V^2 - (3760 + 3728F)\}D; \\ \gamma_0 &= 5\{19E^2V - 3EV - 16V + D(-3572E^2V + 38E^2 + 95EV^2 \\ &\quad + 543EV - 80E - 32V^2 - 3008V)\};\end{aligned}$$

$$\gamma'_0 = 2\{19E^2V + 89/2EV + 24V + D(-3572E^2V + 95E^2 + 95EV^2 - 16717/2EV + 120E + 120V^2 - 4512V)\}. \quad [A2.3]$$

APPENDIX III: NOTATION

		t	Time
		\mathbf{T}	Stress tensor
a	(Outer) radius of the emulsion droplets	$T\langle rr \rangle, T\langle r\theta \rangle$	Stress-tensor components in spherical coordinates
A	Frequency-dependent coefficient of the flow field	T^p	Scalar in the expression of Σ^p
b	Cell radius	u	Physical component of the radial velocity
B	Frequency-dependent coefficient of the flow field	v	Physical component of the tangential velocity
C	Frequency-dependent coefficient of the flow field	\mathbf{v}	Velocity vector
d	Thickness of the interfacial layer (model B)	\mathbf{v}^0	Velocity vector at the sample boundaries
D	Frequency-dependent coefficient of the flow field	V	Total volume
\mathbf{D}	Rate of strain tensor	∂V_c	Cell surface
\mathbf{E}	Surface strain tensor	∂V_p	Particle surface
E_0	Surface elasticity	∂V_s	Sample surface
f	Correction factor	γ, γ'	Interfacial tensions
$f_{1\kappa}, f_{2\kappa}, f_{1\mu}, f_{2\mu}, f_{1\gamma}, f_{2\gamma}$	Dimensionless functions of order unity	Γ	Surfactant surface excess
$g, g_\kappa, g_\mu, g_\gamma$	Functions of R pertinent to η^*	ζ	Dynamic surface-shear viscosity
G	Constant proportional to the applied rate of strain	η	Solvent viscosity
i	$= \sqrt{-1}$	η'	Droplet viscosity
k	Particle index	η''	Interfacial viscosity (model B)
k_H	Huggins coefficient	η^*	$= \eta_1 - i\eta_2$, complex emulsion viscosity
l	Inner radius of the emulsion droplets (model B)	η_{spec}^*	$= \eta^*/\eta - 1$
n	Integer	$[\eta^*]$	$= \lim_{\phi \rightarrow 0} \eta_{spec}^*/\phi$
\mathbf{n}	Unit-normal vector	$\bar{\eta}$	Steady-state viscosity
p	Pressure	θ	Spherical coordinate
p_0	Hydrostatic pressure	κ	Dynamic area elasticity
\mathbf{P}	Surface-stress tensor	λ_1, λ_2	Relaxation times
P_2	Legendre polynomial of the second order	$\lambda_{n,0}$	Relaxation time for $\phi \rightarrow 0$
P'_2	$= dP_2/d\theta$	μ	Dynamic surface-shear elasticity
r	Spherical coordinate	σ	Dynamic area viscosity
\mathbf{r}	Position vector	Σ^p	Part of $\langle \mathbf{T} \rangle$ due to the particles
R	$= b/a$	τ_1, τ_2	Retardation times
S	Area	ϕ	Volume fraction
		ω	Angular frequency

Superscripts

none

Quantity pertinent to region $a < r < b$

'

Quantity pertinent to region $r < a$ (model A) or $r < l$ (model B)

"

Quantity pertinent to region $l < r < a$ (model B)

□

Deviatoric part of a tensor

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