Effect of aggregation processes on the viscosity of suspensions

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This paper examines the effect of aggregation processes on the viscosity of dilute solutions in which the individual clusters contribute additively to the viscosity. The increment in the viscosity is shown to be a nonlinear function of the concentration by weight of the suspended particles. A universal expression for this functional dependence is derived for a broad range of aggregation processes. An example is discussed in which an aggregation process leads to a different (critical) concentration dependence of the viscosity of the suspension. The results derived here also apply to polymer solutions.

INTRODUCTION

Various properties of dilute solutions are usually determined by additive contributions from the individual particles. As a result, the concentration dependence is usually linear. If, however, the particles in the system undergo an aggregation process (and they may do so even at low concentrations), the situation is fundamentally different: The contributions from the individual particles are not additive, so the concentration dependence is nonlinear. Since universal characteristics (e.g., a fractal dimension) exist for various aggregation processes in many problems of physical interest, one might expect that under certain conditions a deviation from linearity in a corresponding concentration dependence would also be of a universal nature. In the present paper we use the example of the concentration dependence of the viscosity to study the conditions under which the effect of aggregation processes on the concentration dependence is universal. We determine this functional dependence.

DISTINCTIVE FEATURES OF SUSPENSIONS WITH AGGREGATION

The contribution to the viscosity of a suspension from the suspended particles is found from the familiar expression[1]

$$\Delta\eta \propto \eta_0 v_0 c, \qquad (1)$$

where η_0 is the viscosity of the liquid in which the particles are suspended, v_0 is the average volume of one particle, and c is the concentration of particles.

Expression (1) is valid if the contribution of the particles of the suspension to the viscosity are additive. In this case the quantity c is understood as the number density of particles in the suspension (the number of particles suspended in a unit volume of the liquid). Actually, what is measured is the concentration by weight of the particles in the suspension. The concentration by weight is proportional to the number density only in the absence of aggregation processes. Predictions regarding the rheological properties of suspensions are based on viscometric measurements carried out for highly dilute suspensions (i.e., in practice, only the viscosity contributions from the individual particles are taken into account) and expression (1).

Expression (1) is usually refined by taking into account the hydrodynamic interaction of the particles. This interaction tends to increase the viscosity of the suspension,[2] although mutual screening can weaken this effect in certain cases.[3] We are interested here in the effect of aggregation processes, which occur at arbitrarily low concentrations of the suspended particles under certain conditions, if the hydrodynamic interaction of the particles can be ignored.

In suspensions with aggregations (if the penetrability of the aggregations is assumed negligible), aggregations of the particles rather than the individual particles contribute to the viscosity. The volume of these aggregations depends on not only the number n of particles making up these aggregations, but also the density with which these particles are packed. This density is characterized by the fractal dimension D:

$$v(n) = v_0 n^{3/D}. \qquad (2)$$

According to Ref. 1, the contribution to the viscosity of a suspension from clusters of n particles is

$$\Delta\eta(n) \propto \eta_0 v(n) u(n), \qquad (3)$$

where $u(n)$ is the number density of clusters consisting of n particles. The densities $u(n)$ are related to the concentration by weight, c, by the normalization condition

$$\sum_n n u(n) = c/m_0 = c_0, \qquad (4)$$

where m_0 is the mass of one particle.

The "size" distribution of the clusters, $u(n)$, which we need to know in order to calculate the contributions to the viscosity from clusters of all types, can be found by solving the Smoluchowski equation, which describes the kinetics of a reversible aggregation process:[4]

$$\frac{\partial u(n)}{\partial t} = \frac{1}{2}\sum_{m<n} p(m, n-m) u(m) u(n-m)$$

$$- \sum_{m \geqslant 1} p(n, m) u(n) u(m)$$

$$- \sum_{m<n} q(n, m) u(n) + 2\sum_{m>n} q(m, n) u(m). \qquad (5)$$

Here $p(n,m)$ is the rate constant for the coalescence of clusters of n and m particles into a cluster of $n+m$ particles; $q(n,m)$ is the rate constant for the breakup of a cluster of n particles into clusters of m and $n-m$ particles.

UNIVERSAL CONCENTRATION DEPENDENCE OF THE VISCOSITY

For the simple case in which the rate constants p and q are independent of the dimensions of the clusters, a solution of Eqs. (5) (more precisely, a solution of a continuous integral approximation of these equations) is known:[4]

$$u(n,t) = \frac{q}{p} \, \text{cth}^2[(c_0pq)^{1/2}t] \exp\{-n(q/pc_0)^{1/2} \, \text{cth}[(c_0pq)^{1/2}t]\}.$$

(6)

At times $t \gg (c_0pq)^{-1/2}$, this solution becomes the steady-state distribution

$$u(n) = \frac{p}{q} \exp\left[-n\left(\frac{q}{pc_0}\right)^{1/2}\right].$$

(7)

Summing the contributions to the viscosity from clusters of all types [more precisely, integrating (3)], and using (2) and (7) (i.e., assuming that the size distribution of the clusters is in a steady state), we find

$$\Delta\eta(n) \propto \eta_0 v_0 (p/q)^{(3-D)/2D} c_0^{(3+D)/2D}.$$

(8)

In the limit $p \to 0$ (no aggregation), we cannot take the continuous limit of n in the derivation of (8). If we use $u(n) = \delta_{n,1}$ as $p \to 0$ in the expression for the situation before the limit is taken, we find our original functional dependence, (1). We will not discuss the case $q = 0$ here.

As was mentioned above, the fractal dimension of aggregations or clusters is a universal characteristic, specifically, $D = 1.76 \pm 0.01$ (Ref. 5; or $D = 1.77$ according to the data in Ref. 4) for a wide range of aggregation processes. This value of D was found through numerical simulation of cluster-cluster aggregation processes[6-9] in which it was established that the fractal dimension D of the aggregations formed in the process does not depend on the relations among the rate constants for the coalescence of clusters of different size. A theoretical foundation for this fact was constructed in Ref. 10. On the other hand, the universal nature of D does not mean that the size distribution of the clusters, $u(n)$, is universal, so we cannot at this point conclude that expression (8) is universal. The reason is that the integral equation describing the steady-state size distribution of the clusters established as the result of a reversible aggregation process with rate constants which depend on the sizes of the clusters,

$$\frac{1}{2}\int_0^n p(y, n-y)u(y)u(n-y)dy - u(n)\int_0^\infty p(n,y)u(y)dy$$

$$-u(n)\int_0^n q(n,y)dy + 2\int_0^\infty q(n,y)u(y) = 0,$$

(9)

supplemented with a continuous approximation of condition (4),

$$\int_0^\infty yu(y)du = c_0,$$

may have solutions other than (7) for arbitrary $p(x,y)$ and $q(x,y)$. Furthermore, Eq. (9) can be solved only for certain special types of rate constants p and q (Ref. 11). In several cases of physical interest, the difficulty which arises can be

overcome, and the functional dependence of interest can be derived without solving Eq. (9). Specifically, if the rate constants for aggregation processes, $p(x,y)$ and $q(x,y)$ have the property of homogeneity,

$$p(x, y) = \lambda^\alpha p(x/\lambda, y/\lambda), \quad q(x, y) = \lambda^\beta p(x/\lambda, y/\lambda), \quad (10)$$

then it follows from (9) that the function

$$\varphi(n) = \lambda^{\alpha-\beta} u(\lambda n)$$

(11)

also satisfies Eq. (9), and the normalization condition (4) for the function φ becomes

$$\int_0^\infty y\varphi(y)dy = c_0 \lambda^{\alpha-\beta-2}.$$

(12)

We choose $\lambda = c_0^{1/(2-\alpha+\beta)}$; i.e., we assume that $\varphi(n)$ is normalized and independent of c_0. The distribution $u(n)$ then depends on the concentration by weight c, in the following way:

$$u(n) = (c/m_0)^{(\alpha-\beta)/(2-\alpha+\beta)}\varphi[(m_0/c)^{1/(2-\alpha+\beta)}n].$$

(13)

Integrating (3) over n, and using (2) and (13), we find

$$\Delta n \propto \eta_0 v_0 c^{[3+D(1+\alpha-\beta)]/(2+\alpha-\beta)D}.$$

(14)

It was shown in Ref. 11 that in essentially all cases of physical interest the coefficients $p(x,y)$ have the necessary property of homogeneity. If we assume that the interaction responsible for the decay of the clusters is the same as that responsible for their formation, then the coefficients $q(x,y)$ also have this property, and the homogeneity indices α and β are the same.

In deriving (14) we ignored the effect of the shape of the clusters on the viscosity of the suspension. As in expression (1), however, incorporating this shape effect changes nothing except the numerical factor (the proportionality coefficient) in (14), and we are now interested in that factor.

For a wide range of aggregation processes, we thus have a universal functional dependence of the incremental viscosity of suspensions with aggregation on the concentration by weight of these suspensions (line a in Fig. 1):
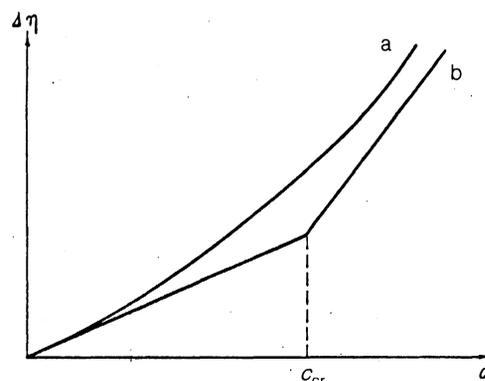
$$\Delta\eta \propto c^{1.36 \pm 0.01}.$$

(15)

FIG. 1. Theoretical behavior of the viscosity increment as a function of the concentration of the suspension. a—Reversible aggregation process with homogeneous rate constants for the reaction; b—system of clusters of three types. Here c_{cr} is the critical concentration for the onset of cluster formation.
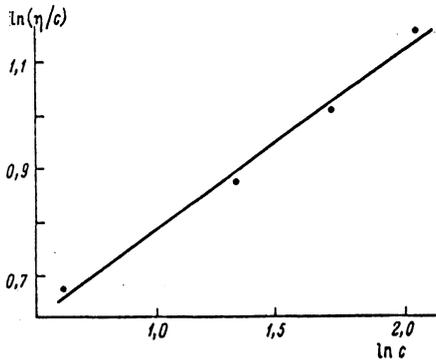
FIG. 2. Experimental $\ln(\eta/c) = k \ln c$ dependence (the points) along with the scaling law $\Delta\eta \propto c^{1+k}$.

The experimental data in the literature support this result. For example, the viscosity of cellulose solutions (in which aggregation processes occur particularly intensely) was reported as a function of the shear stress in Ref. 12 for various concentrations by weight of the cellulose. An extrapolation of those experimental data to a zero shear stress leads the following concentration dependence of the viscosity (Fig. 2):

$$\Delta\eta \propto c_0^{1.36 \pm 0.01}. \qquad (16)$$

This result is in excellent agreement with (15).

EXAMPLE OF A DEVIATION FROM THE UNIVERSAL BEHAVIOR

As was mentioned above, the concentration dependence of the viscosity in (15) is of universal applicability to a wide range of aggregation processes for which the rate constants have homogeneity property (10). Clearly, if the processes by which clusters decay are governed not only by an interaction between the particles of the suspension but also by the external conditions, then the homogeneity index β for the rate constants $q(x,y)$ may not be the same as the index α for the constants $p(x,y)$, or the homogeneity property may not hold at all for the constants $q(x,y)$. As a result, the concentration dependence of the viscosity of the suspension may be markedly different from (15).

As an example we consider the following model aggregation process. Clusters of only three types can exist in the system: small clusters (elementary clusters), intermediate clusters, consisting of two elementary clusters, and large clusters, consisting of three elementary clusters. Larger clusters do not form because of strong external effects. We also ignore the direct formation of an intermediate cluster from two elementary clusters. The kinetic equations describing this aggregation process are then

$$\partial c_1/\partial t = -p_2 c_1 c_2 - p_3 c_1 c_3 + 2 q_2 c_2 + q_3 c_3, \qquad (17)$$
$$\partial c_2/\partial t = -p_2 c_1 c_2 + 2 p_3 c_1 c_3 - q_2 c_2 + q_3 c_3,$$

$$\partial c_3/\partial t = p_2 c_1 c_2 - p_3 c_1 c_3 - q_3 c_3, \quad c_1 + 2 c_2 + 3 c_3 = c/m_1 = c_0.$$

Here c_1, c_2, and c_3 are the concentrations of the small, intermediate, and large clusters; $p_{2,3}$ and $q_{2,3}$ are the coefficients for the coalescence and decay of clusters; c is the concentration by weight of the particles in the system; and m_1 is the mass of one particle.

Skipping over the detailed analysis of the properties of this system, we would like to call attention to one remark-

able property: There is a threshold value of the concentration for the occurrence of aggregation processes in this system. Depending on the value of c_0, the system can have the following equilibrium states:

$$c_1 = c_0, \quad c_2 = c_3 = 0, \quad c_0 \leqslant c_{cr}, \qquad (18a)$$

$$c_1 = c_{cr}, \quad c_2 = \frac{c_1(c_0 - c_1)}{2 c_1 + q_2/p_3}, \quad c_3 = \frac{q_2 c_2}{p_2 c_1}, \quad c_0 \geqslant c_{cr}, \qquad (18b)$$

where

$$c_{cr} = \frac{1}{2}\frac{q_2}{p_2}\left[1 + \left(1 + \frac{4 q_3 p_2}{q_2 p_3}\right)^{1/2}\right].$$

According to our arguments, the concentration dependence of the viscosity is then

$$\Delta\eta \propto \begin{cases} \eta_0 v_1 c_0, & c_0 \leqslant c_{cr}, \\ \eta_0 c_{cr} v_1 + \frac{1}{2}(c_0 - c_{cr})\dfrac{v_2 c_{cr} + v_3 q_2/p_3}{c_{cr} + 3 q_2/2 p_3}, & c_0 \geqslant c_{cr}. \end{cases} \qquad (19)$$

Here $v_{1,2,3}$ are the volumes of respectively small, intermediate, and large clusters. If the packing of the particles in the clusters is not dense (i.e., if the inequalities $v_1 < v_2/2 < v_3/3$ hold), then the concentration dependence in (19) is nontrivial (line b in Fig. 1). If instead the packing is dense ($v_1 = v_2/2 = v_3/3$), concentration dependence (19) becomes trivial and the same as (1).

VISCOSITY OF POLYMER SOLUTIONS

The results derived above for suspensions with aggregation can be extended to polymer solutions, primarily because of the physical similarity of these systems. According to simple scaling models, the contribution of polymer chains to the viscosity of a monodisperse polymer solution is[13]

$$\Delta\eta \propto \eta_0(c/N) R^3, \qquad (20)$$

where N is the degree of polymerization, and R is the hydrodynamic radius of a polymer ball. For flexible-chain linear polymers we would have $R \propto N^{1/D}$, with $D = 2$ in θ solvents and $D = 5/3$ in good solvents. For a polydisperse polymer solution, N and R can be interpreted as respectively the average degree of polymerization and the average radius of the polymer balls. Since the polymerization process is an irreversible aggregation process (particularly in the regime of polycondensation) in which the set of reaction rate constants has the property of homogeneity,[11] the distribution of chains with respect to degree of polymerization has a property similar to (13), as was shown above:

$$u(n) = \varphi(n c^{-1/2}). \qquad (21)$$

Calculating

$$\overline{R^3} = r_0^3 \int_0^\infty n^{3/D} u(n)\,dn \Big/ \int_0^\infty u(n)\,dn,$$

$$\overline{N} = \int_0^\infty n u(n)\,dn \Big/ \int_0^\infty u(n)\,dn,$$

and using (21), we find

$$\Delta\eta \propto \eta_0 r_0^3 c\left[c^{(3+D)/2D} \int_0^\infty x^{3/D}\varphi(x)dx \right]\Big/$$

$$c\int_0^\infty x\varphi(x)dx \propto \eta_0 r_0^3 c^{(3+D)/2D}. \tag{22}$$

This result is exactly the same as (14) in the case $\alpha = \beta$.

Replacing (20) by the more accurate relation[13]

$$\Delta\eta \propto \eta_0(c/N) r_0^3 (R/r_0)^\xi, \tag{23}$$

we find

$$\Delta\eta \propto \eta_0 r_0^3 c^{(\xi + D)/2D}, \tag{24}$$

in which the functional dependence is of the same nature as in (14) (here ξ is a dynamic index which takes on values 2.8–2.9 < 3). In particular, for a good solvent ($D = 5/3$) and $\xi = 2.85$ we have $\Delta\eta \propto c^{1.351}$, which is essentially the same as (15).

CONCLUSION

We would like to point out yet another distinctive feature of an aggregation process: As a result of the cluster formation, the suspension may reach the gel point, even if the relative volume occupied by the suspended particles is much smaller than unity. In the course of an irreversible aggregation, and with a loose packing of the particles in clusters, the gel point is reached at an arbitrarily low concentration of the suspension.[5] In the case of a reversible aggregation, the system reaches the gel point only if the concentration is above a threshold. A gel forms in the system if the volume per cluster is comparable in magnitude to the volume of the cluster itself. From this condition we find an estimate of the gel-formation concentration:

$$c_{gel} \propto \left[v_0 \int_0^\infty x^{3/D}\varphi(x)dx \right]^{-2D/(3+D)} \tag{25}$$

Clearly, as the concentration of the suspension approaches c_{gel}, our original expression, (1), becomes inapplicable, so all the subsequent conclusions are also inapplicable. The range of applicability of universal functional dependence (15) is thus limited by the condition $c_0 \ll c_{gel}$.

On the basis of this analysis we can assert with confidence that aggregation processes which occur in suspensions may lead to significant changes in the viscosity of the suspensions. In certain cases (with $c \sim c_{gel}$), the rheological properties of the suspension may change in a fundamental way.

If the polymer balls in a monodisperse polymer solution undergo aggregation, there may also be a significant change in the viscosity of the solution, since the monodisperse polymer solution becomes a polydisperse solution as a result of the aggregation. The effect of aggregation processes on the viscosity of a polydisperse solution requires separate study.

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Translated by D. Parsons