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Coagulation in a Shear Field Generated by Stirring in a Cylindrical Vessel

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The coagulation of aqueous ZnO dispersions is investigated at various shear rates, in a shear field generated by stirring in a cylindrical vessel, and at different ζ potential values. Laser Doppler anemometry measurements permitted the construction of a model of the shear field by which average shear rates could be calculated. At low shear rates (≤ 200 sec⁻¹), the experimental capture efficiencies are independent of the ζ potential (−20 ζ > −32 mV). At larger shear rates, the capture efficiencies rise with increasing ζ, if the absolute value of the ζ potential is ≤ 30 mV, due to inertial pseudoforces. These are more effective for irregular than for spherical particles, probably because the penetration of the last liquid film between two particles is easier at edges than at smooth surfaces. This effect, however, can be counteracted by electrostatic repulsion. © 1985 Academic Press, Inc.

INTRODUCTION

Recently, a revival of interest in coagulation in a shear field ("orthokinetic coagulation") has occurred. This is distinguished from coagulation caused by Brownian motion ("perikinetic coagulation"). Theoretically, coagulation under influence of shear was treated already by von Smoluchowski (1). On the assumption of rectilinear approach of two equal-sized spherical particles of radius b his equation reads

$$\left(\frac{d \ln n}{dt}\right)_{\text{rectilinear}} = \frac{2}{3} \gamma n(2b)^3,$$  \[1\]

with n = the number of particles per unit volume and \(\gamma\) = the shear rate. For the case of two equal-sized spherical particles in a flow field with constant \(\gamma\), Batchelor and Green (2) calculated the trajectories for two approaching particles, taking into account hydrodynamic interaction. van de Ven and Mason (3) incorporated attraction and electrostatic repulsion into the trajectory equations. They found, by numerical solution of these equations, values for the capture efficiency \(\alpha_0\). Its definition can be written as

$$\alpha_0 = \frac{(d \ln n/dt)_{\text{exp}}}{(d \ln n/dt)_{\text{rectilinear}}},$$  \[2\]

\(\alpha_0\) was calculated by van de Ven and Mason as a function of \(\gamma\), for different values of the double layer potential \(\psi_d\).

In the absence of electrostatic repulsion, \(\alpha_0\) was found to decrease with increasing \(\gamma\), while the influence of repulsion was rather complex: only at intermediate values of the parameter

$$C_A = A/(36\eta_0\gamma b^3),$$  \[3\]

where \(A\) = the Hamaker constant and \(\eta_0\) = the viscosity of the medium; a distinct influence of electrostatic repulsion on \(\alpha_0\) was found.

Thus, \(\gamma\) enters into orthokinetic coagulation theory both as primary cause of collisions (Eq. [1]) and as hydrodynamic friction force (Eq. [3]).

Several differences between the starting points of this theory and experimental conditions limit the applicability of the theory to coagulation experiments: the absence of inertial pseudoforces, the restriction to spherical particles, and the limitation to well-defined shear fields. In a previous paper from
our laboratory (4), the former two restrictions were abandoned: the coagulation of irregular particles (quartz), showing a distinct density difference with the suspension medium, was investigated in a reasonably well-defined shear field between two coaxial cylinders. Some differences with the theoretical productions were observed: (a) at low $\gamma$ values, $a_0$ was considerably smaller than the theoretical value; and (b) $a_0$ was found to decrease with increasing $\gamma$ for particles of about 1 $\mu$m hydrodynamic diameter, in accordance with the theory, but for particles of about 5 $\mu$m the reverse was found.

In the present investigation, these results are extended by studying the coagulation of aqueous ZnO dispersions in a stirred cylindrical cuvette. The present paper is devoted to the influence of shear rate and of electrolyte (KCl) concentration; the effect of different electrolytes and of pretreatment of the ZnO by heating in various atmospheres will be treated in a separate paper.

EXPERIMENTAL

Materials

ZnO, ex Merck, pro analysis; surface area (BET, nitrogen adsorption): 3.66 m$^2$ g$^{-1}$. No hysteresis was noted in the adsorption experiment with increasing or decreasing N$_2$ pressure. The particle size distribution was determined by means of a Sedigraph 5000D Particle Size Analyzer, in an aqueous solution of Vanisisperse CB (4 mg per 100 ml); further additions of vanisperse did not change the measured size distribution. The particle size distribution is characterized by: 20 mass% $< 0.46$ $\mu$m hydrodynamic diameter (h.d.); 40 mass% $< 0.60$ $\mu$m h.d.; 60 mass% $< 0.72$ $\mu$m h.d.; 80 mass% $< 0.93$ $\mu$m h.d.

The sample consists of hexagonal prisms (Fig. 1). Integration of the number fraction curve showed that 1 g ZnO contains $3.3 \times 10^{12}$ particles. A height/hexagon side ratio of 0.25 gives the best fit between the surface area calculated from the particle size distribution, and the BET adsorption surface area.

The ZnO was found, in agreement with data reported by other investigators on similar samples (5–12), to contain both “water” and “CO$_2$.”

The “water” content (hydroxyl groups) determined by Morimoto and Naono’s method (8) amounts to $8.4 \pm 0.3$ OH groups/nm$^2$.

The “CO$_2$” content (carbonate groups) was determined in the same apparatus with a 1 M HCl solution replacing the methyl magnesium iodide reagent employed in the H$_2$O determination. It amounts to 1.7 carbonate groups/nm$^2$.

All other chemicals were ex Merck, pro analysis.

METHODS

Preparation of the Dispersions

Electrolyte solutions were prepared under a flow of nitrogen and transferred to a glove box that was freed of CO$_2$ by a continuous flow of nitrogen. The air in the glove box was pumped continuously over Carbosorb.

An initial suspension was prepared by adding 0.4 g ZnO to 100 ml KCl solution (concentration adjusted to the value ultimately required) of pH 8.70. The pH was adjusted by KOH or HCl solution when necessary. When changes in the pH became less than 0.001 pH unit per minute, the suspension was dispersed by ultrasonic treatment using a Sonicor SC-50-22 apparatus, during 30 min. Afterward, the pH of the suspension was measured and corrected if necessary. This procedure was repeated until the pH did not change any more on sonication. Usually four dispersion procedures were required to obtain a stable pH.

A 0.8-ml volume of this initial suspension was mixed with electrolyte solution and HCl or KOH solutions, and the total volume made up to 25 ml. In this way, a series of dispersions was obtained with equal electrolyte concentration but varying pH. A slave magnet was added, the flask was closed, and the suspension was stirred vigorously. The
flask was stored in the dark until measurement next day. The pH was measured, and 10 ml of the suspension and the slave magnet were transferred to a cylindrical cuvette (diameter 15 mm), fitting into the light extinction apparatus. The remainder of the suspension was used for electrophoresis measurements.

**Light Extinction vs Time Measurements**

The suspension in the cuvette was subjected to ultrasonic treatment, at 25 ± 0.1°C, for 30 min. The tube was placed into a Vitratron MPS spectrophotometer provided with a master magnet, with adjustable stirring speed (200–1200 rpm). The light extinction then was registered as a function of time. Absence of any influence of handling of the suspension between ultrasonic treatment and light extinction measurement was checked by varying the handling time. On subjecting a coagulated suspension to redispersion and renewed coagulation, the coagulation proved to be reproducible.

**Electrophoresis**

Electrophoresis measurements were performed in a Rank Brothers Mark II microelectrophoresis apparatus with a flat cell and platinized platinum electrodes. The ζ potentials were calculated according to Wiersema (13), using an average particle radius of 188 nm.

**Flow Velocity Measurements**

In dummy experiments with the same cuvette and stirring device, average velocities at several points were determined by Laser Doppler Anemometry (14), using a DISA 55X Modular LDA system with a Spectra Physics He–Ne laser (632 nm, 35 mW), in
conjunction with a DISA 55 L 90 a Counter Processor. The apparatus did not, however, include at the time of measurement a Bragg cell, thus only absolute values of velocities could be measured. Flow visualization was effected using a suspension of 6.8 g of aluminum powder in 1 liter of 0.05 M Na dodecyl sulfate solution.

RESULTS

Electrophoresis

The \( \xi \) potentials found in \( 10^{-2} \) M KCl are shown in Fig. 2, as a function of pH. It is seen that in the pH range covered, \( \xi \) potentials are always \( \approx -20 \) mV (i.e., \( |\xi| \approx 20 \) mV). Qualitatively, the shape of the curve agrees with the findings of other investigators (15, 16).

Influence of the Frequency of the Light on the Light Extinction

The initial extinction (\( E_0 \)) of the suspensions was, in the region investigated (366 < \( \lambda \) < 565 nm), independent of \( \lambda \). The same was found for the decay of the extinction as a function of time, in an experiment in which the frequency of the light was switched between different values during a coagulation experiment. Thus, writing the turbidity of the suspensions, following LaMer (17), as proportional to \( (b/\lambda)^y \), we found \( y = 0 \).

Light Extinction vs Time

Figure 3 shows some typical results. In the absence of stirring, no measurable change in the light extinction could be detected, apart from that which had to be ascribed to final sedimentation of the particles.

\[
\frac{d \ln n}{dt} = \frac{1}{0.41} \left( \frac{d \ln E}{dt} \right)_{t=0}.
\]

The initial coagulation rate was calculated by (4)

The main assumptions introduced into the derivation of this equation (see appendix) are: (a) the light removed by a particle from the incident light is proportional to its geometric cross section; (b) \( V_i \), the volume of an aggregate of \( i \) particles can be described by

\[
V_i = f_i \cdot i \cdot V_1,
\]

with \( f_2 = f_1 \); (c) the initial stage of the coagulation is governed by bimolecular reaction kinetics; and (d) in the initial stages of the coagulation, unbranched chains of particles are formed (18).

The Stability Ratio \( W \)

Extending the definition of the stability ratio for the case of perikinetic coagulation (19, 20) to orthokinetic coagulation, we used

\[
W = \frac{\text{(coagulation rate including all interactions except electrocratic repulsion)}}{\text{(coagulation rate including all interactions)}}.
\]

Here both coagulation rates refer to the same stirring rate. The denominator in this quotient is the coagulation rate observed under some specific conditions, while the numerator is the fastest coagulation rate observed at the same stirring rate, at large electrolyte concen-

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trations. Thus, \( W = \frac{a_0(\zeta = 0)}{a_0(\zeta = 0)} \) is the capture efficiency in the absence of double-layer repulsion.

Figure 4 shows some typical data at various electrolyte contents, as a function of stirring rate. In Fig. 5, the same data are plotted against the negative logarithm of the electrolyte concentrations. Similar data were obtained at other pH values.

**Calculation of Shear Rates**

In order to obtain an estimate of the shear rates generated by the stirrer, the flow field in the cuvette was scanned by LDA measurements at four heights above the stirrer.

Typical measurements of velocities at one stirrer speed in tangential and in axial directions are shown in the Figs. 6 and 7, respectively (please note the scale difference between the figures). In these graphs, measurements of the absolute values of the velocities have been plotted. This leads to deviations from the value \( V_x = 0 \) at the center of the cuvette, and to \( V_x \) and \( V_z \) being positive over the whole range of \( r \) values. For the calculations of the average shear rates, the error introduced by this is negligible. By combining tangential velocities at one \( z \) value (\( z = \) height above the stirrer), but at different positions in the cell, the radial velocity \( V_r \) could be calculated by

\[
V_r = \frac{2r}{R} \left( V_a - \frac{d}{r} V_\theta \right),
\]

where \( V_a \) is the tangential velocity measured at \( S \) (see Fig. 8), \( V_\theta \) the velocity measured at \( T \) in the direction parallel to \( V_\theta \) at \( S \). The total average velocity of the fluid at a given position in the cuvette than follows from

\[
|V|^2 = |V_\theta|^2 + |V_r|^2 + |V_z|^2.
\]

Usually, \( V_r \) could be neglected compared to \( V_\theta \) and \( V_z \), except for some positions near the bottom of the cuvette.

The largest shear rates occur in a layer adjacent to the cuvette wall; there is an inner core in which velocity gradients are much smaller. This inner core is taken to be limited at the maximum of \(|V|^2\); its diameter increases with the height above the slave magnet.

In the calculations, the collisions between particles due to the velocity gradients in this inner core are neglected. The whole volume of the liquid in the cuvette is considered as divided into three sections (Fig. 9): (a) the inner core; (b) an outer region; and (c) the space between the slave magnet and the cuvette wall.

In (b) the shear rates were calculated from the equations derived by Stuart (21) for describing the velocities in Taylor vortices between two coaxial cylinders. The radius of the inner cylinder in the equations was taken as equal to the radius of the inner core, thus slightly varying with \( z \); and the velocity of the inner cylinder was taken as that corresponding with the maximum value of \(|V|\) at that particular \( z \) value.

In (c) the shear rates were calculated through the same equations, with the radius of the slave magnet as the radius of the inner cylinder. In both (b) and (c) regions, the

1 After completion of the present investigation, additional apparatus enabled us to measure \( V_\theta \) and \( V_z \) also with regard to their direction. These measurements confirmed that the neglect of shear rates in the inner core is justified.

cuvette radius was taken as the radius of the outer cylinder. The result of the calculations was not critically dependent on the width of the outer region. The assumptions in this model were checked by flow visualization: the onset of Taylor–Goertler vortex-like disturbances of laminar flow occurred near the rotation speed, predicted from the model (150 rpm).

Figure 10 shows the \( \gamma \) values in the (b) region, calculated as

\[
\dot{\gamma} = \left[ \left( \frac{\partial V}{\partial r} - \frac{V_\theta}{r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial V}{\partial \theta} \right)^2 \right] + \left[ \frac{\partial V}{\partial z} \right]^2 \quad [9]
\]

and numerically integrated over the (b) region. The magnitude of \( \dot{\gamma} \) in the outer region does not vary much as a function of \( z \), because of two counteracting effects: the average velocities decrease with increasing \( z \), but the gap between the cuvette wall and the inner core decreases as well.

Figure 11 shows results calculated for different stirring rates. Here the lowest curve represents \( \dot{\gamma} \) in the (b) region, the middle curve that in the (c) region. The upper curve shows the maximum \( \dot{\gamma} \) value that can be expected from Taylor vortex formation at a given stirring speed; it was found by varying the width of the gap for each stirring rate until a maximum value for \( \dot{\gamma} \) was found.

The capture efficiencies \( \alpha_0 \) were calculated from Eqs. [1] and [2] using for \( \dot{\gamma} \) the value

\[
\langle \dot{\gamma} \rangle = \frac{\sum \dot{\gamma}_i V_i}{\sum V_i} . \quad [10]
\]

The \( \alpha_0 \) values found are shown in Fig. 12. The value for \( \dot{\gamma} = 0 \) has been taken from a series of experiments with KNO\(_3\) as electrolyte; it is included in Fig. 12 for comparison's sake.

**DISCUSSION**

From Fig. 5 it is seen that the critical coagulation concentration shifts to higher concentrations with increasing stirrer speed. In other words: electrostatic repulsion becomes more effective with increasing shear rates. These results agree with those reported by Zeichner and Schowalter (22) for latices and with the theoretical predictions of van de Ven and Mason (cf. Fig. 7 in Ref. (3)).

At low stirring rates all \( W \) values tend to unity. This also is in agreement with van de Ven and Mason's calculations, because at low \( \dot{\gamma} \) values the theoretical \( \alpha_0 \) values become independent of electrostatic repulsion effects. The calculated time necessary for decreasing \( n \), the number of particles per unit volume,
that calculated for similar $C_A$ values for spherical particles. This may be due, however, to uncertainties in the $\langle \gamma \rangle$ values. The difference between theoretical and experimental $\alpha_0$ values is smaller for ZnO than for quartz (4). In the latter case, the difference had been ascribed to the irregular shape of the particles, resulting in a lower van der Waals attraction than shown by spherical particles at equal values of the parameter (distance/hydrodynamic radius). The same explanation is thought to be valid here, but the ZnO particles are generally less asymmetrical than the quartz particles in Ref. (4).

At not too large $\xi$ potentials ($|\xi| < 30$ mV), an increase of $\langle \gamma \rangle$ results in an increase of $\alpha_0$. Indeed, theoretical $\alpha_0$ values also increase with increasing $\gamma$ in a certain region (3), due to double-layer effects (3). However, this explanation is excluded by the following considerations:

(a) The theoretical prediction is that $\alpha_0$, as long as it is $\neq 0$, decreases at low $\gamma$ values with increasing double-layer potential, whereas at large $\gamma$ values should approach the same values for low and for large double-layer potentials. Experimentally just the reverse is found in both respects.

When comparing the $\alpha_0$ values found experimentally in $10^{-2}$ M KCl solutions (Fig. 12) with those calculated for spherical particles under neglect of inertial pseudoforces, the following is observed.

At low $\langle \gamma \rangle$ values (up to about 200 sec$^{-1}$), $\alpha_0$ is independent of the $\xi$ potential. This agrees qualitatively with the van de Ven and Mason calculations (3); these authors found electrostatic repulsion only to become operative at $C_A$ values lower than about $2 \times 10^{-2}$ (this limit varies slightly with $\psi_d$). It should be noted that $\langle \gamma \rangle = 200$ sec$^{-1}$ corresponds with $\gamma \approx 700$ sec$^{-1}$ in the (b) region and $\gamma \approx 1400$ sec$^{-1}$ in the (c) region; with a value for the Hamaker constant $A = 3 \times 10^{-20}$ J, $C_A$ would become 0.030 in the (b) region and 0.015 in the (c) region.

The $\alpha_0$ value found ($\approx 0.3$) is lower than
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FIG. 8. Calculation of \( V_r \), the velocity in the radial direction, from measurements velocities at different positions. See text for explanation.

(b) The effect concerned is predicted for \( CR/C_A \) ratios > 200 (where \( C_R = 2\epsilon_0\gamma_d^2/(3\eta_0b^2) \); \( \epsilon_r \) = the relative dielectric constant of the medium, \( \epsilon_0 \) = the permittivity of free space).

Such values are unlikely for aqueous ZnO dispersions with \( |\gamma| < 30 \text{ mV} \).

Thus, the increase of \( \alpha_0 \) with increasing \( \langle \gamma \rangle \) is considered to indicate that inertial pseudoforces are operative similar to the phenomena found with quartz particles of hydrodynamic diameter > 3 \( \mu \text{m} \) at \( \gamma > 20 \text{ sec}^{-1} \) (4).

In order to investigate, whether this conclusion can be justified by the theory for spherical particles, we calculated the trajectories of two approaching particles by a method similar to that used by van de Ven and Mason but incorporating inertial pseudoforces.

The trajectory equations used by van de Ven and Mason were adjusted to a coordinate system with an origin at the point midway between the centers of two approaching particles. This was necessary in order to have a coordinate system not itself subject to accelerations. In this coordinate system, the trajectory equations run as

\[
\frac{d\theta}{dt} = (1 - B)\sin \theta \cos \theta \sin \phi \cos \phi
\]

\[
\frac{d\phi}{dt} = \cos^2 \phi + B(\sin^2 \phi - \cos^2 \phi)/2. \quad [11]
\]

Here \( r \) = the distance between the center of the particles to the origin, divided by the particle radius; \( A \) and \( B \) are the quantities tabulated by Batchelor and Green (2) (thus not those employed by van de Ven and Mason). \( C \) includes, in addition to van der Waals attraction and electrocratic repulsion, a third term for inertial pseudoforces:

\[
F_{\text{inert}} = mV_p^2/r_c, \quad [12]
\]

where \( V_p = \) the velocity of a particle of mass \( m; \) \( r_c = \) the radius of curvature of the trajectory.

Here, the trajectory was approximated as plane. Real trajectories are slightly out of

FIG. 9. Division of the volume of the cuvette into three regions (schematical). I: Inner core; II: outer region; III: region between slave magnet and cuvette wall.

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plane (2), but this is important only when the particles nearly touch. In the calculations, the particle radius was varied between 0.1 and 1 μm; the shear rate between $10^4$ and $10^6 \text{ sec}^{-1}$; the Hamaker constant between $10^{-21}$ and $10^{-19} \text{ J}$; and $\psi_0$ between 0 and 41 mV. A typical result is shown in Fig. 13 (please note that here the distance to the origin is equal to the distance between the center of one particle, and the point midway between the centers of two approaching particles). However, we found for such spherical particles only minor influences of inertial pseudoforces on $\alpha_0$.

Thus, we conclude that inertial forces are much more important for irregular than for spherical particles. This can be understood by considering that edges of irregular particles are able to penetrate the last liquid film between two approaching particles, more efficiently than expected for spherical particles. Similar observations have been reported by Van Boekel and Walstra (25).

An increase in $\zeta$ potential, however, reduces this effect strongly. This is plausible because electrostatic repulsion becomes operative especially at short separations: typical maxima in the potential energy vs distance curve for flat surfaces, with $A = 10^{-20} \text{ J}$, occur at distances of about $20/\kappa \approx 60 \text{ nm}$ in $10^{-2} M 1:1$ electrolyte solution (23).

CONCLUSIONS

(a) The presence of shear causes the critical coagulation concentration to shift to higher values.
(b) On the basis of LDA measurements, the flow field in a stirred cylindrical vessel can be characterized such as to permit the calculation of average shear rates.
(c) Differences between experimental capture efficiencies and those calculated for spherical particles are less pronounced for ZnO than for quartz.
(d) The effect of inertial pseudoforces is more pronounced than expected for spherical particles, but it can be reduced by electrostatic repulsion.

APPENDIX

Derivation of Eq. \[4\] between the Change in Extinction $E$, and the Change in Total Particle Number

From the fact that the extinction is independent of the ratio $b/\lambda$ ($b =$ particle radius,
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Fig. 12. Capture efficiency as a function of $\zeta$ potential at different shear rates. $\langle \gamma \rangle$ (sec$^{-1}$): X, 400; O, 350; ■, 300; △, 250; ●, <200. The datum for $\zeta = 0$ refers to an experiment in 0.01 M KNO$_3$ solution.

$\lambda$ = wavelength of the light), we conclude that the turbidity caused by a particle is proportional to its geometrical cross section. Thus

$$\tau = K \sum_i n_i V_i^{2/3}.$$  \[A-1\]

During the initial stages of the coagulation, the aggregates formed are in majority unbranched chains. Thus, if a parameter $p$ is defined

$$p = \frac{n_0 - n}{n_0}$$  \[A-2\]

(with $n_0$ = the initial number of particles), the following relation is valid (24):

$$n_i = n_0(1 - p)p^{(i-1)}.$$  \[A-3\]

This relation is based on the assumption that every particle has two contact sites which have a probability $p$ to be engaged, and a probability $1 - p$ to be free.

For bimolecular reaction kinetics for the coagulation:

$$\frac{1}{n} - \frac{1}{n_0} = kt,$$  \[A-4\]

where $k$ is the reaction constant. Thus

$$p = 1 - \frac{1}{1 + ktn_0} = \frac{ktn_0}{1 + ktn_0}$$  \[A-5\]

$$1 - p = \frac{1}{1 + ktn_0}$$  \[A-6\]

and on introducing these relations into [A-3], we obtain

$$n_i = n_0 \frac{(ktn_0)^{(i-1)}}{(1 + ktn_0)^{(i+1)}}.$$  \[A-7\]

With $V_i = i f_i V_1$ (see the definition of $f_i$, relation [5]), we obtain

$$\tau = Kn_0^{5/3} V_1^{2/3} \sum_i i^{2/3} f_i^{2/3} \frac{(ktn_0)^{(i-1)}}{(1 + ktn_0)^{(i+1)}}.$$  \[A-8\]

Fig. 13. Trajectories of two spherical ZnO particles. Parameters: $A = 3 \times 10^{-20}$ J; $\psi_d = 20$ mV; $b = 2 \times 10^{-7}$ m; $\gamma \times$, 10$^4$ sec$^{-1}$; △, 10$^3$ sec$^{-1}$; ●, 10$^6$ sec$^{-1}$.

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\[
\frac{d\tau}{dt} = K_n^{5/3} V_1^{2/3} \sum_i \frac{i - 1}{ktn_0} \frac{(i + 1)}{1 + ktn_0} (ktn_0)^{i-1} (1 + ktn_0)^{i+1}, \quad [A-9]
\]

For \( t \to 0 \):
\[
\tau_0 = K_n^{5/3} V_1^{2/3} f_1^{2/3} \quad [A-10]
\]
\[
\left( \frac{d\tau}{dt} \right)_0 = K_n^{5/3} V_1^{2/3} \left[ -f_1^{2/3} \cdot 2 + 2^{2/3} f_2^{2/3} \frac{1}{ktn_0} \right. \\
\left. - \frac{3}{1 + ktn_0} \frac{ktn_0}{(1 + ktn_0)^3} \cdots \right] * kn_0 \quad [A-11]
\]
\[
= K_n^{5/3} V_1^{2/3} f_1^{2/3} \left[ -2 + 2^{2/3} \left( \frac{f_2}{f_1} \right)^{2/3} \right] \cdots \right] \right] \left[ 1 + ktn_0 \right] \quad [A-12]
\]

Thus
\[
\frac{1}{\tau_0} \left( \frac{d\tau}{dt} \right)_0 = \left[ -2 + 2^{2/3} \left( \frac{f_2}{f_1} \right)^{2/3} \right] \left[ 1 + ktn_0 \right] \quad [A-13]
\]

higher terms in the summation being negligible.

For \( f_1 = f_2 \), we obtain
\[
\frac{1}{\tau_0} \left( \frac{d\tau}{dt} \right)_0 = -0.41 kn_0. \quad [A-14]
\]

From [A-4], it follows that
\[
n = \frac{n_0}{1 + ktn_0} \quad [A-15]
\]
and
\[
\frac{dn}{dt} = -\frac{ktn_0^3}{(1 + ktn_0)^2}. \quad [A-16]
\]
Thus
\[
kn_0 = \frac{1}{n_0} \left( \frac{dn}{dt} \right)_{t_0} \quad [A-17]
\]

Introducing this relation into [A-14], we obtain, with
\[
\frac{1}{\tau_0} \left( \frac{d\tau}{dt} \right)_0 = \frac{1}{E_0} \left( \frac{dE}{dt} \right)_0,
\]

relation [4].

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