

CHARACTERIZATION OF FLOCS IN COARSE SUSPENSIONS IN A NON-POLAR MEDIUM

P.J.J.M. VAN MIL*, D.J.A. CROMMELIN[†] and C.J. DE BLAEY[‡]

Department of Pharmaceutics, University of Utrecht, Catharijnesingel 60, 3511 GH Utrecht (The Netherlands)

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ABSTRACT

The flocculation of coarse suspensions of NaCl in liquid paraffin was studied. Floc characteristics such as size, porosity and number of primary particles were investigated for suspensions of NaCl in liquid paraffin by application of the Koglin concept. The dispersed NaCl had a narrow size distribution. Variables under investigation were particle size (mean volume diameter 6.5, 8.1 and 16.2 μm) and solid concentration (0–2% m/m). The results showed that the floc size and floc porosity increased with NaCl concentration up to 2% (m/m). No relationship was found between floc porosity and sediment porosity. For suspensions with small particles and a solid concentration above 3%, a structuring of flocs with high porosity hindered the settling of the flocs.

INTRODUCTION

The formation of flocs in a coarse suspension usually accelerates the settling process. The homogeneity of the suspension at rest, the porosity and the redispersibility of the sediment after settling are strongly affected by flocculation. It is therefore important to gain insight into the mechanisms involved in the flocculation process of coarse suspensions in order to control the state of flocculation by rationale [1]. In the present work the end result of the flocculation process, i.e. the flocs, are studied. Floc formation is usually expressed indirectly by parameters such as the settling rate of the interface between suspension and supernatant [2], sediment volume [3] or in terms of rheological properties of the suspension [4,5]. However, it is of interest to know in more detail the characteristics of the flocs themselves, i.e., floc size, floc porosity and number of primary particles in a floc.

The various methods for particle-size measurement (e.g., Coulter-counter, photometer, sedimentation balance and photosedimentometer [6]) provide

*Present address: Netherlands Institute for Dairy Research (NIZO), P.O. Box 20, 6710 BA Ede, The Netherlands.

[†]To whom correspondence should be addressed.

[‡]Present address: Royal Dutch Society for the Advancement of Pharmacy, Alexanderstraat 11, 2514 JL The Hague, The Netherlands.

only limited information on flocs in suspensions (a size distribution with a mean diameter). Koglin [7] surveyed several methods for determining both size and porosity of flocs in suspensions but could not find a single method suitable for fluffy flocs. Therefore he suggested the use of two independent methods of measuring particle sizes, to obtain information on the mean floc diameter as well as the mean porosity and the number of particles per floc. He derived two equations based on an analysis of sedimentation and light-absorption measurements [7,8]. These equations can be solved provided that (1) data on the mean settling velocity obtained from sedimentation experiments, and on the extinction cross-sectional area obtained from photometer readings (both for the same suspension) are available; (2) the data are collected for a flocculated as well as for a completely non-flocculated system; (3) the ratio between the shape factor of flocs and primary particles is known or can be estimated.

We examined suspensions of a model compound (NaCl) in liquid paraffin, and studied the effect of solid concentration, particle size and the Aerosol-OT concentration (an anti-flocculation agent) on floc size, floc porosity and number of primary particles in a floc. In order to apply the equations derived by Koglin, we used a photometer in combination with a release apparatus to collect the necessary data. The release apparatus provides the means of accurately measuring sedimentation rates of readily water-soluble solids dispersed in non-polar media [9]. Changes observed in floc characteristics induced by variation of the suspension composition were compared with trends in the Stokes diameter and sediment volume.

MATERIALS AND METHODS

The suspensions consisted of NaCl particles dispersed in liquid paraffin. Non-flocculated systems were obtained by dissolving 1 mmol dm^{-3} Aerosol-OT (dioctyl sodium sulphosuccinate) in the liquid paraffin [1].

All experiments were carried out at $25 \pm 0.5^\circ\text{C}$. Chemicals used in the experiments were of pharmaceutical grade.

Sodium chloride was dried (temperature 150°C , pressure $< 2 \text{ kPa}$) and ground (ball mill), dried again and classified by a centrifugal classifier (Alpine). The size fractions were analysed microscopically: from pictures of samples the arithmetic mean particle diameters were determined according to the projected-diameter method [6,10]. More than 100 particles were counted for each fraction. The geometric diameters and geometric standard deviations are given in Table 1. The density of NaCl was 2160 kg m^{-3} , as determined by an air comparison pycnometer (Beckman). The NaCl powder was stored in a stove at 150°C and kept under low pressure ($< 2 \text{ kPa}$) to keep the surface free from NaOH and moisture [9].

Liquid paraffin was purified and dried by adding 15% (m/m) ground, dried NaCl to remove any substances that might have an undesirable influence on the stability of the suspension (e.g., water or surface-active agents);

the supernatant was used in the experiments [9]. The viscosity, as measured with a rotation viscometer (Rheomat 15, Contraves) was 23.1 mPa s. Liquid paraffin had a density of 860 kg m⁻³ as determined by an air comparison pycnometer.

TABLE 1

Particle sizes and standard deviations of the NaCl fractions

Mean diameter (geometric) (μm)	Standard deviation (geometric)	Mean diameter d_v^a (μm)	Mean diameter d_{sto}^b (μm)
15	1.25	16.2	15.6
10.5	1.25	11.3	10.7
7.5	1.25	8.1	7.7
5.5	1.4	6.5	6.3

^a Calculated by the Hatch—Choate Eqns (see Ref. [16]).

^b d_{sto} was calculated from d_v by using $d_{sto}^2 = d_v^2 \sqrt{\psi}$ [15] with $\psi = 0.8$.

Aerosol-OT was dissolved in methanol for purification. The solution was filtered (G3 glass filter) and after evaporation of the methanol, the residue was dried under vacuum at 150°C [11].

The suspensions were prepared by weighing the required amount of dried NaCl into a bottle containing the desired Aerosol-OT/liquid-paraffin solution. The suspension was treated with a high speed mixer (Ultra-Turrax, Janke and Kunkel Ika Werk) in a dry box under nitrogen and sonicated with a probe-type sonicator (Bransonic B12) for 1 min during cooling in ice water. This procedure was followed to ensure complete dispersion of the particles and to keep the suspension water-free. The suspensions were rotated end-over-end (60 rpm) to keep them homogeneous. Just before use, the suspensions were treated briefly ultrasonically (bath-type sonicator, ultrasonic K42) to remove entrapped air.

The absorbance (Abs) of the suspensions was measured with a spectrophotometer (Shimadzu UV-100) at 625 nm in a cell with an optical pathlength of 2 mm. The apparatus was adjusted to meet the requirements of a wide-angle spectrophotometer (WASP; see Ref. [6]). Because of technical restrictions on the absorbance readings, the upper limit for the NaCl concentration was 3% for large particles (16.2 μm) and 2% for the other fractions (8.1 and 6.5 μm). Higher solid concentrations required cells with pathlengths below 2 mm; however, wall effects then prohibited taking proper readings.

The mass flow of the settling suspension was not measured with a sedimentation balance, as is usually done, but with an apparatus originally designed to monitor the release of solids from dispersions in non-polar media to an aqueous phase [9]. This release apparatus (Fig.1) consisted of a glass

vessel with an inner diameter of 100 mm, with a nylon stirrer rotating (80 rpm) in 500 ml of demineralized water at a distance of 10 mm from the bottom. An open siliconized, glass tube with an inner diameter of 37.6 mm was placed eccentrically with its lower end below the water surface. A 10-mm-thick layer of the liquid-paraffin suspension had to be transferred into the tube on top of the water. To ensure a gradual build-up of the layer, the suspension was poured into a syringe which then was emptied against the wall of the tube. The release of the NaCl was followed conductometrically. In the slip-stream of the stirrer an electrode was placed, connected to a conductivity meter (Philips PW 9505) which in turn was connected to a recorder (BD 40, Kipp and Zonen). The mass flow (dm/dt) of the solid through the interface was calculated from the recorded curve. It was found that under the experimental conditions mentioned above, sedimentation was the rate-limiting step in the release process of suspensions with NaCl particles having Stokes diameters of up to $45 \mu\text{m}$.

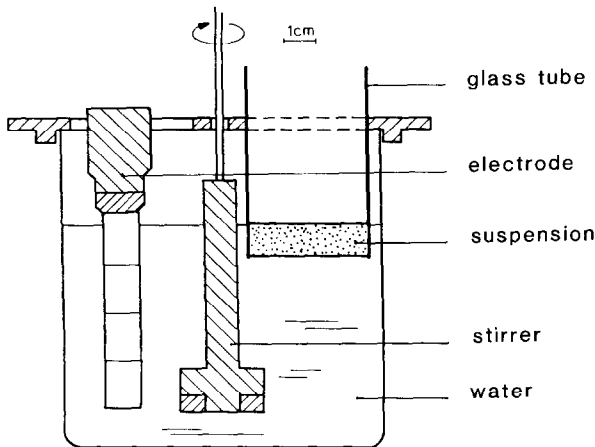


Fig. 1. Apparatus used for determination of the release rate of NaCl (see text).

Equations (1) and (2) are used to calculate floc size, porosity and number of particles of a floc [7,8] (see list of symbols given in Appendix).

$$\frac{\bar{u}_a}{\bar{u}} = \frac{(dm/dt)_a}{dm/dt} = \left(\frac{\psi_a}{\psi}\right)^{1/2} (1-\bar{\epsilon}) \left(\frac{\bar{d}_{v,a}}{d_v}\right)^2 \quad (1)$$

This expression relates the ratio of mean settling velocities of a flocculated (subscript a) and a non-flocculated suspension (containing the same primary particles in the same concentration) to the ratio of mean volume diameter (diameter of a sphere having the same volume as the particle) of floc and primary particle, the mean porosity (ratio of void volume to total floc volume) of the flocs and the ratio of floc and primary particle shape factor (ratio of the surface area of the sphere having the same volume as the particle to its actual surface area).

$$\frac{\bar{A}_{v,a}}{\bar{A}_v} = \frac{Abs_a}{Abs} = \left(\frac{\psi_a}{\psi}\right)^{-1} (1-\bar{\epsilon}) \left(\frac{\bar{d}_{v,a}}{\bar{d}_v}\right)^{-1} \quad (2)$$

This expression relates the ratio of the cross-sectional areas of the same flocculated and non-flocculated suspensions to the same variables. The equations can be solved when the ratio between the shape factors of the flocs and the corresponding primary particles is known or can be estimated. In order to obtain the mean number of primary particles in a floc Koglin gives the relation

$$\bar{k} = (1-\bar{\epsilon}) \left(\frac{\bar{d}_{v,a}}{\bar{d}_v}\right)^3 \quad (3)$$

From the same release curves (amount released versus time) as are used for determination of the mass flow, the average Stokes diameter can be calculated. The average Stokes diameter is calculated by

$$d_{sto} = \left[\frac{18\eta}{\Delta\rho g} \frac{h}{t_{50\%}} \right]^{1/2} \quad (4)$$

in which $t_{50\%}$ stands for the time on the abscissa where a line drawn from the 50% point on the ordinate (% of amount released) touches the release curve [12].

The sedimentation volume (V_u/V_o) measurements were performed by pouring about 15 ml of a suspension into a tube (diameter 10 mm, height 150 mm) and measuring the height of the sediment and that of the total suspension after one day. No change of sediment height was observed after 1 day.

RESULTS AND DISCUSSION

Experiments with suspensions of NaCl in liquid paraffin were performed to study the effect of solid concentration and primary particle size on the floc characteristics: floc size, porosity and number of particles in a floc. Because one of the prerequisites of Koglin's method is that a non-flocculated suspension should be available, two suspensions were made. One suspension was stabilized by 1 mmol dm⁻³ Aerosol-OT [1]. Figure 2 shows the average Stokes diameter, as calculated by Eqn (4), for non-flocculated and flocculated suspensions with different NaCl content. The curves of the suspensions that did not flocculate (closed symbols) indicate that the Stokes diameter increased slightly with NaCl concentration. In a dilute coarse suspension stabilized against flocculation, the dispersed particles will settle individually. For low solid concentrations the average Stokes diameter was therefore identical to the Stokes diameter obtained from microscopic count. When more particles are present, the settling velocity of the particles may increase by mutual interference due to hydrodynamic interaction without floc formation

[6,13,14]. This causes a larger Stokes diameter. In non-flocculated suspensions the settling velocity increases with solid concentration, reaches a maximum and decreases when hindered settling occurs. Then small particles settle faster whilst large particles are withheld compared to their Stokes velocity. No maximum was observed in our experiments, therefore the concentration of solid for which hindered settling exceeds the effect of hydrodynamic interaction was not reached.

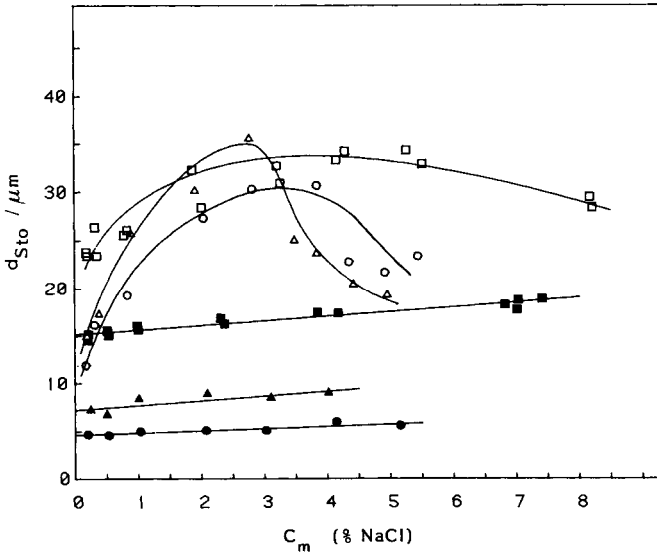


Fig. 2. Average Stokes diameters of particles and flocs of NaCl dispersed in liquid paraffin for various primary particle sizes at different solid concentrations C_m (% by weight); $n=1$.

Open symbols: flocculated suspension (drawn line); closed symbols: stable suspension (least squares regression line); (\square) $d_v = 15.6 \mu m$; (\triangle) $d_v = 8.1 \mu m$; (\circ) $d_v = 6.5 \mu m$.

In the case of suspensions not being stabilized (open symbols) a more pronounced increase in the Stokes diameter with concentration occurred because of flocculation. Three more phenomena can be observed in Fig. 2 for the suspensions that were not stabilized: (1) The increase in average Stokes diameter with concentration levelled off above a concentration of about 3% for suspensions with $15.6\text{-}\mu m$ NaCl particles. This might be a maximum floc size as a result of a balance between flocculation and deflocculation processes. For the suspensions with 7.7- and $6.3\text{-}\mu m$ particles the maximum was reached at a concentration of about 3% NaCl. A further increase in the solid concentration resulted in a smaller Stokes diameter of the flocs. Microscopic observation of those suspensions having a solid concentration (C_m) above 3% revealed that the flocs were highly porous. They tended to form a structure, thus preventing fast settling of individual flocs of small particles (7.7 and $6.3 \mu m$). A very high porosity (> 0.9) was found for 2% C_m suspensions calcu-

lated using Koglin's equations, as will be discussed later. (2) Even at concentrations as low as 0.2% C_m , flocculation occurred. (3) The smaller the Stokes diameter of the primary particles, the larger was the relative increase in the average Stokes diameter after flocculation. For the 6.3- μm particles (0.2% C_m), d_{sto} reached a value of 11.5 μm (+80%); for the 7.7- and 15.6- μm particles, values of 14 μm (+80%) and 24 μm (+55%), respectively, were found.

The absorbances of flocculated and non-flocculated suspensions, together with the size fractions studied, are shown in Fig. 3. A linear relationship was found between absorbance and solid concentration for stabilized suspensions up to the highest concentration that could be measured. The absorbance of the suspensions that were not stabilized was always lower than the absorbance of the corresponding stabilized suspensions.

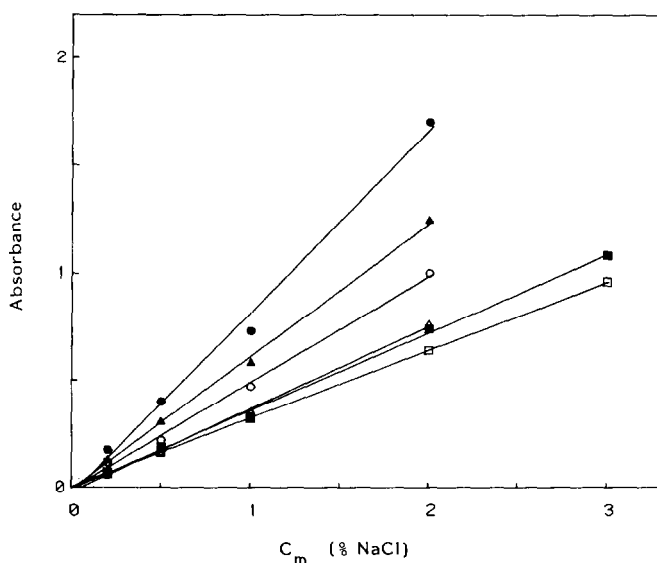


Fig. 3. Light absorbance at 625 nm in a 2-mm cuvette measured with a WASP (symbols as for Fig. 2); least squares regression line.

In order to obtain data on mean size, porosity and number of particles of the flocs formed in the suspensions with primary particles differing in size and concentration, we followed Koglin's method.

The values of the mass flow (dm/dt) and the absorbance (Abs) of the suspension with 1 mmol dm^{-3} Aerosol-OT were taken as the values for the non-flocculated system. Microscopic observation of these suspensions during settling revealed that they were not flocculated. Besides, the experimentally obtained d_{sto} was approximately the same as the d_{sto} calculated from microscopic analysis (prerequisite 2). The shape of the flocs in flocculated suspensions approximated the shape of the single primary particles. Therefore, the shape-factor ratio (ψ_a/ψ) [15] in Eqns (1) and (2) could be set at unity (pre-

requisite 3). Table 2 gives the composition of the flocs in the suspensions calculated according to Eqns (1)–(3). All calculated values in Table 2 have a relative standard deviation of about 20%. An increase in solid concentration resulted in an increase in the mean floc diameter. For suspensions with small particles this increase was more pronounced, as was observed in Fig. 2. For 2.0% NaCl suspensions, the relative increase based on values of the mean volume diameter calculated by Koglin's method was 24 for the small 6.5- μm particles and 15.5 and 3.7 for the 8.1- and 16.2- μm particles, respectively. The number of primary particles in a floc calculated by Eqn (4) also increased with solid concentration and decreasing particle size. At a concentration of 2% the large flocs were very fluffy. The porosity reached a value of almost unity. Figure 2 shows that further increase of the solid concentration resulted in small values of d_{sto} . Presumably, the flocs became so porous and large that a structure of cross-linked small flocs was built in the flocculated suspension. The structuring of a flocculated suspension with a high concentration of solid can be the cause of non-Newtonian behaviour [4,5].

TABLE 2

Mean diameter, mean porosity and mean number of particles in a floc for suspensions with different initial particle size and solid concentration. Calculations made using Eqns (1)–(3)

$d_v = 16.2 \mu\text{m}$				$d_v = 8.1 \mu\text{m}$				$d_v = 6.5 \mu\text{m}$			
C_m (%)	$\bar{d}_{v,a}$ (μm)	$\bar{\epsilon}$	\bar{k}	C_m (%)	$\bar{d}_{v,a}$ (μm)	$\bar{\epsilon}$	\bar{k}	C_m (%)	$\bar{d}_{v,a}$ (μm)	$\bar{\epsilon}$	\bar{k}
0.2	23	0.19	2	0.2	24	0.46	14	0.2	38	0.75	50
0.5	26	0.31	3	0.5	22	0.28	15	0.5	57	0.79	141
1.0	59	0.72	13	1.0	78	0.83	154	1.0	93	0.89	323
2.0	76	0.75	25	2.0	134	0.90	449	2.0	161	0.93	1047

We compared the results of the calculation of floc porosity with sediment heights measured after settling. Figure 4 shows the ratio between sediment volume and suspension volume, normalized for solid concentration, for flocculated and non-flocculated suspensions. The non-flocculated suspensions gave compact sediments with low porosity that were hard to redisperse. In flocculated suspensions porous sediments were formed that were easy to redisperse. The larger the primary particles, the denser the sediment in both the flocculated and corresponding non-flocculated suspensions. The porosity of the sediment did not increase with the solid concentration. This result was in disagreement with the porosity of the flocs as calculated according to Koglin (Table 2, column 3). There, the porosity of the flocs increased with solid concentration. Apparently, settling of the flocs on the bottom of the sedimentation tube diminishes the effect of solid concentration on floc porosity, although it does detect the porosity increase by smaller particle size.

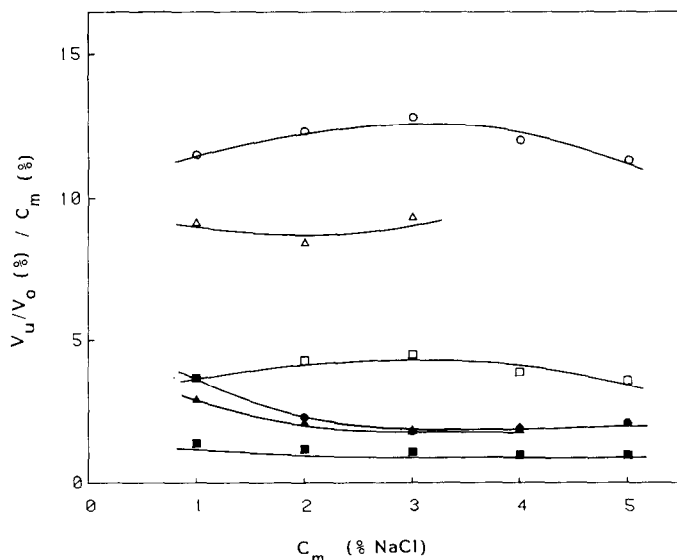


Fig. 4. Sediment to suspension volume ratio (%) normalized to C_m 1.0% (symbols as for Fig. 2); $n = 1$; drawn lines.

Floc porosity and trends in floc porosity with floc size have mostly been studied in colloidal suspensions [17,18]. The suspensions, with monodispersed particles in the colloidal size range, exhibited perikinetic floc formation. Therefore, a comparison of our results on flocs and sediments with results from literature was not made. We also studied the influence of the initial Aerosol-OT concentration on the composition of the flocs for suspensions containing the particle size fraction d_v 11.3 μm . Figure 5 shows that, with increasing Aerosol-OT concentration, the average Stokes diameter of the flocs in the suspension decreased to a value similar to the calculated Stokes diameter (10.7 μm , cf. Table 1). This calculated Stokes diameter was reached at a concentration of Aerosol-OT which depended on the solid concentration. The smaller the surface area of the solid (low solid concentration, large particles) in a suspension, the lower the initial concentration of Aerosol-OT required to reach the minimum value. For a 0.2% C_m suspension, 0.01 mmol dm^{-3} was necessary, while a suspension of 1% C_m required 0.1 mmol dm^{-3} of Aerosol-OT. Here, too, we determined the floc parameters. Table 3 shows that with increasing Aerosol-OT concentration the floc size decreased together with the porosity and the number of primary particles in the floc. Table 3 shows that, at high Aerosol-OT concentration, doublets ($k=2$) were still present in the suspension. However, rounding off the figures (the relative standard deviation of the measurements was 20%) causes this phenomenon. Table 3 also shows that, with increasing solid concentration, the flocs became larger and that the concentration of Aerosol-OT

at which the calculated Stokes diameter was found, i.e., $k=1$, became higher. To complete our experiments we determined the sediment/suspension-volume ratio (V_u/V_o). Figure 6 shows similarly shaped curves as in Fig. 5. Increasing the Aerosol-OT concentration lowered the sediment volume which was to be expected (cf. Fig. 5 and Table 3).

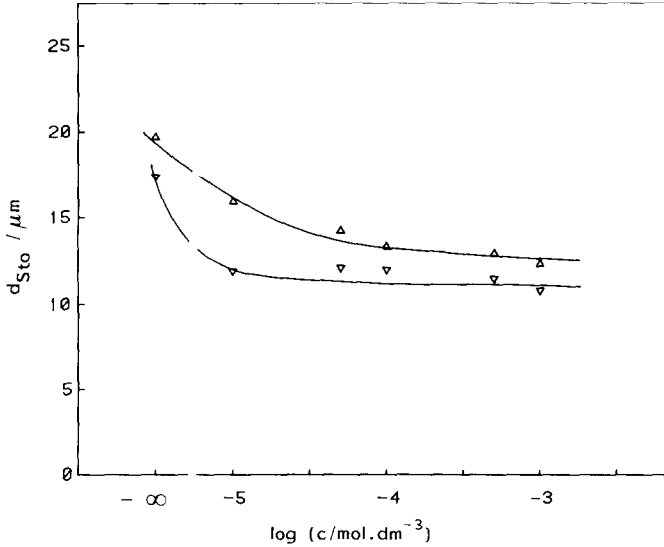


Fig. 5. Average Stokes diameters for suspensions with particles of $d_v = 11.3 \mu\text{m}$ (see Table 1) in liquid paraffin containing various concentrations of Aerosol-OT; $n=2$; drawn lines. (∇) $C_m = 0.2\%$; (Δ) $C_m = 1.0\%$.

TABLE 3

Mean diameter, mean porosity and mean number of particles in a floc for suspensions with different initial Aerosol-OT concentration. Particle size $d_v = 11.3 \mu\text{m}$. Calculations made using Eqns (1)–(3)

$C_m \text{ NaCl} = 0.2\%$				$C_m \text{ NaCl} = 1\%$			
Conc. Aerosol-OT (mmol dm^{-3})	$\bar{d}_{v,a}$ (μm)	$\bar{\epsilon}$	\bar{k}	Conc. Aerosol-OT (mmol dm^{-3})	$\bar{d}_{v,a}$ (μm)	$\bar{\epsilon}$	\bar{k}
0	28	0.59	6	0	34	0.65	10
0.01	17	0.32	2	0.01	23	0.47	4
0.05	16	0.28	2	0.05	15	0.22	2
0.1	15	0.24	2	0.1	13	0.09	1
0.5	15	0.25	2	0.5	12	0.06	1

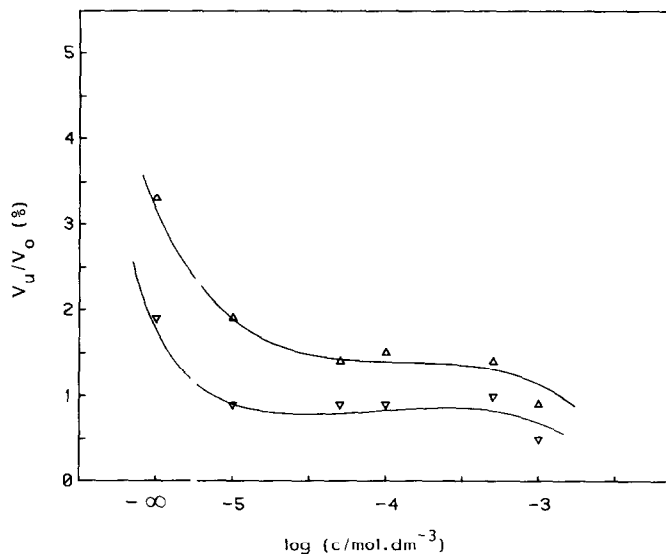


Fig. 6. Sediment to suspension volume ratio (symbols as for Fig. 5); $n = 1$; drawn lines.

CONCLUSIONS

Both the Stokes diameter determined with the release apparatus and the sediment volume give an indication of the state of flocculation of NaCl suspensions in a non-polar medium. Calculations made following Koglin's method yield values of floc size, floc porosity and number of particles in a floc. Under the chosen conditions no data could be obtained above 2% C_m , as no reliable turbidity readings could be taken. An increase was found for these parameters by increasing the solid concentration up to about 2% or by decreasing the particle size. Suspensions with small particles and with a solid concentration above about 3% tend to form a structure. In suspensions with a high concentration and large particles, no structure is formed but above a certain concentration a maximum floc size, independent of concentration, is found. Flocs tend to lose particles because separating forces originating from gravity and shear overrule floc-stabilizing interaction forces.

The porosity of the sediments only partly agreed with the floc porosity as calculated according to Koglin. This discrepancy might be ascribed to the fact that in a sediment, one can discern porosity within a floc and porosity between flocs. In the concept developed by Koglin only floc porosity is taken into account. This concept seems to be much more sensitive to changes in floc characteristics than observations of the floc sediment.

Floc characterization according to Koglin was derived from theory. Substantial evidence that the values for floc size, porosity and number of particles in a floc are true floc dimensions can be found by a method independent of the method used in the Koglin concept. Microscopic observations give only a qualitative impression of the correctness of the charac-

teristics obtained by Koglin's method. Pusch [8] compared the standard deviation of the floc-size distribution calculated according to the Koglin concept with the standard deviation obtained with a Microtrac apparatus (Leeds and Northrup, U.S.A.). Both techniques agreed reasonably well for quartz particles in water flocculated by polymers. As the prerequisites for the Koglin concept were met for our suspensions, we expect that the calculated floc characteristics of settling NaCl particles in a non-polar medium approximate reality.

The release apparatus we used to determine the sedimentation rate of readily water-soluble particles dispersed in a non-polar medium is an excellent alternative to the sedimentation balance. From the release curves, a size distribution can be obtained. The average Stokes diameter thus calculated is in good agreement with the diameter calculated from microscopic observations. Moreover, the apparatus is cheap, simple and easy to handle. An additional advantage is that, with this method, the formation of a large sediment on the pan of a sedimentation balance in the case of flocculated suspensions is avoided.

APPENDIX

Symbols used in the text as follows:

A_v	Extinction cross-sectional area	(m)
Abs	Absorbance	dimensionless
C_m	Concentration of NaCl by weight	dimensionless
c	Concentration of Aerosol-OT	(mol dm ⁻³)
d_{sto}	Stokes diameter	(m)
d_v	Volume diameter	(m)
g	Gravitational acceleration	(m s ⁻²)
h	Suspension height	(m)
k	Number of primary particles in a floc	dimensionless
m	Mass	(kg)
t	Time	(s)
u	Settling velocity	(m s ⁻¹)
V_u	Suspension volume	(m ³)
V_o	Sediment volume	(m ³)
ϵ	Porosity	dimensionless
η	Dynamic viscosity	(Pa s)
$\Delta\rho$	Difference in density between solid and liquid	(kg m ⁻³)
ψ	Shape factor (see Ref. [15])	dimensionless

Subscript a refers to flocculated systems; a bar above the symbol indicates mean values.

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