

DROP COALESCENCE. I.

COALESCENCE OF TWO DROPS; THE SYSTEM WATER-TOLUENE

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An apparatus was constructed for measurements of time of drop coalescence by which times of existence of two drops of a dispersed phase were measured. The drops situated one above the other in the continuous phase acted on themselves only by buoyancy. The obtained results indicate that the drop coalescence is in this case slower than with the meters of the drop-liquid surface type. Further a substantial dependence of time of drop existence on temperature, concentration of surface active matters and on dimensions of the system measured was determined.

An important part of a study of conditions of a continuous polymerization in suspension is the description of mechanism of coalescence of individual drops of dispersed monomers between themselves. At a suspensive polymerization the dispersed spherical drops of monomers are placed closely one along the other in the dispersed environment. It is required that for a successful carrying of suspensive polymerization operations due to a narrow distribution of particle sizes coalescence of individual particles between themselves should not take place. For these reasons we have paid main attention in the study of this operation to determination of the time for which two particles may exist one along the other without the coalescence taking place. As a model liquid was chosen toluene instead of monovinyl or divinyl monomers. This enabled us to study the considered coalescence operation without chemical changes of the dispersed phase. Further this made possible to test a newly designed meter for coalescence studies, the measuring technique, evaluation of the results and their comparison with the published results of other authors obtained by different methods.

The problem of the study of drop coalescence of spherical liquid particles at a continuous suspensive polymerization may be placed into the region of drop agglomeration at conditions when on particles acts mainly the buoyancy or a very slow motion of one particle behind the other. At this motion one particle is pushed by the

next one located closely behind it or an interchange of layers of the particle streams in the horizontal direction takes place. The velocity of this shifting motion is 0.3 to 1.0 m/min. We have paid the attention to study of the coalescence by buoyancy and this condition is for the suspensive polymerization predominant.

These problems are briefly mentioned in the book of Rod, Míšek and Štěrbaček¹ where the results of Gillespie and Rideal² and of Cockbain and Mc Roberts³ are quoted. These authors in the same way as Watanabe and Makoto Kusui⁴ have used the apparatus for measuring of the drop coalescence on the interface between two liquid phases (drop-liquid surface). They were concerned mainly by the agglomeration of oil or water drops on the oil-water interface. Slightly modified similar apparatus for determination of time of existence or of the half-time of existence was used by Charles and Mason⁵ and by Nielsen⁶. The measurement with this type of meter is in literature described most frequently. At this occasion it is also necessary to mention the simple apparatus used by Sawiatovski and James⁷ where again the drop agglomeration on a flat interface takes place. Closest to our problematics is the apparatus of Naoyasu Sato and Iukio Harisaki⁸. They studied the stability of oil drops in a meter formed by a U-tube with three bends. The drops were brought into the U-tube ends by a syringe. After a while (so called "time of growing old") they measured the time of drop existence.

After evaluation of the mentioned meters and methods we came to the conclusion that for our purposes concerning the study of time of drop existence at the suspensive polymerization a new meter must be designed in which the conditions in an actual device of a continuous suspensive polymerization would be simulated at best and at the same time this meter should make possible the study of the effect of basical physical parameters on the time of drop existence. This means to study the coalescence between two drops with a possibility to change their diameter at different temperatures and for different physical properties of the liquid dispersed as well as of the dispersive environment. On the basis of these consideration a new apparatus was designed for the coalescence studies which would be described in the Experimental part.

As for the evaluation of the measured data it was necessary to make use of the results of published papers dealing with similar problems in relation with the batch suspensive polymerization in stirred reactors and further of papers in which the coalescence problematics is studied from a more general point of view. We have paid the main attention to the three factors affecting first of all the drop coalescence. They are: the presence of surface active matters, temperature of the system and size of drops of the dispersed phase. For systems stirred by mechanical mixers which are mostly met in literature, the final size of particles of the system is determined by the both above mentioned factors *i.e.* by the concentration of the surface active matter or of the stabilizer of the suspension, by the temperature and by the work done in the system by the mixer. From this point of view is also further considered the coalescence of formed drops.

With this problematics deals a number of patents⁹⁻¹², in literature the batch suspensive polymerization and in this relation also the particle coalescence is studied by several authors¹³⁻²⁰. From a more general point of view the effect of surface active matters on coalescence is studied

by Sonntag^{2,1-2,3}, Cockbain³ and by Nielsen⁶. The effect of temperature on coalescence is studied by Nielsen⁶, Gillespie² and by Charles⁵. The influence of drop size on their coalescence is described by other authors^{7,8}. On the basis of this literature survey a conclusion may be made that first of all the three above mentioned factors *i.e.* the concentration of the surface active matter, temperature, and the drop size affect the times of drop coalescence. Other factors mentioned in literature such as the effect of pH or of the electrical field cannot be considered significant. It is obvious from this analysis that some authors considered as very important the curvature of the surface on which the coalescence takes place. Mainly this fact and the difference of our problematics of continuous suspensive polymerization from procedures described in literature have caused that we have developed a new apparatus and that we have used it for measuring the coalescence.

EXPERIMENTAL

The apparatus on which our measurements have been made (Fig. 1) consists of several basic parts. They are: the interchangeable metering tube 1 of different inside diameters, the constant temperature jacket 3, vessels for the dispersive medium 4, and for the dispersed liquid 5, syringe 6, connected with a capillary 2. Into the metering tube 1 are by the mean of capillary 2 and syringe 6 brought in the drops of the studied dispersed phase contained in the vessel 5. The dispersive medium which

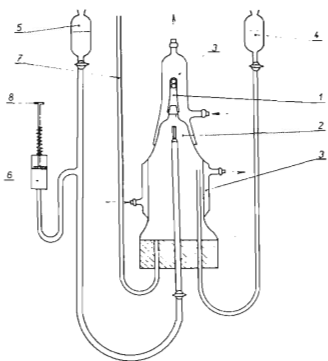


FIG. 1

Schematic View of Apparatus for Measurement of Drop-Drop Coalescence

1 Metering tube, 2 capillary, 3 constant-temperature bath, 4 vessel for the dispersive medium, 5 vessel for the dispersed liquid, 6 syringe, 7 tube for equalizing of volumetric changes in the meter, 8 micrometric screw.

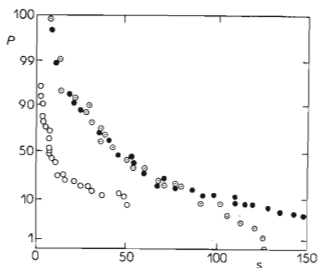


FIG. 2

Time of Drop Existence t Plotted by Use of the Probability Scale

○ $c_{PVA} = 0.01$ weight %, $d_k = 4.8$ mm, $T = 20^\circ\text{C}$; ● $c_{PVA} = 0.01$ weight %, $d_k = 3.5$ mm, $T = 20^\circ\text{C}$; ◐ $c_{PVA} = 1.0$ weight %, $d_k = 2.7$ mm, $T = 80^\circ\text{C}$.

fills the whole space of the apparatus is also in the vessel 4. The temperature of the whole meter is kept constant in the range of $\pm 0.2^\circ\text{C}$ by circulation of water from an ultrathermostat to the water jacket 3.

At first the meter is filled with the dispersive medium from the vessel in an position turned by 180° from that one given in Fig. 1. This motion is possible due to a flexible connection of the meter with both vessels. By this filling air is removed from the system. In this position the meter content is brought to the required temperature so that bubbles of absorbed gases may leave through the tube 7. The meter is then turned into the position given in Fig. 1. By use of the syringe 6 and of the capillary 2, two drops are brought into the metering tube 1. The volume of these drops is measured by a micrometric screw 8 connected with the syringe 6. The metering tube diameter was always chosen so that the drops were one above the other. When the two spherical drops touched each other in the metering tube, the time started to be measured up to the moment when both these particles merged into one. This time is the time of existence of the drops pair. The resulting drop was removed from the metering tube 1 by turning the apparatus into the initial position. The drop from tube 1 came to the tube 7 and the meter was ready for another measurement. From measuring one factor (temperature, concentration or drop size) twenty-five to fifty measurements were made. The above mentioned authors recommend that 30–400 measurements be made.

All described measurements were made with the system toluene–water or aqueous solutions of polyvinyl alcohol (PVA)–toluene. The physico-chemical data of these two liquid phases are given in Table I.

RESULTS

In Fig. 2 are plotted on a probability paper the direct experimental data for regions of drop diameters which were studied by our meter. It is obvious from this plot that for the drop coalescence measurements made by our meter the measured data do not

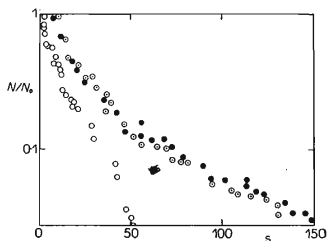


FIG. 3

Time of Drop Existence t in Dependence on Logarithm of Relative Frequency
Symbols used are the same as in Fig. 2.

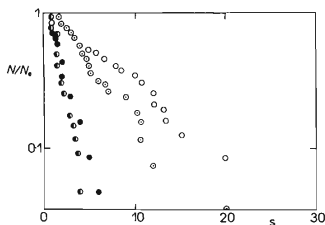


FIG. 4

Comparison of Drop-Drop (○, ⊙) and of Drop-Liquid Surface, (●, ⊙) Measuring Methods for d_k 4.8 mm and d_k 3.8 mm

fit the normal Gauss distribution. From the shape of histograms based on these data the distribution is more close to the binomial one. If these experimental data are plotted in the semilogarithmic plot as is usual with other authors the dependence is of the type given in Fig. 3.

In Fig. 4 are plotted the experimental data of coalescence measured by our meter (drop-drop) and by meters of other authors (drop-liquid surface). This Figure makes possible the comparison of results obtained by both methods at the same experimental

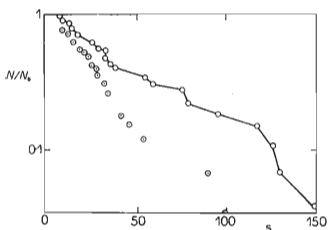


FIG. 5

Dependence of Relative Frequency of Times of Existence of Pairs of Particles

$d_k = 2.9$ mm, $c_{PVA} = 0.5$ weight %; ● at 20°C, ○ 80°C.

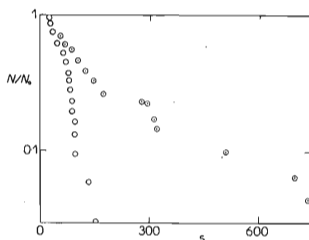


FIG. 6

Dependence of Relative Frequency of Times of Existence of Pairs of Particles

$d_k = 1.7$ mm, $c_{PVA} = 0.5$ weight %; ● at 60°C, ○ at 80°C.

TABLE I

Properties of Liquids Used

Liquid	Concentration weight %	Density $g\ cm^{-3}$	Viscosity cP	Surface tension $dyn\ cm^{-1}$	Refractive index n_{20}
PVA ^a	0.01	0.9987	0.938	21.41	—
PVA	0.1	1.0090	1.057	16.30	—
PVA	0.5	1.0004	1.920	14.63	—
PVA	1	1.0090	2.324	12.08	—
PVA	3	1.0064	16.910	7.19	—
Toluene	pure	0.8671	0.65	—	1.4931

^a Polyviol W 25/140, Farben Fabriken Hoechst, Frankfurt a. Main.

TABLE II
Summary of Experimental Results

Particle diameter mm	PVA concentration weight %	Temperature °C	Mean time of existence s
2.9	0.50	20	49.71
3.5	0.01	20	33.30
3.5	1.01	20	85.27
4.8	0.01	20	10.44
2.7	0.01	40	23.32
2.7	0.50	40	77.24
2.9	0.50	40	18.48
2.9	1.00	40	187.39
3.5	0.01	40	14.51
3.5	1.00	40	34.32
3.5	2.00	40	417.02
2.2	0.01	50	57.53
2.7	0.50	50	30.98
2.7	0.50	50	32.84
1.7	0.10	60	49.80
1.7	0.50	60	182.77
2.2	0.01	40	56.05
2.7	0.01	60	15.03
2.7	0.50	60	25.21
2.7	0.50	60	26.08
2.7	1.00	60	350.68
2.9	0.50	60	11.99
2.9	1.00	60	79.77
3.5	0.01	60	6.86
3.5	1.00	60	15.96
3.5	2.00	60	112.30
2.2	0.01	70	23.70
2.2	0.50	70	208.45
2.7	1.00	70	173.07
1.7	0.10	80	28.95
1.7	0.50	80	53.37
2.2	0.01	80	5.39
2.2	0.50	80	70.84
2.7	0.01	80	5.26
2.7	0.50	80	11.84
2.7	0.50	80	12.15
2.7	1.00	80	41.50
2.7	2.00	80	69.92
3.5	1.00	80	10.74
3.5	2.00	80	70.90

conditions. From these dependences is obvious that measurements made with the system drop-drop gives at the same physical conditions higher values of time existence than the measurements made with the system drop-liquid surface. As is obvious from this figure these results are so different that we have not made the statistical test of significance of differences measured by both mentioned methods. From these results we may expect for the system drop-drop longer times of drop existence and their larger spread than for coalescence in the system drop-liquid surface. On this basis we may conclude that the coalescence of two drops slightly differs from the coalescence drop-liquid surface. This is also the reason of our efforts to approximate by this modelling the conditions in a continuous polymerization reactor as closely as possible.

The times of existence of toluene drops were measured at temperatures from 20°C to 80°C. The drop diameters measured for pairs of drops were in the range of levels $d_k = 1.2$ mm, 1.7 mm, 2.2 mm, 2.7 mm, 2.9 mm, 3.5 mm, and 4.8 mm. Each experiment at a certain combination of individual factors was repeated at least 25 times. From this number of measurements the average values of times of existence of a pair of particles were calculated in dependence on temperature, PVA concentration and on drop size. Our most important results are summarized in Table II which gives the mean times of existence of pairs of spherical particles obtained as averages of measurements made at a certain combination of three basic factors. For a graphical presentation of results measured in individual series a semilogarithmic plot was used.

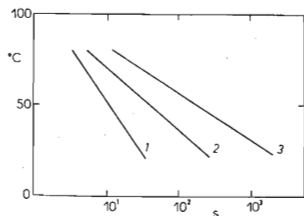


FIG. 7

Dependence of Mean Time of Existence on Temperature

- 1 $d_k = 2.9$ mm, $c_{PVA} = 0.5$ weight %;
- 2 $d_k = 2.7$ mm, $c_{PVA} = 0.5$ weight %;
- 3 $d_k = 1.7$ mm, $c_{VAP} = 0.01$ weight %.

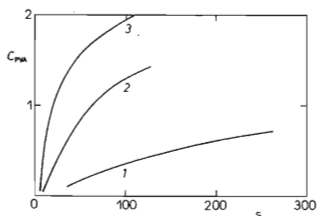


FIG. 8

Dependence of Mean Time of Existence on PVA Concentration

- 1 $d_k = 1.7$ mm, $T = 80^\circ\text{C}$;
- 2 $d_k = 2.2$ mm, $T = 60^\circ\text{C}$;
- 3 $d_k = 3.5$ mm, $T = 60^\circ\text{C}$.

The typical dependences selected from number of measurements are plotted in Fig. 5 and 6. For a strict connection of individual experimental points a zig zag line plotted on Fig. 5 is obtained. Similar character of experimental dependences is mentioned in papers of some other authors⁶.

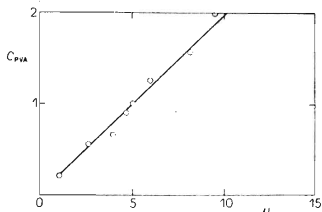


FIG. 9

Dependence of Relative Particle Size on PVA Concentration for Mean Time 100 s of a Pair Existence

In Fig. 7 is plotted the dependence of the mean time of existence on temperature for different drop diameters at a constant concentration of PVA solution 0.1 weight %. From that is obvious that with a decreasing diameter of dispersed particles their time of existence is significantly prolonged. A similar characteristic dependences have the solutions with concentrations of PVA 0.01, 0.5 and 1.0 weight %.

The dependence of the mean time of existence of particles on PVA concentration at other parameters constant. From Fig. 8 is obvious that the stabilizing effect of PVA solutions is decreasing with an increasing particle diameter. From the dependence in this and other similar figures which may be plotted from the experimental data, an effort was made to derive a new relation. If at constant temperature the mean time of existence 100 s is taken as a basis and if the particle diameter is related to the diameter of the smallest measured particle 1.7 mm, we obtain the dependence given in Fig. 9. From this graph it may be assumed that there is a direct proportionality between the PVA concentration of solutions and the third power of ratio of particle diameters. This means that the concentration of PVA solutions by which a stabilizing effect for dispersion is obtained is in direct proportionality to the particle volume.

LIST OF SYMBOLS

t	time of drop existence [s]
c_{PVA}	PVA concentration [weight %]
d_k	drop diameter [mm]
T	temperature [°C]
N	number of drops which have not merged
N_0	total number of measured drops
P	frequency of occurrence
$u = d_k^3/d_{k,\text{min}}^3$	relative drop size

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