DROP COALESCENCE. II.*

THE SYSTEM: WATER–TOLUENE
MATHEMATIC-STATISTICAL EVALUATION
OF DROP COALESCENCE

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This paper presents the dependence of rate constant of drop coalescence on drop diameter, on concentration of the stabilizer, and on temperature and further the comparison of model and experimental values. For testing the effect of these variables was chosen the method of linear and quadratic regression dependences.

The coalescence process is at best characterized by rate constants calculated from the power model.

The study of drop coalescence in a two-phase system concentrates on the change in quantity of confluenced particles with time, as it was mentioned in our previous paper. We are dealing with the effect of temperature, drop size, and concentration of polyvinyl alcohol (PVA) on the time of existence of drop-pairs in the water–toluene system. Such factors as drop deformation, pressure effect, effect of the medium undulation, eventually the effect of electric or other fields on the coalescence of particles are not considered.

Cockbain and McRoberts[1] found the dependence for the above mentioned process in the medium stabilized with soap which can be written in form of equation

$$\lg N/N_0 = -kt . \qquad (1)$$

Constant k in Eq. (1) represents the rate constant. Large values of k indicate a sharp distribution of life times. Graphical presentation of the dependence (1) gives in actual cases a curve which systematically deviates from a straight line[2–4]. Gillespie and Rideal[5] derived for probability of drop coalescence the differential equation

$$-(1/N)\,(dN/dt) = K(t - t_0)^{1/2} , \qquad (2)$$

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where the rate constant K is a function of drop radius, interphase tension, liquid viscosity, temperature etc. Solution of the differential equation (2) can be written as

$$\ln (N/N_0) = -K(t - t_0)^{3/2} . \tag{3}$$

Nielsen and coworkers[2] introduce the half-life time $t_{1/2}$ which is in general easier to reproduce than the minimum t_{min} or maximum t_{max} life-times of drops. The effect of concentration of the stabilizing agent on the half-life of the drop existence is described by these authors by a simple equation

$$t_{1/2} = mC^n , \tag{4}$$

where C is concentration of the stabilizing agent, m and n are empirical constants. Value of constant n varies usually from 0·3 to 0·45. By the use of half-life time, the shortest and the longest life time can be approximated by value of the rate constant in the Cockbain-McRoberts equation (1). By Nielsen[2] we may write it either

$$k = 3/(t_{max} - t_{1/2}) \tag{5}$$

or in the form

$$\log k = 0·279 - 1·013 \log (t_{1/2} - t_{min}). \tag{6}$$

Equation (6) was obtained by statistical processing of a great number of data. Further we try to express the rate constant as a function of drop diameter, concentration of the stabilizing agent and of temperature.

THEORETICAL

Differential equation which describes the change in the number of coalesced particles (drops) N in the time t is written in a general form

$$dN/dt = f(t, N/i, P_i) , \tag{7}$$

in which the functional $f(t, N/i, P_i)$ on the right side is a non-specified function of time t, number of coalesced drops N, and i parameters of P_i which determine the coalescence process. Let us assume that the functional $f(t, N/i, P_i)$ is continuous and limited in the two-dimensional range of solutions $D(t, N)$ and that in this range is fulfills the Lipschitz condition[6,7]. With these assumptions fulfilled it is secured that through each point of range $D(t, N)$ passes just one solution of differential equation (7). Fulfillment of above mentioned conditions also secures the expansion of solutions of equation (7) into power series (8) and, *vice versa*, that power series (8) is the solution of equation (7):

$$N/N_0 = \sum_{j=0}^{\infty} a_j t^j. \tag{8}$$

In practical cases of rapid convergence of the power series (8), we can limit ourselves to only several of the lowest members of the series. From the form of solution (8) is obvious that the expansion coefficients a_j are functions of the existing determination parameters P_1. We consider in this work 3 parameters: diameter of confluenced drops $P_1 = d$, concentration of the stabilizing agent (polyvinyl alcohol) $P_2 = c_{PVA}$ (mass percent) and temperature of medium $P_3 = T(°C)$. Thus we can write

$$dN/dt = f\left(t, N/d, c_{PVA}, T\right),$$

$$y = N/N_0 = \sum_{j=0}^{k} a_j t^j, \qquad (9)$$

$$a_j = a_j(d, c_{PVA}, T),$$

where k is the final integer number.

The rate v of drop coalescence determined in equations (1) and (2) by use of the rate constant k, can be described in case of solution by the power series

$$v = \sum_{j=0}^{n} j a_j t^{j-1}, \qquad (10)$$

where all symbols have their usual meaning.

When we know the exact expression of the function f on the right side of equation (9) and the initial conditions, we can directly find the exact solution of equation (9) in dependence on existing parameters (diameter of confluencing drops, concentration of the stabilizer and temperature of medium). In case that expression of functional dependence $f(t, N/D, c_{PVA}, T)$ is not known, the expansion coefficients a_j may be determined by least square method from experimental dependences of the number of confluenced drops on time. In this way we obtain a set of expansion coefficients a_j, $j = 0, 1 \ldots, n$ for each three used parameters. For expressing the functional dependence of particular expansion coefficients on diameter of confluencing drops, concentration of the stabilizing agent, and temperature of the medium, we can use for inst. the multiple regression (linear or non-linear). In this way, the combination of the two latter equations in system (9) expresses the general dependence of the course of coalescence on time t and conditioning parameters. This way of expression of the functional dependence of the number of confluencing drops on time, diameter of confluencing drops, concentration of the stabilizer and temperature of the medium is very laborions and the results obtained are not clearly arranged. The above mentioned way of calculation (by use of the Stiefel algorithm[8,10]) does not lead to practically usuable results in the studied system. Far simpler and more effective is the expression of this dependence in the form

$$\ln y = \varkappa t^{\alpha}, \qquad (11)$$

where $\varkappa$ is the rate constant independent on time t, $y = N/N_0$, α is the exponent whose value may differ from that of Cockbain[1] or Gillespie and Rideal[5].

Dependence of the rate constant on determining parameters is assumed in the form

$$\varkappa = k_0 d^{\beta_1} c_{PVA}^{\beta_2} T^{\beta_3} . \tag{12}$$

We determine the constant k_0 and exponents β_1, β_2, and β_3 by the use of multiple linear regression dependence of the rate constant logarithm on diameter of coalescing particles, concentration of the stabilizer and temperature of the medium:

$$\log \varkappa = \log k_0 + \beta_1 \log d + \beta_2 \log c_{PVA} + \beta_3 \log T . \tag{13}$$

Distribution curve of coalesced particles can be thus written in the form

$$\ln N/N_0 = k_0 d^{\beta_1} c_{PVA}^{\beta_2} T^{\beta_3} t^{\alpha} . \tag{14}$$

RESULTS

In studying the coalescence, we have concentrated our attention on coalescence of two spherical particles which are affected by no external force except the upward pressure. The experimental part is a subject of the previous paper[11]. This study deals with mathematic-statistical description of coalescence of two drops according to relations in the theoretical part. Following tables comprise results of elaboration of dependences of times of existence of drops and rate constants on drop diameter d(v mm), concentration of the stabilizer c_{PVA} (mass %) and temperature of the medium $T(°C)$. All numerical calculations were made on the computer NCR Elliott 4130. Table I gives the values of parameters d, c_{PVA} and T, the measured values of the minimum, half, and maximum life times of drops t_{min}, $t_{1/2}$, and t_{max}, further the calculated values of rate constants k_1 (by equation (5)) and k_2 (by equation (6)). Let us note that values of the rate constants calculated by Eq. (6) are more probable than the values k_1 calculated by Eq. (5), because the life times $t_{1/2}$ and t_{min} can be determined with more accuracy than t_{max}. For testing the effect of diameter of coalescing drops, concentration of PVA, and temperature of the medium on life times t_{min}, $t_{1/2}$, and t_{max} of coalescing drops and an expansion coefficients a_i of polynomials, we have chosen the linear and quadratic regression dependences (with interactions between the particular variables).

Table II gives comparison of standard deviations of linear and quadratic regression dependences of life times t_{min}, t_{max} and $t_{1/2}$ on the drop diameter, concentration of the stabilizer and temperature of the medium. The quadratic dependence includes the linear dependence and mutual interactions between the considered parameters. Quadratic dependences have the standard deviations only slightly lower than are the

TABLE I

Lifetimes and Rate Constants k_1 and k_2 at the Coalescence of Two Drops (Equations (5) and (6))

d	c_{PVA}	T	t_{min}	t_{max}	$t_{1/2}$	k_1	k_2
4·8	0·01	20	1·6	47·8	5·1	0·07026	0·5343
4·8	0·01	40	2·2	17·2	6·5	0·28037	0·4338
4·8	0·01	60	1	15	4	0·27273	0·6247
4·8	0·01	80	1	13·8	3·5	0·29126	0·7515
3·5	0·01	20	2·8	157	27·3	0·02033	0·0354
3·5	0·01	40	1·8	108	5·9	0·02318	0·0745
3·5	0·01	60	1	21	4·4	0·02938	0·4550
3·5	0·01	80	1	27	2·6	0·18072	0·5502
3·5	1	20	14	265	71·7	0·12295	1·1810
3·5	1	40	6·8	160	23·5	0·01552	0·0313
3·5	1	60	5·2	53	14·1	0·02198	0·1098
3·5	1	80	2·2	25·4	9·95	0·07712	0·2076
2·5	2	80	6	204·6	57	0·19934	0·2388
2·9	0·5	20	6	161·4	32·2	0·02322	0·0696
2·9	0·5	40	3·8	51·4	16·1	0·08499	0·1496
2·9	0·5	60	3·4	35·8	9·6	0·11450	0·2995
2·9	0·5	80	6·6	100·2	21	0·03788	0·1275
2·9	1	40	47·8	355·2	188·5	0·01800	0·0127
2·9	1	60	2·3	285	55·75	0·01309	0·0338
2·7	0·01	40	2	83·4	8·2	0·03989	0·2994
2·7	0·01	60	1·8	52·5	11·8	0·07426	0·1845
2·7	0·01	80	1·4	16·4	3·6	0·23438	0·8554
2·7	0·5	40	20·4	187·2	69·6	0·02551	0·0367
2·7	0·5	50	5	83	29	0·05556	0·0760
2·7	0·5	60	7	58·2	22	0·08287	0·1312
2·7	0·5	80	3	25·4	11·4	0·21429	0·2204
2·7	1	60	25·2	1 001·2	306·1	0·00432	0·0063
2·7	1	70	6·8	798·6	84·9	0·00420	0·0230
2·7	1	80	7·2	114·4	36·7	0·03861	0·0617
2·2	0·01	50	2	385·4	19·6	0·00820	0·1041
2·2	0·01	60	2·2	357·4	12·6	0·00870	0·1773
2·2	0·01	70	2	150·6	9·4	0·02125	0·2503
2·2	0·01	80	1·6	10·2	5·5	0·63829	0·4789
2·2	0·01	70	25·4	600	188·9	0·00730	0·0109
2·2	0·01	80	18·1	150·4	66·3	0·03567	0·0174
1·7	0·5	60	15·2	816·4	102·4	0·00420	0·0206
1·7	0·5	80	9·8	150·2	61	0·03360	0·0354
1·7	0·1	60	11	125·8	48·6	0·03886	0·0482
1·7	0·1	80	4·2	105·4	27·7	0·03861	0·0776

standard deviations of linear dependences. Standard deviations of quadratic dependences for lifetimes of drops equal approximately to mean values of these times. Table III gives the ratio of regression coefficients for particular parameters b to their standard deviations σ_b for the linear and quadratic type of regression dependences of lifetimes of drops on parameters d, c_{PVA} and T. In both models plays the most important role the concentration of the stabilizer (longest values of ratio $t = b/\sigma_b$) respectively their interactions with the drop diameter and temperature of the medium.

When we express the dependences of rate constants k_1 and k_2 on the diameter of coalescing particles, concentration of the stabilizer and temperature of the medium. equation (13), we obtain — for the value of log k_0 and values of exponents β_1, β_2, and β_3 — values given in Table IV.

TABLE II

Comparison of Standard Deviations at Multiple Linear and Quadratic Regressions

Dependence	Standard deviation		Mean values of independent variable
	linear	quadratic	
t_{min}	8·203	7·384	7·659
t_{max}	203·814	189·898	187·974
$t_{1/2}$	55·597	48·420	44·300

TABLE III

Statistical Significance Tests of Variables in the Linear and Quadratic Models of Regression Dependences

Variable	Linear dependence			Quadratic dependence		
	t_{max}	t_{min}	$t_{1/2}$	t_{max}	t_{min}	$t_{1/2}$
d	2·06	1·89	1·78	0·63	0·86	0·47
c_{PVA}	2·83	3·90	3·75	0·81	3·09	2·51
T	1·35	1·92	1·38	0·20	0·63	0·22
d^2	—	—	—	0·52	0·80	0·41
$d \cdot c_{PVA}$	—	—	—	1·87	3·13	3·28
$d \cdot T$	—	—	—	0·62	0·99	0·70
c_{PVA}^2	—	—	—	2·31	1·25	2·07
$c_{PVA} \cdot T$	—	—	—	0·51	2·50	1·76
T^2	—	—	—	0·68	0·02	0·55

TABLE IV
Power Model of Dependence of Rate Constant of Coalescence on Determining Conditions

Dependence	k_1	k_2
$\log k_0$	$-4\cdot2400$	$-3\cdot2022$
β_1	$2\cdot2412$	$2\cdot1037$
β_2	$-0\cdot1415$	$-0\cdot3049$
β_3	$0\cdot9901$	$0\cdot5906$
t_1	$3\cdot17$	$3\cdot25$
t_2	$1\cdot61$	$3\cdot78$
t_3	$2\cdot15$	$1\cdot40$
Coefficient of multiple regression R	$0\cdot5643$	$0\cdot6880$
Degree of freedom	34	34
Level of statistical significance	$0\cdot1\%$	$0\cdot1\%$
Residual variance	$0\cdot4849$	$0\cdot4441$
k_0	$0\cdot000575$	$0\cdot006278$

First line of Table IV gives the values of $\log k_0$ (see Eq. (13)), the following three lines the values of exponents (β_1 for the diameter of coalescing particles, β_2 for the concentration of PVA, and β_3 for the temperature of the medium, the fifth up to the eight line the significance tests of particular variables (ratio of the regression coefficient to its variance). The ninth and tenth lines give the values of regression coefficient and degree of freedom followed by values of the level of statistical significance found from the tables of critical values (10), residual variance, and finally by the antilogarithm of the rate constant k_0 independent of the considered parameters and of time. The first column of Table IV gives values of regression for dependence of the rate constant k_1 calculated from experimental data according to Eq. (5) — see also Table I; the second column, of rate constants k_2 calculated from experimental data according to Eq. (6) — see Table I. The variance of logarithm of rate constants values k_2 are half the variance to logarithms of rate constants k_1 which is in accordance with the note to Table I. This fact is also confirmed by the significance tests of variables d, c_{PVA} and T.

In the mentioned dependence, the most important are the size of coalescing drops and temperature of the medium, while concentration of the stabilizer in the given type of dependence and at the used values of particular variables is of less importance. We can thus write for the rate constant k_1 calculated from equation (5) the following equation

$$k_1 = 0\cdot000575 d^{2\cdot241} c_{PVA}^{-0\cdot142} T^{0\cdot99} , \qquad (15)$$

and for the rate constant k_2 calculated from equation (6) we may write

$$k_2 = 0\cdot00628 d^{2\cdot104} c_{PVA}^{-0\cdot305} T^{0\cdot591} , \qquad (16)$$

where the notation used is obvious. Let us note that equation (16) is statistically more significant than equation (15) due to providing values of rate constants for the regression. As it can be seen from the last two equations, the values of rate constants k_1 and k_2 are about proportional to the second power of diameter of coalescing spherical drops. The significance of equations (15) and (16) lies in that by use of four constants we characterize the coalescence of particles in a two-phase system. The mentioned equations may be used for estimate of rate constants k from the values of diameters of coalescing drops, concentration of the stabilizer and temperature of the medium even though the lifetimes of drops t_{min}, $t_{1/2}$, or t_{max}, are not known. Let us add that by a suitable expression of dependence of inter-phase pressure on concentration of the stabilizer and temperature, also dependence of the rate constant k on the inter-phase pressure can be expressed. Power equations (15) and (16) are numerically not very suitable for estimate of the rate constant. Table V gives parameters of the linear dependence of the rate constants k_1 and k_2 on ratios of confluencing particle diameters, concentration of the stabilizer and temperature of the medium. Quantities given in Table V are analogous to those in Table IV. Power and linear dependences are statistically significant already in testing on a 0.1% level of statistical significance. Use of the linear dependence has a further advantage as for estimation of values of rate constants no tables are needed which facilitates and speeds up the calculation. Further if we compare values of variances given in Tables IV and V we can see that in the linear model the dependence k_1 has a five-times smaller variance than the power model, while with k_2 the value of ratio of varian-

TABLE V

Linear Model of Dependence of Rate Constants of Coalescences k_1 and k_2 on Determining Conditions

Dependence	k_1	k_2
a_0, absolute term	−0.20694	−0.56990
a_1, coefficient with d	0.06059	0.19769
a_2, coefficient with c_{PVA}	−0.08895	−0.32132
a_3, coefficient with T	0.00279	0.00629
t_1	2.85	6.45
t_2	2.52	6.32
t_3	3.03	4.74
Coefficient of multiple regression R	0.5884	0.8458
Degree of freedom	35	35
Level of statistical significance	0.1%	0.1%
Residual variance S	0.10430	0.15014

TABLE VI

Comparison of Experimental Values of Rate Constants k_1 and k_2 with Values Calculated by the Linear and Power Models

d	c_{PVA}	T	k_1			k_2		
			measured	linear	power	measured	linear	power
4·8	0·01	20	0·0703	0·145	0·0720	0·5343	0·497	0·4062
4·8	0·01	40	0·2804	0·205	0·1430	0·4338	0·617	0·6117
4·8	0·01	60	0·2727	0·265	0·2137	0·6247	0·737	0·7769
4·8	0·01	80	0·2913	0·325	0·2841	0·7515	0·857	0·9209
3·5	0·01	20	0·0203	0·066	0·0355	0·0354	0·240	0·2092
3·5	0·01	40	0·0232	0·126	0·0705	0·0745	0·350	0·3150
3·5	0·01	60	0·029	0·186	0·1053	0·4550	0·470	0·4001
3·5	0·01	80	0·1807	0·246	0·1401	0·5502	0·600	0·4744
3·5	1	20	0·1229	−0·023	0·0185	1·1810	−0·078	0·0514
3·5	1	40	0·0155	0·038	0·0368	0·0313	0·042	0·0773
3·5	1	60	0·0220	0·097	0·0549	0·1098	0·162	0·0983
3·5	1	80	0·0771	0·158	0·0730	0·2076	0·282	0·1166
3·5	2	80	0·1993	0·069	0·0662	0·2388	0·201	0·0943
2·9	0·5	20	0·0232	−0·015	0·0134	0·0696	−0·036	0·0427
2·9	0·5	40	0·0849	0·045	0·0266	0·1496	0·084	0·0642
2·9	0·5	60	0·1145	0·105	0·0397	0·2995	0·204	0·0816
2·9	0·5	80	0·0379	0·165	0·0527	0·1275	0·324	0·0967
2·9	1	40	0·0180	0·009	0·0241	0·0127	−0·076	0·0520
2·9	1	60	0·0131	0·061	0·0359	0·0338	0·163	0·0660
2·7	0·01	40	0·0390	0·077	0·0394	0·2994	0·202	0·1822
2·7	0·01	60	0·0743	0·137	0·0588	0·1845	0·322	0·2316
2·7	0·01	80	0·2344	0·197	0·0782	0·8554	0·482	0·2745
2·7	0·5	40	0·0255	0·033	0·0226	0·0367	0·045	0·0552
2·7	0·5	60	0·0829	0·093	0·0338	0·1312	0·165	0·0702
2·7	0·5	80	0·2143	0·153	0·0449	0·2204	0·285	0·0832
2·7	1	60	0·0043	0·048	0·0306	0·0063	0·005	0·0568
2·7	1	70	0·0042	0·079	0·0357	0·0230	0·065	0·0161
2·7	1	80	0·0386	0·109	0·0408	0·0617	0·125	0·0673
2·2	0·01	50	0·0082	0·076	0·0310	0·1041	0·162	0·1351
2·2	0·01	60	0·0087	0·106	0·0372	0·1773	0·222	0·1504
2·2	0·01	70	0·0213	0·136	0·0433	0·2503	0·282	0·1649
2·2	0·01	80	0·6384	0·166	0·0494	0·4789	0·302	0·1783
2·2	1	70	0·0073	0·048	0·0226	0·0109	−0·035	0·0405
2·2	1	80	0·0357	0·078	0·0257	0·0174	0·024	0·0438
1·7	0·1	60	0·0389	0·68	0·01504	0·0482	0·095	0·0433
1·7	0·01	80	0·0386	0·128	0·0200	0·0776	0·215	0·0532
1·7	0·5	60	0·0042	0·032	0·0120	0·0206	−0·034	0·0265
1·7	0·5	80	0·0336	0·092	0·0159	0·0354	0·086	0·0314

ces is slightly higher. Therefore, we can use for calculation of rate constants k_1 and k_2 empirical equations (17) and (18):

$$k_1 = -0 \cdot 207 + 0 \cdot 061d - 0 \cdot 089c_{PVA} + 0 \cdot 003T, \tag{17}$$

$$k_2 = -0 \cdot 570 + 0 \cdot 198d - 0 \cdot 321c_{PVA} + 0 \cdot 006T, \tag{18}$$

where the meaning of used symbols is evident.

When the equations of the linear and power models are compared mutually we can see that in both cases the rate constant of coalescence increases with the increase of diameter of coalescing particles and with increase of temperature of the medium, while it decreases with the increasing concentration of the stabilizer. In Table VI are given the rate constant k_1 and k_2 predicted by the linear and exponential models in comparison with the experimental values. In accordance with conclusions made from Tables IV and V the rate constants k_2 calculated by the power model express in a better way the character of the coalescence process than rate constants k_1. Negative values of rate constants k_1 and k_2 in the linear model are caused by smoothing the experimental data which at the ends of regions of used parameters neglects the actual character of the process.

LIST OF SYMBOLS

a_i	expansion coefficients of polynomials, coefficients in regression equation; $i = 0, 1, 2, 3$
c_{PVA}	concentration of PVA (mass %)
d	drop diameter (mm)
K, k_1, k_2	rate constants
N	number of not-coalesced drops in time t
N_0	total number of measured drops
t	time
T	temperature (°C)
$t_i = a_i/\sigma_{a_1}$	
t_{min}	minimum life time of drop
t_{max}	maximum life time of drop
$t_{1/2}$	half-life time of drop
β_i	exponents with parameters d, c_{PVA}, T; $i = 1, 2, 3$
σ_{a_1}	standard deviation of the regression coefficient a_i; $i = 0, 1, 2, 3$

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