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# INVESTIGATION OF PHYSICAL DISSOLUTION OF BENZOIC ACID POLYDISPERSE MIXTURE

***Dmytro Symak*[1], *Jaroslaw Gumnitsky*[1], *Volodymyr Atamaniuk*[1, *], *Oleg Nagurskyy*[1]**

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**Abstract**. The dissolving process of benzoic acid polydisperse mixture in the gas-liquid flow has been examined. On the basis of criterial dependence and the theory of local isotropic turbulence the mass-transfer coefficient was determined experimentally and theoretically and their values were compared. Theoretical calculation of polydisperse mixture dissolution was performed during periodic dissolution under variable driving force. Theoretical and experimental results were compared.

**Keywords:** polydisperse mixture, periodic dissolution, mass-transfer coefficient, distribution function.

## 1. Introduction

Benzoic acid ($C_6H_5COOH$), which is widely used in various fields of chemical and food industries, as well as in medicine, is solid crystals of various shapes.

There are different technologies of obtaining this product. At present the main attention is focused at the obtaining of high purity product, development of low-waste technology, increase of resulting product yield and reduction of waste products [1, 2]. Benzoic acid is used for the production of caprolactam, viscose, dyes (aniline blue, anthraquinone dyes), in medicine as an antimicrobial and fungicidal agent. Benzoic acid and its salts – sodium, potassium and calcium benzoates – are used as the preservative in food industry [3, 4].

In most cases, the use of benzoic acid is possible after its dissolution in water, which is the first stage in the technological process. The processes of physical dissolution are well analyzed in the scientific literature. The focus is on defining mass-transfer coefficient and its presentation in the form of criterial equations. All definitions and calculations are based on the analysis of monodisperse phase dissolution, *i.e.* a mixture of particles of the same diameter. For the theoretical calculations some averaged diameter of the solid phase is taken as a typical linear size. In fact, the real polydisperse system is dissolved, that complicates the mathematical modeling of polydisperse mixture dissolution process. In addition, the analysis of dissolution is conducted at a constant driving force. In fact, in the batch reactors the driving force is changed due to the increase in concentration of dissolved component.

Benzoic acid is the starting material to produce many products, most of which are obtained through their dissolution in different solvents. Typically, the process of dissolution is considered in two aspects: the study of solubility and kinetics of the process of analysis methods for intensification.

The solubility of benzoic acid in water at different temperatures is well researched and presented in many references. Values of benzoic acid dissolution in binary mixture of solvent (benzyl alcohol and benzaldehyde) at 298.35–355.65 K and atmospheric pressure are given in [5]. It was determined that at constant composition of binary mixture the increase in temperature increases solubility. The increase in benzaldehyde acid concentrations decreases solubility. Q.Yang *et al.* [6] studied the solubility of benzoic acid depending on temperature; the experimental data are described by the Wilson equation. The authors consider their data to be important for the predicting of organic substances behavior in the environment. The solubility of benzoic acid in ethanol, benzene, ethyl acetate and acetic acid and its mathematical correlation is given in [7]. The problem of dissolving solids of monodisperse and polydisperse composition is focused in monographs [8, 9]. Some aspects of this process are discussed in [10], where the dissolution of polydisperse solid phase in a stationary bed of solid particles is analyzed. Much attention is paid to the dissolution in halurgy technologies, for which it is the first and main stage. Then other stages are required to produce a specific fertilizer composition, mainly potassium [11, 12]. Conducting the process in batch apparatus creates non-stationary aspects, *i.e.* the process is not only described by the spatial coordinates, but also depends on time [13]. In the experimental studies the determination of mass-transfer coefficient is of special attention.

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[1] Lviv Polytechnic National University
12 S. Bandery St., 79013, Lviv, Ukraine
* *atamanyuk@ukr.net*

Previously we determined the mass-transfer coefficient based on local isotropic turbulence [14, 16]. The kinetics of sodium chloride dissolution in carboxylic acid ammonium salts is given in [17]. The kinetics of dissolution is shown to be dependent on the concentration of ammonia characterized by salting-out action. Mathematic dependencies to determine the mass-transfer coefficient are presented. Kinetic peculiarities of solid melts dissolving are given in [18]. The authors proposed an equation for determining the mass-transfer coefficient. The intensification of dissolution process is described in [16, 19]. Non-stationary aspects at the variable driving force in a stationary bed of dispersed material are considered in [15]. Application of the local isotropic turbulence theory requires the external energy necessary to keep the particles in a suspension state and prevent them to be captured by liquid flows. This can be achieved by introducing the gaseous phase into solid–liquid two-phase system, which intensifies the process of dissolution and converts the system into three-phase one [16, 20]. B. Kulikov *et al.* [21] determined the process area (diffusion, transition, kinetic).

The analysis of references shows that the dissolution process was investigated for monodisperse systems. In industry the solid phase is a polydisperse phase which requires new approaches to the process calculation. So, the aim of this work is experimental and theoretical study of non-stationary dissolution of benzoic acid polydisperse mixture in water at an alternating driving force.

To achieve this goal the following tasks were accomplished:

– experimental and theoretical defining of the mass-transfer coefficient for particles of various diameters;

– construction of the particles distribution function relative to their diameters and determination of characteristic function based on kinetic equations and material balance;

– determination of the dissolution degree depending on dimensionless time by means of graphical dependencies.

## 2. Experimental

Experimental study of polydisperse solid phase dissolution was carried out on an experimental setup. Its scheme is shown in Fig. 1. The main part of the setup is a vertical column, with a gas distribution grid in the bottom. The column was filled by 1 dm$^3$ of distilled water and air was fed with a velocity of $1 \cdot 10^{-4}$ m$^3$/s. This velocity corresponds to an intensive stirring and keeping the particles in a suspension state. Taking into account that the column diameter is 0.1 m, air velocity divided by the cross-sectional area of the column is expressed as $n_C = 0.0133$ m/s. Then a sample of polydisperse mixture, which was in a gas-liquid flow in the suspension state, was loaded. Liquid samples were withdrawn every 600 s. The mass-transfer coefficient $b$ was determined by dissolving individual particles of benzoic acid in the gas-liquid environment. The experiments were conducted at 293±0.5 K.

Determination of the mass-transfer coefficient was based on the determination of mass loss of benzoic acid particle in water for definite dissolution time. The process driving force in this case is determined only by the saturation concentration, because the acid concentration is practically zero. Experimental values of the mass-transfer coefficient were determined according to Eq. (1) [8]:

$$b = \frac{\Delta M}{F \cdot C_S \cdot \Delta t} \qquad (1)$$

where $\Delta M$ – weight of the particle dissolved during time $\Delta t$; $F$ – dissolution surface area; $C_S$ – saturation concentration of benzoic acid ($C_S = 2.9$ kg/m$^3$).

Experimental dissolution of particles with different diameters allows to establish that the mass-transfer coefficient for these particles are actually identical, and their averaged value, which was determined experimentally, may be accepted as $b = 3.79 \cdot 10^{-5}$ m/s.

The particles with $d < 6$ mm were selected and 100 g of polydisperse mixture was weighted. Sieve distribution provided the distribution function of the mixture depending on the average diameter of the fraction. Distribution function $F(d)$ is given in mass parts allowing to equate the area under the distribution function curve to one. Table 1 shows the particles distribution relative to their diameters. Points in Fig. 2 show the experimental data about the distribution function of particles of benzoic acid polydisperse mixture.

*Table 1*

**Distribution function of the particles relative to their diameters**

| Particles fraction, mm | 0–1 | 1–2 | 2–3 | 3–4 | 4–5 | 5–6 |
|---|---|---|---|---|---|---|
| Distribution function $F(d)$, mass parts | 0.03 | 0.08 | 0.21 | 0.38 | 0.23 | 0.07 |

*Table 2*

**Kinetics of benzoic acid polydisperse mixture dissolution**

| Sampling time $t$, s | 600 | 1200 | 1800 | 2400 | 3000 | 3600 |
|---|---|---|---|---|---|---|
| Benzoic acid concentration $C$, kg/m$^3$ | 0.21 | 0.45 | 0.61 | 0.75 | 0.92 | 0.98 |

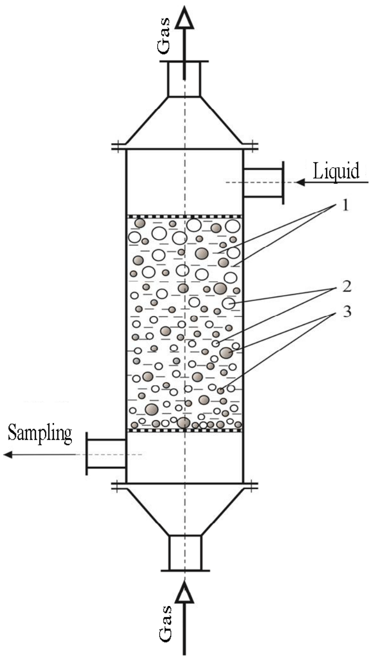

**Fig. 1.** Scheme of the experimental setup: liquid (1); air bubbles (2) and solid particles (3);
1 – continuous phase; 2 and 3 – dispersed phases

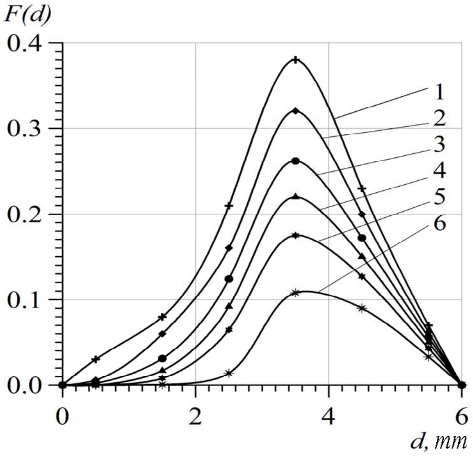

**Fig. 2.** The distribution function of particles relative to their diameter: original size (1); reduction of particle size by the value (mm) of 0.2 (2); 0.4 (3); 0.6 (4); 0.8 (5) and 1.2 (6)

After stead-state conditions were achieved, 10 g of benzoic acid polydisperse mixture was added and stopwatch was turned on. After certain intervals of time (600 s) the acid concentration was measured in the samples. The results are represented in Table 2.

## 3. Results and Discussion

### 3.1. Theoretical Analysis of Mass-Transfer Coefficient Determination during Solid Particles Dissolution

For the theoretical analysis of this type of dissolution it is necessary to establish two aspects. The first aspect is the theoretical determination of mass-transfer coefficient and its comparison with the experimental one. This determination is based on the theory of generalized variables, as well as local isotropic turbulence.

In the first case we found that particles suspension state does not affect the dependence of mass-transfer coefficient on particles size and hydrodynamic situation can be described by the Archimedes number [8]:

$$Sh = 0.28(Sc \cdot Ar)^{0.33} \qquad (2)$$

where $Sh = (\beta \cdot d)/D$ – Sherwood number; $Sc = n/D$ – Schmidt number; $Ar = (g \cdot d^3/n^2) \cdot (r_s - r)/r$ – Archimedes number; $d$ – particle diameter; $D$ – coefficient of benzoic acid molecular diffusion in water at 293 K; $n$ – coefficient of water kinematic viscosity; $r_s$ and $r$ – density of benzoic acid and water, respectively.

As a consequence of Eq. (2), self-similarity occurs, *i.e.* independence of mass-transfer coefficient on particles size.

The obtained values $Ar$ = 21190, $Sc$ = 869.6, $Sh$ = 72.28 allow to determine the coefficient $b = 3.87 \cdot 10^{-5}$ m/s.

The second method to determine mass-transfer coefficient is called the theory of local isotropic turbulence. Turbulence defines the hydrodynamic situation in the system and significantly affects mass transfer and mass transfer coefficient [14]. When comparing isotropic turbulence in devices with mechanical and pneumatic stirring we may assert that it is more possible to achieve isotropic turbulence during the pneumatic mixing due to the uniform distribution of the gas phase in the apparatus cross-section. Mechanical mixing creates non-uniform pulsing of the liquid phase at different distances from the stirring device. Theoretical dependence for determining the mass-transfer coefficient has the form [8]:

$$b = 0.276(e_0 \cdot n)^{0.25} \cdot Sc^{-0.75} \qquad (3)$$

where $e_0 = N/(W \cdot r)$ – dissipation specific energy in the liquid; $N = V_C \cdot \Delta P$ –energy introduced to the liquid per unit of time; $W$ – liquid volume.

Calculated by dependence (3) the mass-transfer coefficient is equal to $3.13\cdot10^{-5}$ m/s. The difference between two theoretical values of $b$ is 19 %. The value determined by Eq. (2) is closer to the experimental value. Whereas the theoretical value is determined for spherical particles, and the actual particles slightly deviate from a spherical shape, we used experimentally determined value $b$ for calculations.

## 3.2. Theoretical Analysis of Polydisperse Mixtures Dissolution

The theoretical description of the dissolution process and its analysis are grounded on the material balance equation:

$$M_0 - M = WC \tag{4}$$

where $M_0$ and $M$ – initial and running masses of the solid phase at time $t$; $W$ – liquid volume; $C$ – salt concentration in the liquid phase.

Kinetic equation for each particle in differential form looks like:

$$-\frac{dM}{dt} = b \cdot F \cdot \left(C_S - C\right) \tag{5}$$

where $F$ – variable surface of the solid phase during dissolution; $C_S$ – salt saturation concentration in water; $b$ – mass-transfer coefficient.

Eq. (5) contains four variables: $M$, $t$, $F$ and $C$. The mass can be expressed through the linear dimensions of the system. For spherical particles the values of $M$ and $F$ may be determined by the diameter:

$$M = N \cdot r_S \cdot \frac{p \cdot d^3}{6}; \quad F = N \cdot p \cdot d^2 \tag{6}$$

where $N$ – number of particles; $d$ – diameter.

Substituting Eq. (6) into Eq. (5) we can write the kinetics equation in the form of:

$$-\frac{d(d)}{dt} = \frac{2 \cdot b}{r_S}\left(C_S - C\right) \tag{7}$$

The equation of material balance can be written in the form that can express the running concentration $C$, variable in time, relative to the parameters of the solid phase:

$$C = C_{\max} \cdot (1 - y) \tag{8}$$

where $y = M/M_0$; $C_{\max} = M_0/W$.

By denoting the change of particle size as $\Delta = d_0 - d$, the kinetic Eq. (7) takes the form:

$$\frac{d\Delta}{dt} = \frac{2 \cdot b}{r_S}\left[C_S - C_{\max} \cdot (1 - y)\right] \tag{9}$$

In Eq. (9) three values $\Delta$, $y$, $t$ are variable, *i.e.* apart from time and particle linear dimensions, the concentration is changed. In the mass-transfer equation it expresses a variable driving force. The solution of this equation can be obtained by using a graphical distribution function.

In Fig. 2 the distribution function 1 shows the particles distribution at the initial time when the diameter of every fraction corresponds to the initial diameter $d_0$. The area under the *curve* 1 multiplied by the appropriate scale is equal to 1, *i.e.* the mass fraction of all particles is equal to 1. Taking into account the independence of mass-transfer coefficient on the particles size (Eq. (2)), the reduction of solid particles size for time $t$ by the value $\Delta$ is identical for all sizes of solid phase. At the same time the particles with the size less than $\Delta$ are fully dissolved. The mass of all particles which remain at time $t$, is decreased by the value proportional to the particle size in the third degree $((d_0 - \Delta)/d_0)^3$.

The distribution function for any value of the particles diameter is equal to:

$$F\left(d_i\right) = F\left(d_0\right)\left(\frac{d_0 - \Delta}{d_0}\right)^3 \tag{10}$$

In Fig. 2, apart from for the initial distribution function (*curve* 1), we plotted a distribution function for five values of $\Delta$. The areas under distribution curves 2, 3, 4, 5 and 6 are numerically equal to the mass fraction of solid phase remained after dissolving and decrease in the particles diameter by appropriate value $\Delta$. The value of the mass fraction is defined as:

$$y = \int_{\Delta}^{d_{\max}} \left(\frac{d_0 - \Delta}{d_0}\right)^3 \cdot F\left(d_0\right) \cdot d\left(d_0\right) \tag{11}$$

Eq. (11) is a characteristic function because it is fully determined by the initial distribution of the particles according to their size $F(d_0)$. The characteristic functions is represented as a relationship $(1–y) = f(\gamma)$, where $\gamma = \Delta/d_{0\max}$.

This presentation allows you to submit parameters of the process in a dimensionless form. The value of $d_{0\max}$ means the diameter of spherical particles, which corresponds to the maximum on the curve of decomposition function. Fig. 3 shows a characteristic function as a curve, which represents the share of dissolved benzoic acid, depending on the dimensionless simplex $\gamma$.

It is possible to establish the theoretical dependence *via* Eq. (9), which can be represented by the following differential equation:

$$d\left(\frac{\Delta}{d_{0\max}}\right) = \frac{2 \cdot b \cdot C_S}{r_S \cdot d_{0\max}}\left[1 - \frac{C_{\max}}{C_S} \cdot (1 - y)\right] \cdot dt \tag{12}$$

After introducing dimensionless complexes $t = 2^{x}b^{x}C_S^{x}t/(r_S^{x}d_{0\max})$; $\gamma = \Delta/d_{0\max}$; $w = C_{\max}/C_S$, Eq. (12) is written in the dimensionless form:

$$\frac{dg}{dt} = 1 - w\left(1 - y\right) \tag{13}$$

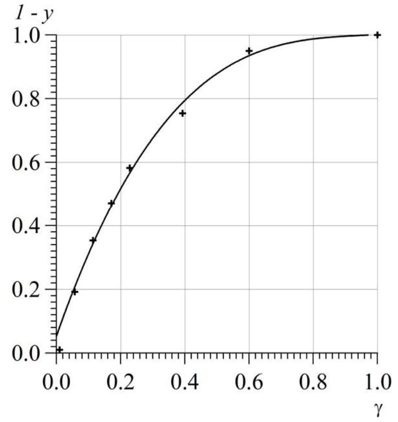

**Fig. 3.** Characteristic function 1–*y* = *f*(*g*) for polydisperse mixture of benzoic acid during its dissolution

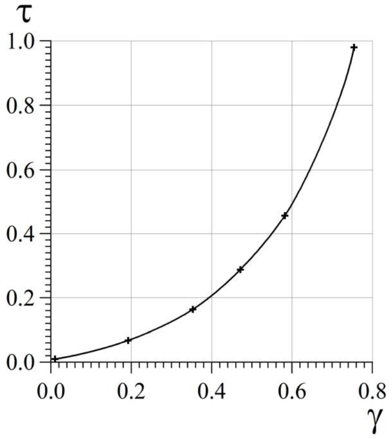

**Fig. 4.** Dimensionless time *vs*. particles relative size

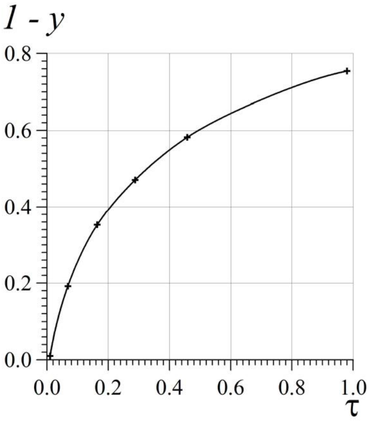

**Fig. 5**. Dissolution degree *vs*. dimensionless time

From Eq. (13) we can determine the time of dissolution $\tau$ at which the degree of dissolution (1–*y*) is achieved:

$$t = \int \frac{dg}{1-w\left(1-y\right)} \tag{14}$$

Polydisperse mixture dissolution $\omega$ is conducted with the initial mass $M_0$ = 10 g in the liquid volume $W$ = = 4.0 m$^3$, and is equal to 0.862.

Using the values of characteristic function (Fig. 3) we calculate the integrand in Eq. (14) for the values (1 – $\gamma$) and find magnitude dimensionless time $\gamma$ depending on $\gamma$. It is graphically presented in Fig. 4.

We obtained the values of the characteristic function (1–*y*) = $f(\gamma)$ and $\gamma = f(\tau)$ for the polydisperse mixture. The calculated value of (1–*y*) = $f(\tau)$ is shown in Fig. 5.

## 3.3. Dissolution of Benzoic Acid Polydisperse Mixture

Experimental results about the concentration of dissolved benzoic acid as a function of time are shown in Table 2, compared with theoretically calculated values. Theoretically calculated values of dissolution degree (1–*y*) as a function of dimensionless time which are shown in Fig. 4, can be recalculated for the concentration of benzoic acid *C* and real time *t*. The transition from the dissolution degree to the concentration is determined by Eq. (15):

$$C_t = \frac{\left(1-y\right)\cdot M_0}{W} \tag{15}$$

The transition from dimensionless time $\tau$ to real time *t* occurs in accordance with Eq. (16):

$$t = \frac{r_S \cdot d_{0\max}}{2 \cdot b \cdot C_S} \cdot t \tag{16}$$

All theoretically calculated values of concentrations depending on time are plotted as a curve (Fig. 6). The experimental values are given in Table 2 and plotted as points in Fig. 6.

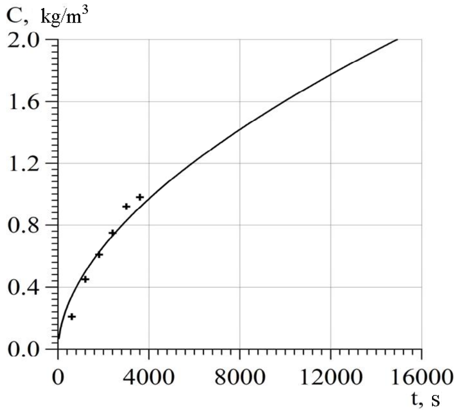

**Fig. 6.** Comparison of theoretically calculated values of benzoic acid concentration (curve) with the experimental values (points)

There is a satisfactory coincidence between calculated and experimental values; the average deviation does not exceed 9 %. Using this method of calculation, we can calculate the time of dissolution, the value of which is necessary when calculating the volume of the device. For example, reducing the size of the particles by $\Delta$ = 1.2 mm demands time of 15400 s; the concentration of benzoic acid in water will be 1.855 kg/m$^3$.

## 4. Conclusions

1. The process of dissolving benzoic acid polydisperse mixture in the gas-liquid system was studied,

mass-transfer coefficient was determined ($b = 3.79 \cdot 10^{-5}$ m/s), its independence on the particles size was confirmed. Theoretical values were calculated on the basis of local isotropic turbulence theory and criterial dependence. The comparison of theoretically calculated and experimentally determined average values showed their satisfactory coincidence.

2. Characteristic function of mass particles depending on dimensionless diameter was determined and plotted on the basis of distribution function curves according to the particles diameter. The method of graphic calculation for the dissolution process of benzoic acid polydisperse mixture at variable driving force was developed and the efficiency of its application was shown to calculate complex processes of solid phases polydisperse mixtures dissolution at variable driving force.

3. The dissolved compound concentration was calculated depending on time and its satisfactory coincidence with experimental data was confirmed. The method can be used for theoretical calculation of polydisperse mixtures dissolution.

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## ДОСЛІДЖЕННЯ ФІЗИЧНОГО РОЗЧИНЕННЯ ПОЛІДИСПЕРСНОЇ СУМІШІ БЕНЗЕНОВОЇ КИСЛОТИ

***Анотація.*** *Розглянуто процес розчинення полідисперсної суміші частинок бензенової кислоти у газорідинному потоці. Експериментально та теоретично на основі критеріальної залежності та теорії локальної ізотропної турбулентності визначено коефіцієнт масовіддачі та порівняно їх значення. Виконано теоретичний розрахунок розчинення полідисперсної суміші під час періодичного розчинення за умови перемінної рушійної сили. Дано порівняння теоретичних та експериментальних результатів.*

***Ключові слова:*** *полідисперсна суміш, періодичне розчинення, коефіцієнт масовіддачі, функція розподілення.*