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Experimental Determination of Mass Transfer Coefficients in Dissolution Processes

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Abstract: In this paper it is followed the influence of several parameters (substance nature, hydrodynamic conditions, temperature, compacting pressure) over the dissolution process and it is calculated the total mass transfer coefficients. The substances used in experimental determination are: acetylsalicylic acid, citric acid, sodium benzoate, sodium chloride, Penicillin G-potassium salt, and pentaerythriol, respectively. The microcrystalline material was compacted in tablets shape, with or without conditioning addition.

Keywords: dissolution, mass transfer coefficient

1. Introduction

The first approach to explain the dissolution rate of a solid was developed by Noyes and Whitney. They claimed the dissolution rate to be proportional to the difference between bulk concentration and concentration at the dissolving interface. Nernst introduced the diffusion layer model. They assumed that dissolution at the solid-liquid interface is rapid and transport of the solute to the bulk is completely determined by diffusion through a stagnant boundary layer surrounding the dissolving interface. The dissolution rate of a solid is then given by:

$$\frac{dm}{dt} = A \cdot \frac{D}{\delta} \cdot \left(C^* - C\right) \qquad (1)$$

in which dm/dt is the dissolution rate ($kg \cdot s^{-1}$), A represents the area available for dissolution, D the diffusivity of the dissolving compound in the solvent, δ the thickness of stagnant boundary layer, C^* is the equilibrium solubility and C is the concentration in the bulk [1].

Nernst theory has the disadvantage that the thickness of the diffusion layer, respectively its dependence of the liquid rate and dissolved mass flow, cannot be calculated with this theory. The subsequent studies have determined the dependence between the diffusion layer thickness and liquid rate :

$$\delta = \frac{1}{v^n} \qquad (2)$$

where :

v - liquid rate ($m \cdot s^{-1}$) and n - exponent depending on the experimental conditions, n∈ (0,5÷1).

Dissolution is a physico-chemical process which spread in two stages:

-at the solid-liquid contact surface take place the passing of the component from the solid phase into the liquid phase (component dissolution by bonds burst inside it);

- from the contact surface the component spread into the liquid phase volume (mass transfer of the component by liquid phase). The propagation of solid component molecules between the dissolving molecules depends on its polarity and leads to new solvent-solute bonds.

Comparing the rates of the two elementary processes it is possible to establish the rate determining elementary process [2].

The dissolution of solide substances in solvents is encouraged by the temperature increase, the grows of contact surface, by stirring and particles dimensions decrease. Not all substances have the same solubility. This parameter depends generally by the compound intern structure, and presents different variations with temperature.

The dissolution process involves mass transfer accordingly the relation:

$$\Delta m = K \cdot A \cdot \Delta c \cdot \tau \qquad (3)$$

where:

Δm - amount of dissolved substance, (kg) ;

K - total mass transfer coefficient , ($kg \cdot m^{-2} \cdot s^{-1}$) ;

A - contact surface, (m^2) ;

$\Delta c = c^* - c$, difference between the equilibrium concentration (saturation) and the real substance concentration in solvent, ($kg \cdot kg^{-1}$) ;

τ - dissolution time, (s) [3].

Comparing the relations (1) and (3) it emphasize the direct proportionality between the total mass transfer coefficient K and the diffusion coefficient (D) and the inverse proportionality with the thickness of diffusion layer (δ).

The partial mass transfer coefficients are entailed by Sherwood criterium, *Sh* :

$$Sh = \frac{k_{l,s} \cdot d_{ech.}}{D_l} \tag{4}$$

in which :

$k_{l,s}$ - partial mass transfer coefficient, ($kg \cdot m^{-2} \cdot s^{-1}$) ;

$d_{ech.}$ - granule equivalent diameter, (m);

D_l – solid-liquid diffusion coefficient, ($m^2 \cdot s^{-1}$).

The system physical properties are represented by Schmidt criterium, *Sc* :

$$Sc = \frac{\rho_l}{D_l \cdot \eta_l} \tag{5}$$

where:

ρ_l - liquid density, ($kg \cdot m^{-3}$) ;

η_l - liquid dynamic viscosity, ($kg \cdot m^{-1} \cdot s^{-1}$).

The dependence between the *Sh* criterium, *Sc* criterium and hydrodynamic conditions *Re*, are represented by the general relation:

$$Sh = a \cdot \mathrm{Re}^b \cdot Sc^c \tag{6}$$

where *a*, *b* and *c* represents the system specific constants [4-8].

For different particulary situations at the dissolution of benzoic acid in water are proposed the following relations:

- Benzoic acid tablets (Re=2.10^4÷ 10^5):

$$Sh = 3{,}3 \cdot \mathrm{Re}^{0{,}55} \cdot Sc^{0{,}3} \tag{6.1}$$

- Benzoic acid granules (Re=10^4÷10^6):

$$Sh = 0{,}052 \cdot \mathrm{Re}^{0{,}83} \cdot Sc^{0{,}5} \tag{6.2}$$

2. Materials and methods

The features of tablets obtained from the substances whose dissolution behavior was studied are presented in Table 1.

TABLE 1. Features of tablets which contain the studied substances

Substance	Dimensions, d_0 x h_0 [mm]	Volume, V x 10^8 [m^3]	Equivalent diameter $d_{ech.}$ [mm]	Area, A_0 x 10^4 [m^2]	Mass, m_0 [g]	Density,ρ [kg/m^3]
Acetylsalicylic acid	9,75 x 9,0	6,72	10,8	4,25	0,9833	1465
Citric acid	9,75 x 9,5	7,09	11,1	4,40	1,0830	1530
Sodium benzoate	9,75 x 9,8	7,31	11,2	4,50	0,9800	1340
Sodium chloride	9,75 x 8,0	5,97	10,4	3,94	1,2316	2060
Penicillin G, potasium salt	9,75 x 2,9	2,16	3,45	2,37	0,3000	1390
Pentaerytrite	9,75 x 11,0	8,21	11,6	4,86	1,1008	1340

The samples for analyse were obtained by powdery material pressing in cylindrical stamps at the reference pressure of P_1=700 MPa (7000 atm).

Equivalent diameter was considered as the diameter of a spherical granule with volume equivalent with that of the tablet, and the density of tableted substances has been calculated from its mass and volume.

Tablets dissolution is realized in a certain water amount (100 g), at t=20°C, tablets being arranged in a parallelipipedic nacelle (50 x 20 x 10 mm) with holey walls, fitted on the stirrer shaft with a well determined stirring rate (1÷27 rot x min^{-1}), which allows the estimation of hydroynamic conditions (Reynolds number-Re),figure 1.

The contact surface is considered as mid-range between the value A_0 coresponding to the initial dimensions and the one resulting by mass decrease, Δm_1, as a result of the dissolution in time $\Delta\tau_1$. At cylindrical tablets, considering the proportionality between the height and the diameter (h=a·d), the corrected area value is:

$$A_1 = A_0 \cdot \left(\frac{m_0 - \Delta m_1}{m_0} \right)^{2/3} \tag{7}$$

For mass transfer total coefficient detemination K it is used the relation (3). The amount of dissolved substance Δm_1 was determined by weighting at several spells $\Delta\tau$ and by spectrofotometry (in case of Penicilline G potasium salt).

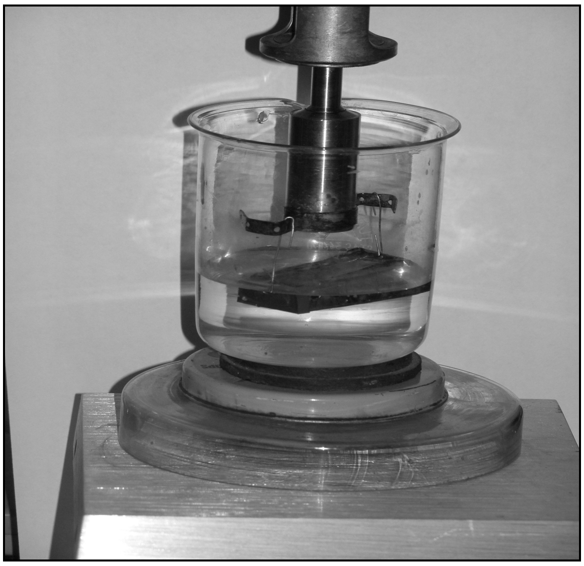

Figure 1. Experimental equipment

3. Results and discussion

3.1. The influence of hydrodynamic conditions

To established the criterial equations of the vessel-stirrer system was realised an experimental equipment which allows the measurement of the stirring rate n, torsion moment M_t (so the resistance force F_{rez}) and of consumed power during the stirring process ***P***, with system adaptation to a Rheotest-2 rotational viscosimeter. With this experimental determinations can be calculated the Reynolds (**Re**) and Euler (**Eu**) criteria at stirring and their corelation. The dependence relation is:

$$Eu = c \cdot \mathrm{Re}^{-m} \tag{9}$$

where :

$$\mathrm{Re} = \frac{n \cdot d^2 \cdot \rho}{\eta}; \qquad Eu = \frac{P}{\rho \cdot n^3 \cdot d^5}$$

$$P = 2\pi \cdot n \cdot M_t; \qquad M_t = F_{rez} \cdot \frac{d}{2} \tag{10}$$

where :

c, m - characteristic constants for pot-stirrer system
n - stirring rate , s^{-1}
d - stirrer diameter, m
η - medium viscosity, Pa s
P - consumed power, W
M_t - torsion moment, N m
ρ - medium density, kg .m^{-3}
F_{rez}- stirring resistance force, N

The constants c and m are obtained by plot lgEu = f (lgRe) of logaritmic equation:

$$\lg Eu = \lg c - m \cdot \lg \mathrm{Re} \tag{11}$$

The characterization of stirring system is realized for water at t= 20˚C, for which $\rho = 1000\, kg \cdot m^{-3}$ and dynamic viscosity is $\eta = 1\, cP = 1 \cdot 10^{-3}\ Pa \cdot s$.

For the stirring system which contains a cylindric vessel with diameter of D = 80 mm and height of H = 95 mm, and a stirrer with diameter of d = 50 mm, D/d = 1,6, respectively, the particular form of ecuation (11) is:

$$\lg Eu = 5.726 - 1.484 \cdot \lg \mathrm{Re} \tag{11.1}$$

and the constants values are: *c = 532108,3* and *m = 1.484.*

The influence of hydrodynamic conditions over the dissolution of Penicillin G potasium salt tablets was studied in two cases:

a) the tablets were placed in nacella with holey walls fitted on the stirrer shaft;

b) the tablets were placed to the bottom of the vessel, and the liquid was involved in a speed of revolution with the help of a blender with two holey palettes inclined at 45°.

In figure 2 is represented the Penicillin G potasium salt mass variation, when the tablets are placed in nacella, at two stirring intensities.

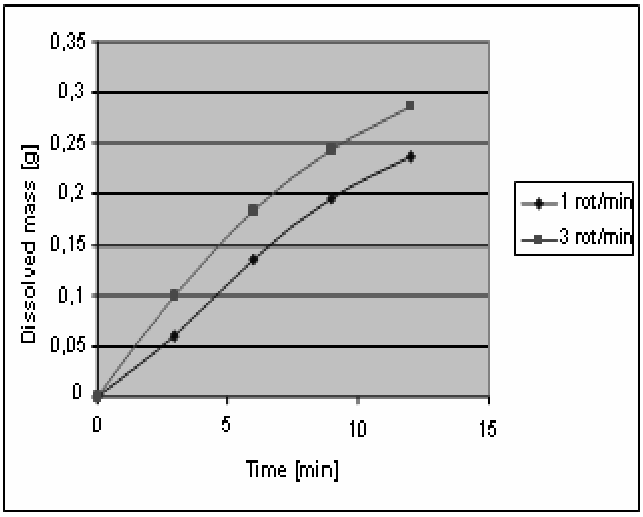

Figure 2. The influence of the hydrodynamic conditions over the dissolution process of Penicillin G potasium salt (case a)

From the figure 2 is find that the intensification of the hydrodynamic conditions has a favorable effect over the dissolution process.

In the second case is find a less significant influence of the hydrodynamic conditions over the tablets dissolution (figure 3).

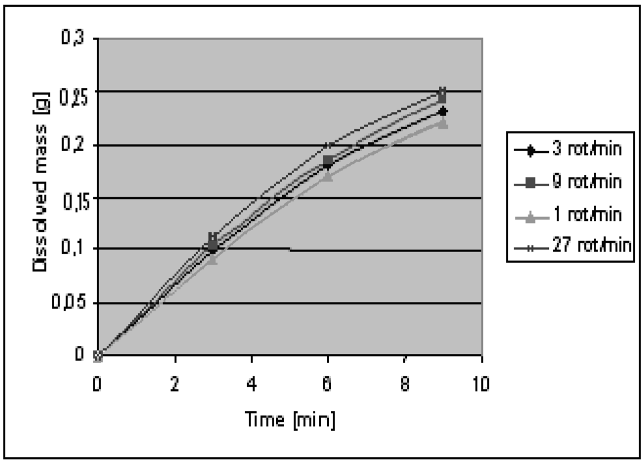

Figure 3. The influence of the hydrodynamic conditions over the dissolution process of Penicillin G potasium salt (case b)

Studying comparatively the dissolution process of Penicillin G potasium salt in that two cases, at the same stirring rate values, is observed that the mass transfer is intensified when the tablets were placed to the bottom of vessel. This is confirmed both the dissolved substance amount in the same speel and the values of mass transfer coefficients K (Table 2).

Comparing the values of total mass transfer coefficient at dissolution K, is observed that the intensifying of hydrodynamic conditions, by stirring rate increase, has a favorable effect over the dissolution process, increasing the K coefficient value.

TABLE 2. Mass transfer coefficient K values determinated in those two cases : a) and b) at Penicillin G potasium salt dissolution

Disolution method	Stirring rate, n [min^{-1}]	Dissolved mass Δm_1, [g]	Time $\Delta\tau$, [s]	Surface $A_m \cdot 10^4$ [m^2]	Sat. conc. C^* [kg/kg]	Real conc. C [kg/kg]	Coef. K 10^3 [kg/m^{2}s]
Tablet in nacella	1	0,1054	360	2,06	0,10	0,0010	14,6
	3	0,1840	360	1,84	0,10	0,0018	28,4
Tablet on pot base	1	0,1810	360	1,72	0,10	0,00181	29,8
	3	0,1857	360	1,75	0,10	0,00186	30

3.2. The influence of compacting pressure

The influence of this parameter is studied for the sodium benzoate tablets, tablets that were obtained by powdery material pressing in cylindrical stamps at the reference pressure of P_1=700 MPa and P_2=350 MPa. The oil primary pressure for hydraulic action was p_1= 50 at (5 MPa), p_2=25 at (2,5 MPa), respectively.

From the amounts of dissolved substance in pre-established speels, as well from the decrease of solid-liquid contact surface were calculated the total mass transfer coefficients K, that are presented in Table 3.

TABLE 3. Mass transfer coefficients for sodium benzoate dissolution in water

Stirring rate, n [min^{-1}]	Pressure P [at]	Mass Δm_1 [g]	Time $\Delta\tau$ [s]	Surface $A_m \cdot 10^4$ [m^2]	Sat. conc. C^* [kg/kg]	Real conc. C [kg/kg]	Coefficient K 10^3 [kg/m^{2}s]
3	50	0,9846	600	7,30	0,63	0,0098	3,62
	20	1,0261	600	7,20	0,63	0,0103	3,83

It can be observed that the tablets compacting degree hasn't a significant influence over the amount of dissolved substance and, implicitly over the total mass transfer coefficient.

3.3. The influence of substance nature

The influence of substance nature over the dissolution process is studied experimental for three substances that are different in what concerning the solubility degree in water and the domain where they are applicable.

In figure 4 is represented the evolution in time of the dissolved mass for citric acid, NaCl and Penicillin G potasium salt (PGK).

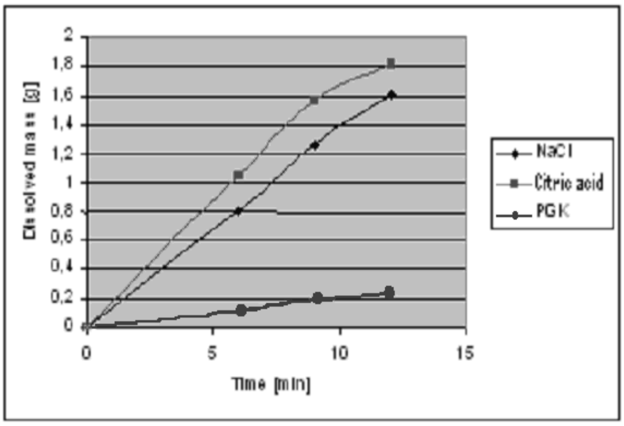

Figure 4. The influence of substance nature over the dissolution process

It can be observed that exist a very good correlation between the amount of dissolved substance in pre-established speel and its solubility.

In table 4 are presented the saturation concentrations of that three studied substances and the total mass transfer coefficients K. The determinations were made at a stirring rate of 1 rot/min, at speel of $\Delta\tau$ = 6 min.

For the determinations made at citric acid and sodium chloride dissolution were used 2 tablets, but for Penicillin G potasium salt just 1 tablet.

Comparing the values of total mass transfer coefficients K, it is observed that the values are as bigger as the studied substances solubility is smaller. That is explained by the mass transfer coefficient compensation with the concentration difference.

3.4. The influence of temperature

The experimental study of temperature influence over the dissolution processes and calculation of the corresponding mass transfer total coefficients K was made over the acetylsalicylic acid, at room temperature (t_1 = 20 °C) and at a different temperature (t_2 = 55 °C).

In Table 5 are presented the total mass transfer coefficients for acetylsalicylic acid at two studied temperatures. The experimental determinations were made at a stirring rate of 9 rot/min, in speel of $\Delta\tau$ = 12 min.

It is observed that the temperature influences significant the dissolution process, solid-liquid contact surface decrease with the temperature increasing and, finally, the total mass transfer coefficient increase significantly with the temperature increasing

TABLE 4. Mass transfer coefficients for three substances

Substance	Dissolved mass Δm_1, [g]	Surface $A_m \cdot 10^4$, [m^2]	Sat. conc. C^*, [kg/kg]	Real conc. C, [kg/kg]	Coefficient $k \cdot 10^3$, [kg/m^{2}s]
Citric acid	1,0605	7,20	1,33	0,0106	3,10
Sodium chloride	1,2634	7,88	0,36	0,0126	12,8
Penicillin G potasium salt	0,1054	2,06	0,10	0,0010	14,6

TABLE 5. Mass transfer total coefficients for acetylsalicylic acid

Temp. [^{o}C]	Dissolved mass Δm_1, [g]	Surface $A_m \cdot 10^4$, [m^2]	Sat. conc. C^*, [kg/kg]	Real conc. C, [kg/kg]	Coefficient $k \cdot 10^3$, [kg/m^{2}s]
20	0,0726	4,18	0,01	0,00072	25,9
53	0,0983	4,24	0,01	0,00098	32,5

3.5. Variation of mass transfer total coefficients during the dissolution process

The variation of mass transfer total coefficients is experimental studied for acetylsalicylic acid, citric acid and Penicillin G potasium salt. The studies were made in the same conditions with those presented for the previous determinations.

It was represented the plot evolution of dissolved substance mass in time vs. the substance saturation concentration, then the plot was divided in 4 domains, each one coresponding at 3 min.

The difference between the curve and the saturation concentration C^* represents the concentration variation, value which is used to calculated the total mass transfer coefficients K.

In figures 5 and 6 are presented the variations in time of acetylsalicylic acid and penicillin G potasium salt concentration.

With this values were calculated the total mass transfer coeficients K for that 4 domains.

The values of this coefficients as well as the value of the tablets surface as a result of their mass decrease through dissolution, are presented in Table 6.

It is observed the gradually increase of the mass transfer coefficient during the dissolution process. That is explained by decreasing of tablets dimensions, which leads to the change of the limit layer thickness, as well as the existence of solvent (water) diffusion process inside the granule.

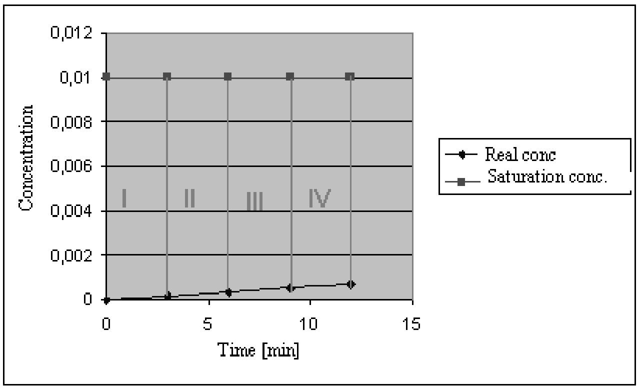

Figure 5. The variation of acetylsalicylic acid concentration in time

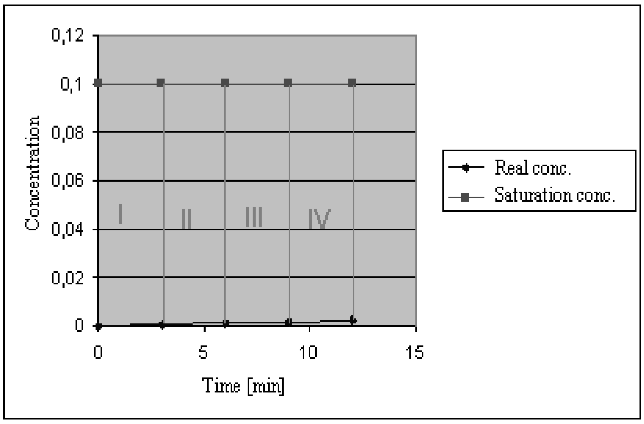

Figure 6. The variation of penicillin G potasium salt concentration in time

TABLE 6. The evolution of total mass transfer coefficients during the dissolution process (I-IV domains), for the three substances

Substance	Domain I		Domain II		Domain III		Domain IV	
	$K \cdot 10^3$	$A \cdot 10^4$	$K \cdot 10^3$	$A \cdot 10^4$	$K \cdot 10^3$	$A \cdot 10^4$	$K \cdot 10^3$	$A \cdot 10^4$
Acetylsalicylic acid	24,05	4,24	24,71	4,21	25,29	4,19	25,95	4,15
Citric acid	4,55	4,35	5,38	3,68	6,72	2,95	9,44	2,10
Penicillin G potasium salt	14,3	2,38	16,7	2,05	20,4	1,69	26,8	1,29

4. Conclusions

- It is presented an experimental method for determination of mass transfer coefficients at dissolution;
- The experimental determinations had as objectives the change of total mass transfer coefficient K under the influence of several parameters: hydrodynamic conditions, compacting pressure, temperature, substance nature etc;
- The substances tested at dissolution is converted in tablets with pre-established dimensions by powdery material pressing in cylindrical stamps at different reference pressures; the tablets compacting degree hasn't a significant influence over the amount of dissolved substance and, implicitly over the total mass transfer coefficient;
- By use of a rotating system, is intensified the effect of hydrodynamic conditions (blender). During the determinations, the Reynolds number (Re) has attained values of 10^3;
- At the substances with high saturation solubility, smaller values of the mass transfer coefficients is explained by the balance with the difference between the saturation concentration and the real concentration;
- The dissolution process is so intense as the temperature is bigger, solid-liquid contact surface is decreasing with the temperature increase, and the significant total mass transfer coefficient increase with temperature increasing.

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