Correlations between kinetic and thermodynamic parameters of the extraction of tobacco leaves

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Abstract: The correlations between thermodynamic and kinetic parameters in the extraction of tobacco leaves (solid – liquid system) were determined. The values of the parameters internal molecular diffusio coefficient, activation energy and entropy were used in the calculation procedure presented in the study, with regard to the extraction process of leaves of three types of tobacco (Virginia, Burley and Oriental), carried out with 50% ethanol as a solvent at different temperatures (20, 30, 40, 50, 60 and 70°C) and duration (10, 20, 30, 40, 50 and 60 min). On the basis of the Arrhenius law the effective diffusion coefficient in solid – liquid system and the reaction rate constant of the three types of tobacco were computed.

1. Introduction

Extraction is a process of transferring one or more components of a complex solid with a porous structure into a liquid medium (solvent). According the Benda [1] this process is performed on the basis of selective solubility of each substance(s) of the solid material.

The extraction process is often called diffusion, as is the driving force of transfer. The diffusion of extracted components of the starting mixture in the extractant is based on the difference in their concentration [1-6].

The diffusion coefficient is a major characteristic of the diffusion setting and is an important parameter in the theory of all diffusion processes [1-12]. The ideal thermodynamic system would represent an ensemble of non-interacting particles, which diffuse as a result of the chaotic movement. The theory of chaotic motion model is based on the strict laws of static mechanics and is sufficiently accurate. In this reason, the diffusion coefficient in a given case can be calculated accurate enough, so as to create the conditions for the development of theories of the complex diffusion process.

For example, the molecular diffusion coefficient represents only a physical constant characterizing the ability of a substance to penetrate through diffusion into an immobile environment, not dependent on the hydrodynamic conditions in which the process runs. The molecular diffusion coefficient is a function of the properties of the extracted substance and the setting, in which it diffuses, as well as of temperature and pressure. Usually the molecular diffusion coefficient increases with increasing the
temperature and decreasing the pressure (for gases). In some specific cases, the molecular diffusion coefficient was determined by experimental data or in theoretical or semi-empirical equations, taking into account the influence of the temperature and the pressure at which the diffusion proceeds [3-7, 13-15]. According to several authors [6, 7, 16-18] the molecular diffusion coefficient was also called a conductivity coefficient for the solid-liquid system.

Often an effective diffusion coefficient was used instead of an internal molecular diffusion coefficient, which gives the optimal value of the diffusion coefficient for the solid-liquid extraction and can be used for its application in electronic devices for controlling the extraction process.

According to literature data [16, 18-22] there are results for determining an effective diffusion coefficient depending on the value of the internal molecular diffusion coefficient. In some of the publications Arrhenius law was used for the determination of the effective diffusion coefficient based on a constant value of the diffusion coefficient. Some authors [22-24] prepared mathematical models for calculating the effective diffusion coefficient in dependence with the structure of the solid, the temperature and the type of solvent used. Castillo-Santos et al. [25] and Simeonov et al. [9] calculated an effective diffusion coefficient based on the different porosity of the raw material.

Some authors [11, 12, 20, 21, 26, 27] represent the influence of temperature on the process by the Arrhenius law to determine the reaction rate constant (k) in the extraction process. On this basis were presented the graphical dependencies between lnk and the extraction temperature 1/T and the activation energy of the system was determined as well as the entropy and enthalpy.

The effective diffusion coefficient calculated according to the Arrhenius law establishes the relationship between the kinetic (coefficient of internal molecular diffusion and temperature) and thermodynamic (activation energy and temperature) parameters of the extraction process.

The reaction rate constant calculated for a given thermodynamic system provides information to determine the order of the reaction, its speed, and the mechanism of the reaction. It can be used to optimize a process.

Ivanova et al. [13-15] presented the results of the investigations of the extraction process of leaves from three types of tobacco (Oriental, Virginia and Burley) with 50% ethanol solvent, namely: the calculated values of the internal molecular diffusion coefficient and the activation energy of the thermodynamic liquid extraction system.

The purpose of the present work is to calculate the effective diffusion coefficient and the reaction rate constant for liquid extracts from three types of tobacco leaves - Virginia, Oriental and Burley, with 50% ethanol solvent, as well as to establish a relationship between the kinetic and thermodynamic parameters of the extraction process of the three types of tobacco.

2. Materials and methods

In the extraction of capillary-pore material the process is carried out by molecular diffusion. The density of the diffuse stream in the material relative to a unit of its surface was described by Fick’s law using the effective diffusion coefficient $D_e$ (coefficient of mass conductivity). The dependence of the effective diffusion coefficient on the parameters of the porous structure was characterized by the equation (1):

$$D_e = D \cdot e \cdot \Pi = D \cdot m$$  (1)

where: $D$ is the coefficient of diffusion in a homogeneous setting (in a pure liquid); $\Pi$ - coefficient of diffusion permeability; $m$ - parameter depending on the porous structure [4, 9].

According to Castillo-Santos et al. [25] and Simeonov et al. [9] the porosity of the raw material can be used.

Effective diffusion coefficient can be determined, which connects the kinetic and thermodynamic parameters of the extraction process according to equation (2) [28]:

$$D_e = D_0 \cdot e^{\frac{E_a}{RT}}$$  (2)
where: \( D_e \) is the effective diffusion coefficient, m\(^2\)/s; \( D_0 \) - pre-exponential factor or internal molecular diffusion coefficient, m\(^2\)/s; \( E_a \) - activation energy in the system, J/mol; \( R \) - universal gas constant, J/mol·K; \( T \) - extraction temperature, K.

The effective diffusion coefficient in dependence with the temperature of the Arrhenius law was calculated based on the values of the internal molecular diffusion coefficient for liquid extracts of Oriental, Virginia and Burley tobacco types, provided by Ivanova et al. [13-15], according to equation (2).

Temperature is a parameter that affects the diffusion properties of substances being extracted, as well as the running of the process. Its influence was expressed by a reaction rate constant, according to equation (3) [11, 12, 20, 21, 26, 29, 30]:

\[
k = A \cdot e^{-\frac{E_a}{RT}}
\]

where: \( k \) is the reaction rate constant; \( E_a \) - activation energy, J/mol; \( R \) - universal gas constant, J/mol·K; \( T \) - absolute temperature, K.

To determine the reaction rate constant and Arrhenius constant value the activation energy and entropy of the thermodynamic system were used. Calculations prepared for liquid extracts obtained from the extraction of three types of tobacco, extracted with ethanol solvent at concentration 50%, provided by Popova et al. [19, 31, 32].

Arrhenius constant (A) or frequency factor can be calculated according to equation (4) [11, 26]:

\[
A = \frac{R \cdot T}{N \cdot h} e^{\frac{\Delta S}{R}}
\]

where: \( N \) is the Avogadro number; \( h \) - Plank constant; \( \Delta S \) - activation entropy in the system; \( R \) - universal gas constant, J/mol·K.

3. Results and discussion

In Table 1 were presented results obtained after calculation of effective diffusion coefficient on the basis of the Arrhenius law, which takes into account the temperature influence on the extraction process. The values obtained for effective diffusion coefficient were calculated with parameters of an internal molecular diffusion of the three types of tobacco (Virginia, Burley and Oriental) with ethanol solvent at a concentration 50% according to Ivanova at al. [13-15].

As it can be seen from the presented results, the determined effective diffusion coefficient of the three types of tobacco exhibited values between 3.68 and 888.78.10\(^{-9}\) m\(^2\)/s (Table 1). It was observed good correlation between results in this work and literature data.

The values of the effective diffusion coefficient \( D_e \) depended on the type of the raw material, the solvent used, the particle size, as well as on the raw material: solvent ratio. After reaching a maximum the effective diffusion coefficient decreases (increases the resistance in the solid phase), because of the changes occurring in the structure of the solid phase. From the data presented in Table 1 it can be seen that the values of effective diffusion coefficient \( D_e \) for a certain temperature also reach the maximum, and then decrease.

At 30 and 60°C temperature, the maximum value of effective diffusion coefficient \( D_e \) coincided with the end of the process for all three types of tobacco. Consequently, it can be concluded that these values were optimal in terms of the temperature and duration of the solvent extraction process with 50% ethanol for tobacco. For the solid phase used under these conditions there was no change in structure as a result of the extraction process.

Scientific literature describes values of the effective diffusion coefficient of different plant materials, which vary considerably depending on the characteristics of the material, the extractant, the extraction conditions and the calculation procedure (Table 2).
Table 1. Effective diffusion coefficient ($D_e$) for extraction of tobacco leaves with solvent 50% ethanol

| $t$, °C | $\tau$, min | $D_e \cdot 10^9$, m²/s | Oriental | Virginia | Burley |
|---------|-------------|------------------------|---------|----------|--------|
| 20      | 10          | 3.68                   | 3.72    | 87.01    |
| 20      | 20          | 5.10                   | 5.99    | 310.76   |
| 20      | 30          | 5.90                   | 5.63    | 279.69   |
| 20      | 40          | 6.76                   | 6.15    | 296.78   |
| 20      | 50          | 5.25                   | 5.91    | 377.58   |
| 20      | 60          | 5.52                   | 5.93    | 367.62   |
| 30      | 10          | 4.26                   | 4.05    | 128.97   |
| 30      | 20          | 5.75                   | 5.26    | 295.22   |
| 30      | 30          | 5.10                   | 6.28    | 298.33   |
| 30      | 40          | 4.95                   | 5.87    | 315.42   |
| 30      | 50          | 5.40                   | 6.40    | 296.78   |
| 30      | 60          | 6.19                   | 8.52    | 378.51   |
| 40      | 10          | 4.97                   | 5.71    | 152.28   |
| 40      | 20          | 7.72                   | 6.52    | 259.48   |
| 40      | 30          | 10.12                  | 6.56    | 289.00   |
| 40      | 40          | 9.31                   | 6.60    | 337.18   |
| 40      | 50          | 9.92                   | 7.25    | 400.88   |
| 40      | 60          | 10.70                  | 7.22    | 547.91   |
| 50      | 10          | 5.80                   | 13.08   | 220.63   |
| 50      | 20          | 9.72                   | 19.43   | 441.28   |
| 50      | 30          | 10.25                  | 22.67   | 428.85   |
| 50      | 40          | 8.87                   | 25.99   | 427.30   |
| 50      | 50          | 9.16                   | 47.37   | 626.18   |
| 50      | 60          | 10.54                  | 46.69   | 612.74   |
| 60      | 10          | 7.65                   | 7.81    | 413.31   |
| 60      | 20          | 11.03                  | 10.57   | 551.60   |
| 60      | 30          | 10.55                  | 12.39   | 658.82   |
| 60      | 40          | 11.68                  | 12.87   | 649.49   |
| 60      | 50          | 12.44                  | 12.35   | 596.66   |
| 60      | 60          | 14.50                  | 13.80   | 749.96   |
| 70      | 10          | 38.96                  | 20.49   | 170.92   |
| 70      | 20          | 62.51                  | 37.13   | 888.78   |
| 70      | 30          | 50.44                  | 23.12   | 739.61   |
| 70      | 40          | 5049                   | 17.05   | 680.57   |
| 70      | 50          | 67.52                  | 13.48   | 560.93   |
| 70      | 60          | 69.65                  | 14.62   | 621.52   |

Table 2. Effective diffusion coefficient values for different plant raw materials.

| Plant material | Conditions | $D_e$ (m²/s) | Reference |
|---------------|------------|-------------|-----------|
| Vanilla beans | 60% (w/w) ethanol-water solvent; at 30, 40 and 50°C; fixed particle size | 1.22 - 2.43$\cdot 10^{11}$ | [25] |
| Birch bark    | Ethanol as a solvent; at boiling temperature; with mixing; for different solid particle sizes | 7.12 - 47.2$\cdot 10^{11}$ | [5] |
Mangrove barks  Water as a solvent; isothermal extraction; temperature range 20-75°C; a simple pore diffusion model with constant diffusivity 5.0 - 7.5.10^{11} [10]

Oak barks  Water as a solvent; isothermal extraction; temperature range 20-75°C; a simple pore diffusion model with constant diffusivity 4.35 - 5.10^{11} [10]

Geranium  Ethanol as a solvent, with 70% concentration:
- depending on the calculated function of the effective coefficient 1.04 - 3.70.10^{10} [33]
- depending on the method of the regular calculated regime 1.58 - 5.25.10^{11} [24]
- taking into account the influence of other process parameters 1.2097 - 5.0567.10^{10} [24]

Tobacco  Water as a solvent 0.28064 - 0.47784.10^{10} [24]

Peanut kernels  Hexane as a solvent; at 25°C; for different thickness of the solid particles (seed slices) 0.49 - 1.26.10^{13} [28]

Tung seeds  Different petroleum distillation products as solvents; at 30, 50, and 70°C; for different thickness of the solid particles (seed slices) 15.0 - 44.5.10^{13} [28]

Chickpea  Grounded chickpea, a mixture of hexane and isopropanol (75:25, v/v) as a solvent; at 60°C 0.13 - 2.04.10^{13} [28]

Depending on the calculated values of the reaction rate constant (k) by equation (3), in Figures 1-3 were presented its variation on the temperature and the duration of the process for the three types of tobacco.

It is determined that reaction rate constant values increased with the increase of process duration and temperature. These results can be explained by the exponential type of the Arrhenius law (equation (4)). In future investigations the values of the reaction rate constant will be used to determine the order of the reaction, velocity and mechanism of the reaction.

In Figure 4 was presented the graphical dependence InK versus 1/T for the three types of tobacco (Oriental, Virginia, Burley). These graphical presentations were used to determine the angle of linear dependence, from where the activation energy and enthalpy of the process can be determined, in the absence of system data. The linear dependences were confirmed from literature data [11, 12, 20, 21, 26, 30].

**Figure 1.** Reaction rate constant (k) in dependence with temperature and duration of the extraction process for Oriental tobacco.
As it can be seen from the presented results the temperature had a very significant influence on the process of the extracted substances. Beside this factor, the structure of the solid, its size and the raw material: solvent ratio influences the process. All of these parameters will be taken into account in future studies of the solid-liquid extraction process.

4. Conclusions
There were determined relations between kinetic and thermodynamic parameters involved in extraction process, related to the influence of temperature on the diffusion of substances and the degree of their extraction from the solid. The values of the effective diffusion coefficient for leaved from three tobacco types were calculated, which were within the following ranges: for Oriental tobacco - between 3.68 and 69.65·10^{-9}\text{m}^2/\text{s}, for Virginia flue-cured tobacco – between 3.72 and 47.37·10^{-9}\text{m}^2/\text{s} and for Burley tobacco - between 87.01 and 888.78·10^{-9}\text{m}^2/\text{s}. The maximum values of the effective diffusion coefficient $D_e$ can be used in practice for the characterization of the extraction process. Moreover, they can be applied for optimization of the process and its intensification against parameters influencing it.
Figure 4. Graphical dependence between lnK versus 1/T for three tobacco types:
   a) Oriental, b) Virginia, c) Burley.

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