Mathematical modeling of metal ions extraction process using a single drop technique

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Abstract

One of the main ways of determining the mechanism of the process is to study the kinetics of the process, the dependencies of the kinetics on various parameters and adopt the proper mathematical models to the obtained results. Generally, the correctness of such a course is mostly dependent on the derived model - assumptions taken, the type of solution and variables taken into consideration. This work presents a mathematical modeling of an extraction using a single drop method, where metal ions are being extracted in a form of complex with metal to extractant ratio of 1:2. This kind of complex has been observed for example in the extraction of metal dications using imidazole derivatives. Two mathematical models assuming different limiting stages of process have been derived and the course for determining the one most appropriate for individual system has been presented.

1. Introduction

Extraction processes can be used for the precipitation of both organic and inorganic compounds. Various extractants present various ways of actual extraction process due to a different mechanisms of compound transport from water to organic phase. Generally, the extraction is caused due to the difference in solubility of compounds in water and organic phases, though many chemical reactions can occur during the extraction and compounds can be extracted in various chemical states. Very often compounds are being transported in a form of complexes containing these compounds and extractant molecules. For the determination of such complexes compositions the extraction kinetics studies can be applied.

Some of the main techniques used in the studies of kinetics extraction include intensively stirred tanks (both phases are stirred creating droplets of one phase throughout the other phase), constant interfacial area cells (both phases are stirred, but in the way that does not disturb the interfacial area that remains constant during the measurements), short phase contact time (used for very fast reactions occurring during extraction where the diffusion steps could disturb the measurements for higher times) and moving drop methods [1,2]. The last group introduces techniques, where the drop of one phase is being formed in the other phase and then travels through it, either upwards or downwards, depending on the densities of both fluids. The former is called the rising drop method, while the latter - the falling drop method. Both of them enable kinetics measurements using very small amounts of dispersed phase (drop) while simulating the hydrodynamic conditions of a drop found for example in the extraction columns (excluding interactions between drops). Main problems associated with these techniques are drop formation at the orifice or nozzle and drop collection.

These stages are quite difficult to describe and they can introduce errors connected with not taking them into consideration in the modeling of extraction.

While modeling the extraction using a single drop method many processes should be taken into consideration to create an exact mathematical model, though they increase the complexity of a solution, which very often is difficult to obtain. Thus, some simplifying assumptions are usually applied. Most of them concern chemical reactions occurring at the interfacial area, diffusional processes and determining the limiting stage of the extraction. Creating various models with different assumptions can help to determine the most appropriate one for the experimental conditions.

This work introduces the course for mathematical modeling of extraction of metal dications using extractants such as imidazole derivatives, that create complexes with metal to extractant ratio of 2:1 [3,4,5] and the way to determine the limiting stage of such an extraction.

2. Modeling

For the extraction of metal dications using a single drop method the following chemical reaction equations can be adopted:

$$M_{aq}^{2+} + Ex_{org} \leftrightarrow MEx^{2+}$$
$$MEx^{2+} + Ex_{org} \leftrightarrow MEx_{2,org}^{2+} \quad ' \tag{1}$$

where M and Ex denotes respectively metal and extractant molecules, while *aq* and *org* stand for aqueous and organic phases. Two different approaches can be made assuming that either first or second stage is the slower one, thus limiting the rate of whole extraction process. The faster stage is then described using equations corresponding to equilibrium. Thus, two models have been considered, namely model 1 and model 2, describing respectively processes where first or second stage in equation (1) is the limiting one. Equation (1) can be written then as:

— model 1:

$$M_{aq}^{2+} + Ex_{org} \underset{k_b}{\overset{k_f}{\leftrightarrow}} MEx^{2+}$$
$$MEx^{2+} + Ex_{org} \overset{K}{\rightarrow} MEx_{2,org}^{2+} \quad , \tag{2}$$

— model 2:

$$M_{aq}^{2+} + Ex_{org} \overset{K}{\rightarrow} MEx^{2+}$$
$$MEx^{2+} + Ex_{org} \underset{k_b}{\overset{k_f}{\leftrightarrow}} MEx_{2,org}^{2+} \quad , \tag{3}$$

where: k_f, k_b – forward and backward reaction rate constants,
    K – reactions equilibrium constant.

During the modeling of a single drop extraction some simplifying assumptions can be made. In this modeling the drop is being made of an organic phase (with extractant dissolved in it), while the water phase (containing metal dications) forms continuous phase. The volume of the continuous phase is usually much bigger than volume of a drop, so constant concentrations can be assumed in the water phase. While combining it with high concentrations in the water phase, the convective and diffusional processes outside the drop can be neglected. Inside the drop usually turbulent circulation is assumed [6] thus reducing the modeling to the interfacial reaction step.

Initially, the stage of a drop formation has been considered. The spherical cap shape of emerging drop has been assumed. It was necessary to create functions of volume V and surface A of a drop dependent on time. The main dimension quantities of a spherical cap, that is radius and height have been made dependent on time resulting in equations:

$$r = \frac{\dot{V} t}{\pi} h^{-2} + \frac{1}{3} h ,$$ (4)

$$h = \sqrt[3]{\frac{6\dot{V}t}{2\pi} - \sqrt{\left(-\frac{6\dot{V}t}{2\pi}\right)^2 + \left(\frac{\pi^2 d^4}{16}\right)^2}} + \sqrt[3]{\frac{6\dot{V}t}{2\pi} + \sqrt{\left(-\frac{6\dot{V}t}{2\pi}\right)^2 + \left(\frac{\pi^2 d^4}{16}\right)^2}} ,$$ (5)

where: r – radius of spherical cap,
h – height of spherical cap,
t – time,
d – diameter of a nozzle,
$\dot{V}$ – volumetric flow of an organic phase.

Using equations (3) and (4) volume and surface of a drop can be described as:

$$V = \pi \left(rh^2 - \frac{h^3}{3} \right) ,$$ (6)

$$A = 2\pi r h .$$ (7)

All of the above equations are necessary to solve the kinetic equations due to the extraction rate being dependent on both interfacial surface and volume of organic phase.

For the drop formation stage kinetic equations have to include not only the rate of chemical reactions shown in equations (1) but also the phenomena of drops increasing volume and fresh doses of organic phase of fixed extractants concentration being delivered into the drop. Assuming that the concentration of metal dications outside the drop is constant (as described earlier) three equations characterizing the rate of concentrations change of three components are needed to describe the process kinetics:

— model 1:

$$
\begin{cases}
\dfrac{d[MEx]}{dt} = \dfrac{A}{V}\left(k_f[M][Ex] - k_b[MEx]\right) - \dfrac{[MEx]}{t} \\[2mm]
\dfrac{d[Ex]}{dt} = \dfrac{A}{V}\left(k_b[MEx] - k_f[M][Ex]\right) - \dfrac{[Ex]}{t} + \dfrac{[Ex]^0}{t} \\[2mm]
\qquad\qquad [MEx_2] = K[MEx][Ex]
\end{cases}
$$

(8)

— model 2:

$$
\begin{cases}
\dfrac{d[MEx_2]}{dt} = \dfrac{A}{V}\left(k_f K[M][Ex]^2 - k_b[MEx_2]\right) - \dfrac{[MEx_2]}{t} \\[2mm]
\dfrac{d[Ex]}{dt} = \dfrac{A}{V}\left(k_b[MEx_2] - k_f K[M][Ex]^2\right) - \dfrac{[Ex]}{t} + \dfrac{[Ex]^0}{t} \\[2mm]
\qquad\qquad [MEx] = K[M][Ex]
\end{cases}
$$

(9)

The charges of all ions have been neglected in the notation. In the above differential equations the first term at the right side always describes the rate of chemical reaction, while the second term refers to the dilution of compounds due to the growing of the drop (change of volume). In the equations describing the rate of extractants concentration change a third term appears that characterizes the flux of an extractant being pumped into the drop with a fresh organic phase (concentration $[Ex]^0$). Set of equations describing each model (equations (8) and (9)) along with equations (4)-(7) had to be solved numerically because no analytical solutions were found.

The stage of drop travel through the continuous phase has also been considered. The same equations as equations (8) and (9) has been used but some changes have been applied. First of all, the drops shape has been assumed a sphere during the travel and both drops surface and volume are time-independent. Also, the terms referring to the dilution and extractants flux are omitted. Thus, the sets of equations for the drop travel stage are presented as follow:

— model 1:

$$
\begin{cases}
\dfrac{d[MEx]}{dt} = \dfrac{A}{V}\left(k_f[M][Ex] - k_b[MEx]\right) \\[2mm]
\dfrac{d[Ex]}{dt} = \dfrac{A}{V}\left(k_b[MEx] - k_f[M][Ex]\right) \\[2mm]
\qquad\qquad [MEx_2] = K[MEx][Ex]
\end{cases}
$$

(10)

– model 2:

$$\begin{cases} \dfrac{d[MEx_2]}{dt} = \dfrac{A}{V}\left(k_f K[M][Ex]^2 - k_b[MEx_2]\right) \\ \dfrac{d[Ex]}{dt} = \dfrac{A}{V}\left(k_b[MEx_2] - k_f K[M][Ex]^2\right) \\ [MEx] = K[M][Ex] \end{cases} \qquad (11)$$

Sets of equations (10) and (11) have been solved numerically because no analytical solutions were found. The surface and volume of the drop have been calculated using equations for the sphere for the assumed time of drop formation with constant volumetric flux of organic phase.

3. Results

The results of numerical solving of equations (8)-(11) have been presented in the figures 1-16. The comparison between models can be made and some characteristic features differing them can be found.

The effect of change of the forward reaction rate constant on extraction kinetics has been studied (fig. 1-4) for both models. In figure 1, presenting results for drop formation stage of model 1, a line of maximum values can be clearly seen. This kind of maximum does not appear in the figure 2 for model 2. It is worth to notice, that the maximum point location depends on both values of k_f and time. It means, that in practice we can obtain maximum point only for the systems that can be described using model 1, that is in the systems, where the limiting step of extraction is a reaction between metal dication and first molecule of an extractant. For model 2 no maximum values have been found in the whole range of examined values of time and k_f. The same conclusions refer to the drop travel stage (figures 3 and 4), where the maximum remains only in case of model 1 and, what is more, it is visibly steeper.
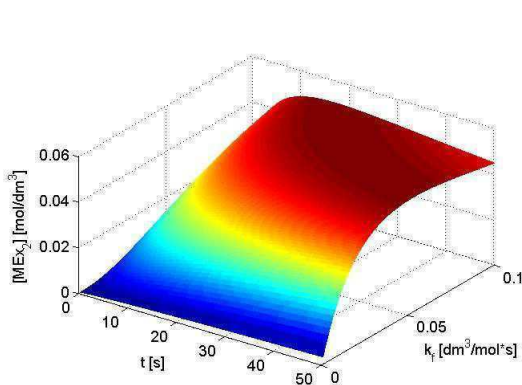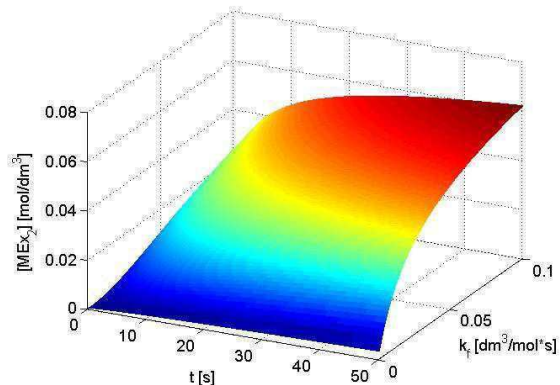

Fig. 1. The kinetics dependency on forward reaction rate constant during the drop formation stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_b=10⁻³ m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20).

Fig. 2. The kinetics dependency on forward reaction rate constant during the drop formation stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_b=10⁻³ m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20).
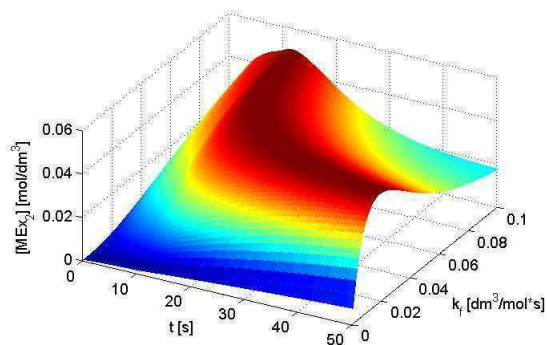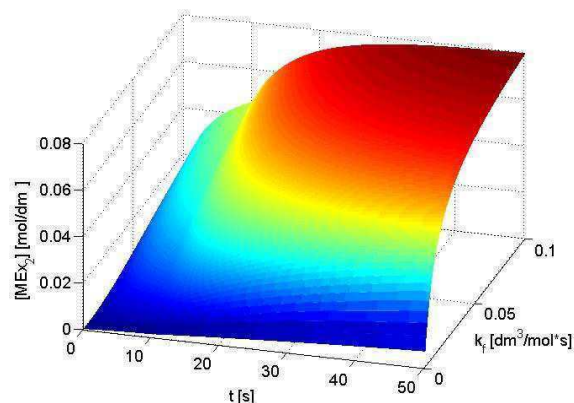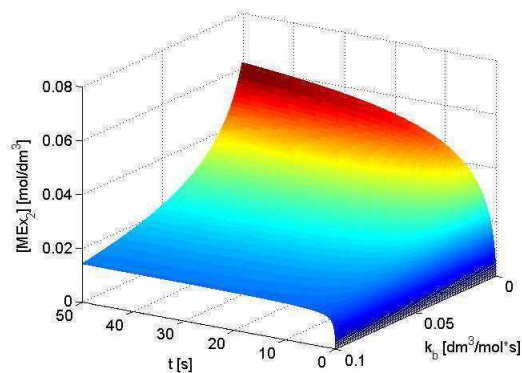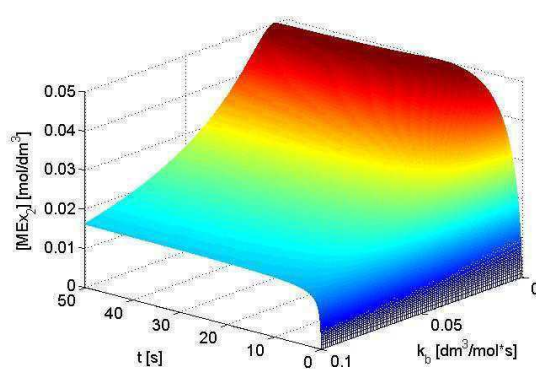
Fig. 3. The kinetics dependency on forward reaction rate constant during the drop travel stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_b=10⁻³ m/s, $[Ex]$=0.1 mol/dm³, K=20, t_{df}=10 s).
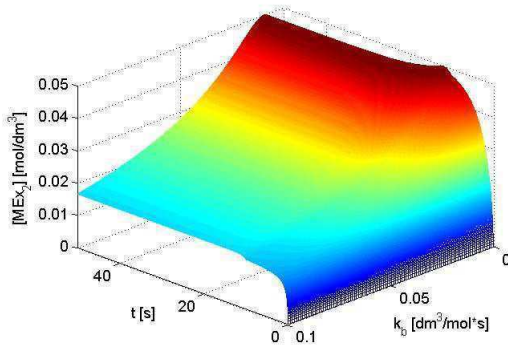

Fig. 4. The kinetics dependency on forward reaction rate constant during the drop travel stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_b=10⁻³ m/s, $[Ex]$=0.1 mol/dm³, K=20, t_{df}=10 s).

Analyzing the kinetics dependence on the backward reaction rate constant derived models can also be distinguished. For model 2 (in figures 6 and 8) a visible plateaus for time dependency can be seen for all values of k_b. In figure 5 the different behaviour of kinetic curve can be seen in case of model 1. What is more, for the drop travel stage for model 1 (figure 7) the maximum values can be found corresponding to small values of backward reaction rate constant. The maxima location is independent on time for wide range of examined values of time.

Fig. 5. The kinetics dependency on backward reaction rate constant during the drop formation stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_f=10⁻² m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20).

Fig. 6. The kinetics dependency on backward reaction rate constant during the drop formation stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_f=10⁻² m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20).
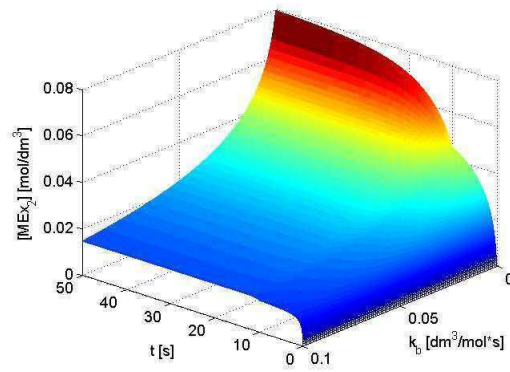
Fig. 7. The kinetics dependency on backward reaction rate constant during the drop travel stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_f=10⁻² m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20, t_{df}=10 s).

Fig. 8. The kinetics dependency on backward reaction rate constant during the drop travel stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, $[M]$=0.1 mol/dm³, k_f=10⁻² m⁴/(mol·s), $[Ex]$=0.1 mol/dm³, K=20, t_{df}=10 s).

The dependencies of extraction kinetics on the initial metal concentration in continuous phase for two models during the drop formation stage (figures 9 and 10) show no distinctive differences between models. In both cases the kinetics are improved with an increase in metal concentration. The situation changes when we consider the drop travel stage in the range of examined values of time (figures 11 and 12). In the figure 11 the maximum values line can be seen, similar to the one shown in the figure 3. In the case of model 2 (figure 12) no maximum has been found.
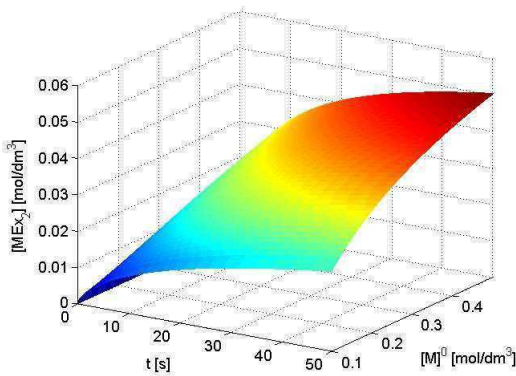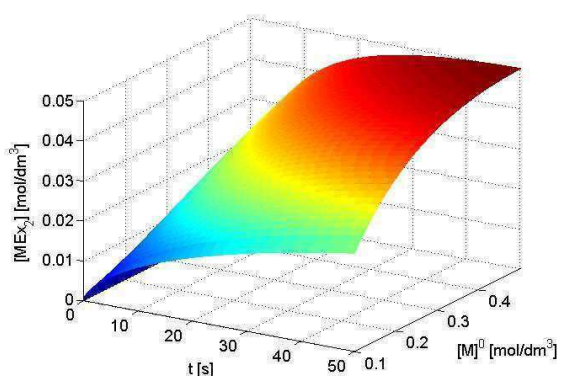

Fig. 9. The kinetics dependency on initial metal concentration during the drop formation stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10⁻² m⁴/(mol·s), k_b=10⁻³ m/s, $[Ex]$=0.1 mol/dm³, K=20).

Fig. 10. The kinetics dependency on initial metal concentration during the drop formation stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10⁻² m⁴/(mol·s), k_b=10⁻³ m/s, $[Ex]$=0.1 mol/dm³, K=20).
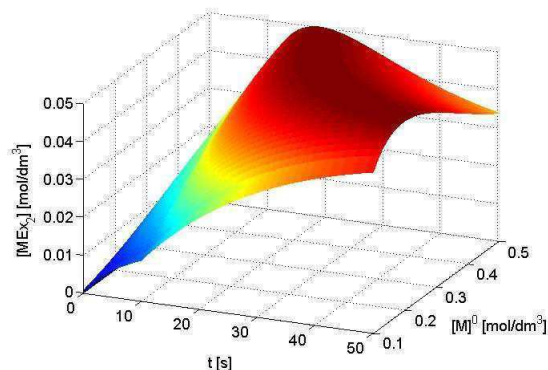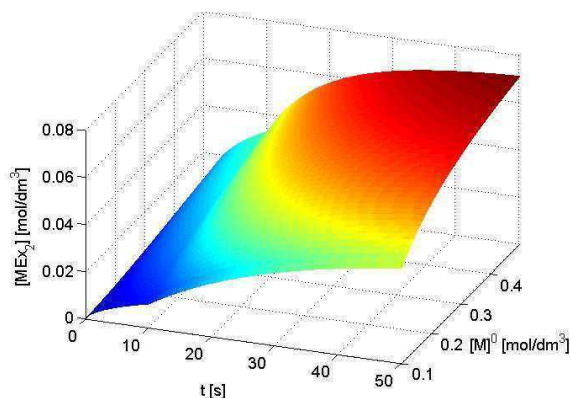
Fig. 11. The kinetics dependency on initial metal concentration during the drop travel stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, *[Ex]*=0.1 mol/dm^3, K=20, t_{df}=10 s).

Fig. 12. The kinetics dependency on initial metal concentration during the drop travel stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, *[Ex]*=0.1 mol/dm^3, K=20, t_{df}=10 s).

Finally, the kinetics dependencies on the initial extractant concentration in organic phase have been investigated. As it could be predicted, an increase in the extractant concentration affects positively the extraction kinetics (figures 13-16) although no distinction can be made between models 1 and 2 both in case of a drop formation stage (figures 13 and 14) and the drop travel stage (figures 15 and 16).
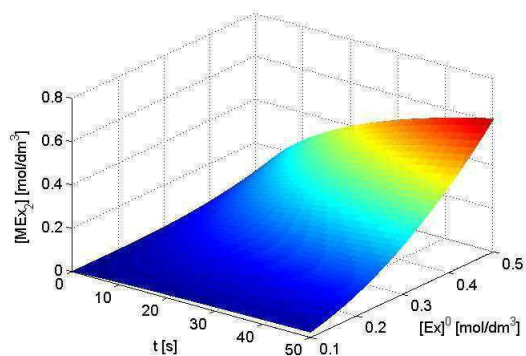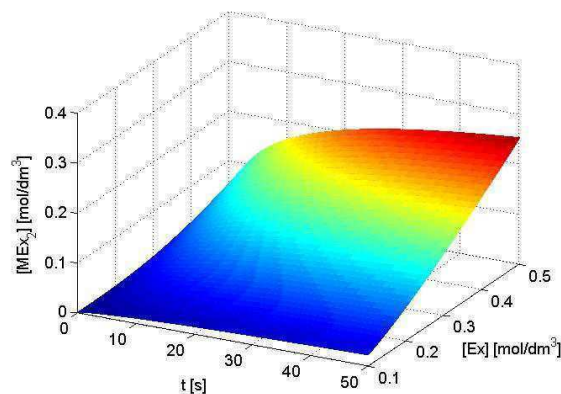

Fig. 13. The kinetics dependency on initial extractant concentration during the drop formation stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, *[M]*=0.1 mol/dm^3, K=20).

Fig. 14. The kinetics dependency on initial extractant concentration during the drop formation stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, *[M]*=0.1 mol/dm^3, K=20).
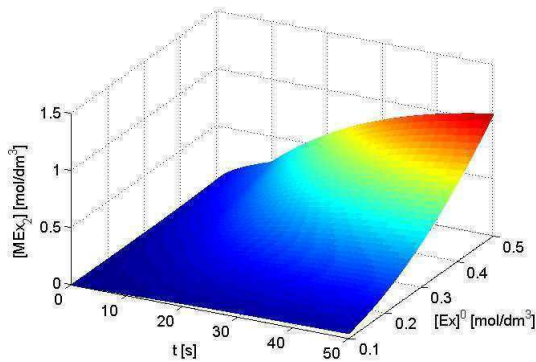
Fig. 15. The kinetics dependency on initial extractant concentration during the drop travel stage for model 1 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, $[M]$=0.1 mol/dm^3, K=20, t_{df}=10 s).
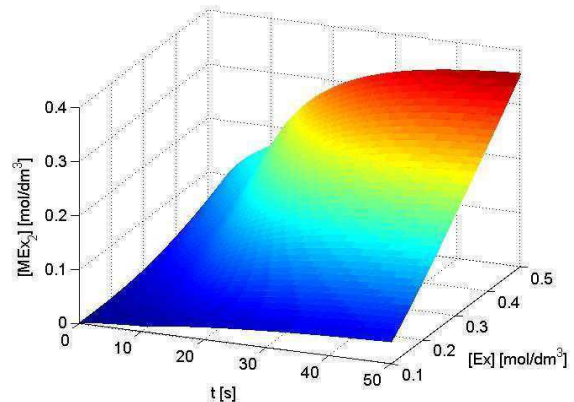
Fig. 16. The kinetics dependency on initial extractant concentration during the drop travel stage for model 2 (parameters used for calculations: V=0.01 ml/s, d=0.04 dm, k_f=10^{-2} m^4/(mol·s), k_b=10^{-3} m/s, $[M]$=0.1 mol/dm^3, K=20, t_{df}=10 s).

4. Summary

Two models of extraction kinetics for the described systems have been presented. The main aim of this study was to find a course of determining the limiting stage of extraction and some differences that may help to distinguish between the two derived models.

Model 1 is characterized by the existence of maxima in the dependencies of extraction kinetics on reaction rate constants k_f and k_b, and on initial metal concentration in aqueous phase. Such phenomenon does not occur in model 2. That indicates, that the easiest way to determine the limiting stage of such an extraction is to change the initial metal dication concentration and to check whether maximum exists. Derived model can then be used to calculate the rate constants that are very helpful in designing processes comprising investigated extraction process. The limiting stage of a process can be determined and described.

Moreover, these models can be used to find an optimal conditions for an extraction process, especially for model 1, where a clear maximum can be found. The optimal parameters that can be calculated include the extraction time, drop formation time and concentrations of all compounds used in the process.

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