Non-linear Dynamics of Mass Transfer Process with an Interphase Fractal Structure in Liquid-liquid System

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Abstract. As a liquid-liquid system is away from equilibrium state, the phase thickness is variable when mass transfer process with chemical reaction occurs in interphase region, and a dispersible transitional layer called the interphase dispersed zone (IDZ) is formed. It is found that some small voltage electrostatic field applied to the liquid-liquid mass transfer reaction system can trigger a jump of mass transfer rate. To elucidate experimental results, this study simplifies IDZ to a dynamic layer -- σ phase model, of which the porosity varies with time. The models of non-equilibrium thermodynamic mass transfer and the fractal reaction mass transfer kinetics are applied to obtain the experimental data through the stripping system of DEHPA-Cu²⁺-CCl₄/H₂O to which is added surfactant and applied 15v electrostatic field. The evaluative regularity of parameters obtained from the experiments such as interfacial thickness, disjoining pressure, porosity of interphase layer etc. explains the non-linear mass transfer characteristics of the experimental process, which indicates that the above models can sufficiently reflect the connotation of the model for IDZ in the liquid-liquid phase system.

1. Introduction

Traditional methods assumed that each phase in interface liquid-liquid system was unchangeable even in the interface and the thickness of the interphase layer was ignored completely. Actually in the mass transfer process, the phase region always evolves with time, accompanying with chemical reaction, hydromechanics instability, automatic dispersion, the formation of the interphase layer, the absorption and coalescence of dispersed particles, and the formation of interphase layer structure. Synthetically analyzing the phenomena of the process, the interphase dispersed zone (IDZ) model in liquid-liquid system is demonstrated in this study, which takes the interphase microemulsion process as the core [2].

Based on observation of the process, phenomena in the mass transfer process of the stripping liquid-liquid system are analyzed. Due to the effect of coordinate chemical binding between extraction agent and metal ion, and as well as intermolecular function between the chemical complexes and the solvent molecules, when the metal ion carries the extraction agent and solvent particles dispersing near the inorganic interphase layer in the process of transferring from...
organic to inorganic phase, the extraction agent and the solvent after separating from the metal ion can form the O/W type of micro-emulsion near the inorganic interphase zone under the competition of water molecules in the inorganic phase or other stripping agents. Similarly, the metal ion in the inorganic phase in liquid-liquid extraction system also can form the W/O type of micro-emulsion near the organic interphase layer.

Under the effect of the thermal movement of molecule and concentration driving force, the two types of micro-emulsion come into being and very dynamically in mass transfer process. Moreover, the O / W micro-emulsion near the inorganic interphase and the W/O micro-emulsion near the organic interphase can come into being simultaneously in the interphase layer of the mass transfer process. It is inferable that the double continuous phase type of micro-emulsion also can be produced between the O/W micro-emulsion and W/O micro-emulsion of the interphase layer. That is to say, in the equilibrium state of mass transfer, the heat movement of molecules possibly produces some interphase micro-emulsion layer. This process is generally known as mass transfer micro-emulsion process in liquid-liquid system interface [2]. The model for interface mass transfer or reaction mass transfer process is called the model of IDZ. In the research of mathematical simulation, the model of the mass transfer interphase layer is assumed to be simplified into non-continuous fluid film model with interspaces, which is called \( \sigma \)-phase model.

In the process of non-homogeneous mass transfer process, gradual changing of material concentration of the system, as well as the effects of machinery, electric field, magnetic field, gravitational field and sound field on the system, lead to the bifurcation of mass transfer rate, which is hard to be explained by Fick’s law used to describe mass transfer process. Therefore, the non-equilibrium propelling force of the IDZ in the mass transfer reaction of the liquid-liquid system and the model of fractal reaction mass transfer kinetics are introduced to simulate the non-linear reaction mass transfer kinetics characteristics obtained from the experiment. Combining with the theory of IDZ, this paper will explain how the low-voltage electrostatic field triggers the non-linear mass transfer kinetics in interface of the liquid-liquid system.

2. Experimental study
This study applies an improved constant interface cell (see in figure 1) to study the non-linear dynamics of interfacial mass transfer in liquid-liquid reaction system. The size of the constant interface cell is 52 x35x120mm, and the ratio of two-phase contact area to phase volume is 0.241 cm\(^{-1}\).

2-ethylhexyl phosphate (DEHPA, shortened form as HR) is taken as extraction agent and the carbon tetrachloride as the solvent for extracting cupric sulfate (see formula (1)), and then deionized water is used to strip cupric ion in the organic phase (see formula (2))

\[
\text{Cu}^{2+} + [\text{HR}]_{2+n} \rightleftharpoons \text{CuR}_2(\text{HR})_n + 2H^+ \quad (1)
\]

\[
\text{CuR}_2(\text{HR})_n + \text{H}_2\text{O} \rightleftharpoons [\text{HR}]_{2+n} + \text{Cu}^{2+} + 2\text{OH}^- \quad (2)
\]

In the experiment, the variation of material concentration in the interfacial mass transfer process in the improved Lewis cell, the stimulation of external electrostatic field and mechanical stimulation to the interface of the system, as well as the effect of different surfactants on dynamics of the interfacial mass transfer process are observed.

In the experiment, the stirring speed of stirrer in two-phase and the constant temperature are fixed respectively at 510rpm/min and 29.2\(^\circ\)C. Fig. 2 describes the changing curves of cupric ion concentration in the inorganic phase along with the changing of mass transfer process in the conditions of adding SDS and applying non-electric field or 15 V electric field vertical to the mass transfer direction, To save the length of the paper, we takes the data obtained from fig. 2 as an example to conduct calculations.
**Fig. 1** the improved constant interface cell

1- computer; 2-Digital switch-device; 3-concentration detector; 4-sensor; 5-constant speed motor; 6-speed device; 7-reciprocating device; 8- ribbon; 9- heat preserved water-jacket; 10- electric fields 11-stirrers.

**Figure 2:** The changing of Cu$^{2+}$ concentration in inorganic-phase along with the mass transfer process.

In the experiment, online data in each 0.5 second are collected. In order to measure the equilibrium concentration, the system is adequately mixed and then remained static for a whole day and night in each end of experiment. The rate of dynamic mass transfer is calculated according to formula (3).

$$\beta_c = \frac{dc}{dt} \frac{(c_p - c_r)(S/V)}{c_r}$$  \hspace{1cm} (3)

3. The impetus of non-equilibrium thermodynamics

The process of reaction mass transfer firstly comes from the organic phase (Cu$^{2+}$-DEHPA - CCl$_4$) , then goes through the interphase layer and at last arrives at the inorganic phase (aqueous-phase). $\sigma$-phase model is applied to simplify the model of the reaction mass transfer in the IDZ.

The pore of the dynamic layer changing with time manifests the thermodynamic instability of the O/W and W/O micro emulsions. Non-consecutive $\sigma$- phase is similar to porous media which the extracted components are diffused . This porous structure can be studied from the angle of fractal geometry [3,4]. Otherwise, with the model of non-equilibrium thermodynamics mass
transfer, variations of partial properties such as phase thickness, density, concentration, polarization, tension and so on can be studied.

Researches on non-equilibrium thermodynamics of extraction show that effective mass transfer coefficients need to be added the propelling force containing thermodynamics components. Based on the mechanism of micro-multiphase and non-equilibrium thermodynamics, the comprehensive propelling force is composed of three parts:

\[
X_{\sigma} = \left[ \frac{\mu_{\sigma}}{T_{\sigma}} - \mu \right] + i \left[ \frac{1}{T} - \frac{1}{T_{\sigma}} \right] + \frac{1}{\rho \cdot T} \left[ \rho \cdot P - \rho \cdot P_{\sigma} \right]
\]  

(4)

The first item of formula (4) denotes non-equilibrium nature in each phase, the second item denotes the uneven quality of temperature in phase, and the third item signifies the effect of surface strength. Considering that the thermal effect of extracting reaction process is not remarkable, \( \mu_{\sigma} = \mu_{0} + R \cdot T \cdot \ln c \) is adopted, and the mass transfer flow is calculated as following:

\[
J_{\sigma} = \beta \cdot \left[ 1 - \frac{c_{p}}{c_{p} - c} \cdot \frac{\pi}{\rho \cdot R \cdot T} \right] \cdot (c_{p} - c)
\]  

(5)

Comparing the differences between formula (5) and formula (3) of classical mass transfer flow, we can find the effective mass transfer coefficient in formula (6):

\[
\beta_{i} = \beta \cdot \left[ 1 - \frac{c_{p}}{c_{p} - c} \cdot \frac{\pi}{\rho \cdot R \cdot T} \right]
\]  

(6)

Formula (6) provides an approach calculating disjoining pressure (\( \pi = P - P_{\sigma} \)) in the experiment of mass transfer dynamics, also conditions and its dynamics effect on \( \pi \) value can be discussed. Through simple transformation, formula (6) can be transformed into (7) and (8), consequently, the \( \pi \) value and mass transfer coefficient at sometime also can be calculated (here :\( d_{j} = c_{p}/(c_{p} - c) \)):

\[
\left( \frac{\pi}{\rho \cdot R \cdot T} \right)^{(i)} = \left[ \frac{\beta_{i}^{o} \cdot d_{i}^{o} - \beta_{i}^{i} \cdot d_{i}^{i}}{\beta_{i}^{i} \cdot d_{i}^{o} - \beta_{i}^{o} \cdot d_{i}^{i}} \right]
\]  

(7)

\[
\beta_{i}^{i} = \frac{\beta_{i}^{o}}{1 - d_{i}^{i}} \left( \frac{\pi}{\rho \cdot R \cdot T} \right)^{(i)}
\]  

(8)

The mass transfer coefficient and the dynamic value of disjoining pressure indicate informations of the interphase layer. Disjoining pressure value are calculated (see in figure 3). To obtain the expressions of interphase thickness, we carry out the following transformations according to \( \pi = d \xi / dh \):

\[
\pi = -\frac{d\xi}{dh} \cdot \frac{dh}{d\psi} \cdot \frac{dh}{d\psi} = \frac{d\xi}{d\psi}
\]  

(9)

Using formula \( \xi = \xi_{p} - B \cdot \ln(1 + A \cdot \psi) \), \( dh/d\psi = a_{0} + a_{1} \cdot t_{p} \), we can obtain the expressions of the interphase thickness and the pressure difference:

\[
h = (a_{0} + a_{1} \cdot t_{p}) \cdot \psi + h_{0}
\]  

(10)

\[
\pi = \frac{A \cdot B}{(1 + A \cdot \psi)(a_{0} + a_{1} \cdot t_{p})}
\]  

(11)
These unknown parameters $A, B, a_0, a_1, \rho$ are obtained by the analytical method of minimum variance:

$$\min(R) = \sum_{j=1}^{N} \left[ \frac{\pi_j - \pi_k}{\pi_j} \right]^2$$

Figure 3 Curves of the disjoining pressure evolving with time contrasting with external electrostatic field.

Figure 4 Curves of the interphase layer film thickness evolving with time contrasting with external electrostatic field.

Figure 2, figure 3 and figure 4 illustrate that the electrostatic field applied to vertical direction of mass transfer in the external experiment device has changed the mass transfer rate and the disjoining pressure in interphase layer, which indicates that the vertical electrostatic field applied to the external system has changed the formation of the IDZ.

4. Fractal kinetics of the IDZ

In the process of mass transfer of the interphase layer, of which the thickness is $h$, the IDZ model ($\sigma$-phase) can be simplified with the differential equation containing decimal dimension, see in formula (12).

$$\frac{\partial^\alpha c_\sigma}{\partial t^\alpha} = D_\sigma \frac{\partial^2 c_\sigma}{\partial x^2} + K_\sigma c_\sigma$$

(12)
In order to obtain diffusion coefficient and reaction rate of $\sigma$-phase region, we make the triple integral in both sides of formula (13), which results in the equation manifesting the variation of mass transfer flow containing decimal differential of time (13).

$$\frac{\partial^a m_{\sigma}}{\partial t^a} = F \left( D_{\sigma} \frac{\partial c}{\partial x} - D_{\sigma} \frac{\partial c}{\partial x}_{m} \right) + K_{\sigma} c \cdot h \cdot F$$

(13)

$$I_{\sigma} = F \left( D_{\sigma} \frac{\partial c}{\partial x}_{m} - D_{\sigma} \frac{\partial c}{\partial x}_{m} \right) + K_{\sigma} c \cdot h \cdot F$$

Here, making integral decimally for the equation (13) in $[t_0, t]$, we can get formula (14):

$$m_{\sigma}^{f} = \frac{\partial^{a-\alpha} m_{\sigma}}{\partial t^{a-\alpha}} = \frac{1}{\Gamma(\alpha)} \int_{t_0}^{t} I_{\sigma} (t-\tau)^{a-1} d\tau$$

(14)

Narrowing the time interval $[t_0, t]$, $\overline{T}_{\sigma}$ is the mean value in $[t_0, t]$, then:

$$m_{\sigma}^{f} = \frac{\partial^{a-\alpha} m_{\sigma}}{\partial t^{a-\alpha}} = \frac{1}{\Gamma(\alpha)} \overline{T}_{\sigma} \left[ \frac{d\tau}{(t-\tau)^{a-\alpha}} \right] = \frac{1}{\Gamma(\alpha)} \overline{T}_{\sigma} \left[ \frac{(t-\tau)^{a-\alpha}}{\alpha} \right] = \frac{1}{\Gamma(\alpha)} \overline{T}_{\sigma} \frac{(t-t_0)^{a-1}}{\alpha}$$

(15)

In terms of the equation (15), calculating the differential in infinitely small time frame, non-decimal differential equation which the rate of component quality varies with time can be obtained (16)

$$\frac{dm_{\sigma}}{dt} = \frac{\overline{T}_{\sigma}}{\Gamma(\alpha) (t-t_0)^{a-\alpha}}$$

(16)

Supposing the concentration gradient of Cu^{2+} in the $\sigma$ interphase and the vertical direction of aqueous phase is zero, for his process of research is irreversible, and experimental volume ratio of two-phase is 1, then it is argued that when material completely transfers from the organic phase to the aqueous phase, its concentration in the organic phase of quasi-equilibrium state is zero $c_\rho = 0$. So the concentration gradient between $\sigma$-phase and the diffused boundary layer has the following form:

$$\frac{\partial c}{\partial x}_{\sigma_1} \approx \frac{c_\sigma - c_\rho}{h} = \frac{c_\sigma}{h}$$

(17)

Basing on deduction above, we can calculate $\overline{T}_{\sigma}$:

$$\overline{T}_{\sigma} = F \cdot D_{\sigma} \cdot c_{\sigma} \cdot h + K_{\sigma} \cdot c_{\sigma} \cdot h \cdot F$$

(18)

Thus, the function relation for the changing of material component quality in $\sigma$-phase is
\[ \frac{\partial m_\sigma}{\partial t} = \left\{ \frac{F \cdot D_\sigma \cdot c_\sigma + K_\sigma \cdot c_\sigma \cdot h \cdot F}{h} \right\} \frac{1}{\Gamma(\alpha)(t-t_0)^{1-\alpha}} \]  

Incorporating the formula (19) into

\[ \frac{dm_\sigma}{dt} = \beta_{\sigma} \cdot (c_\sigma - c_p) \cdot F \]

it can be obtained that

\[ \beta_{\sigma} = \frac{(D_\sigma / h + K_\sigma h)}{\Gamma(\alpha)(t-t_0)^{1-\alpha}} \]  

\[ \frac{\partial m_\sigma}{\partial t} \]

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\( \alpha \) Fractal dimension, porosity: the volume of micro-emulsion in \( \sigma \)-phase/ total volume, \( 0 < \alpha < 1 \)

\( \beta \) The mass transfer coefficient

\( \beta_e \) The effective mass transfer coefficient

\( \beta_m \) The mass transfer coefficient witch is derived from the relation of the membranous thickness and mass transfer

\( \pi, \pi_n, \pi_e \) membrane, disjoining pressure and the experimental data

\( \xi, \xi_0 \) surface tension, the surface tension without surfactant

\( \mu \) Chemistry potential of phase

\( \nu \) molar volume of diffused chemical substances

\( \mu_{i0} \) standard chemistry potential of main phase

\( \rho \) Inorganic density

Subscript \( \sigma \) Representative the nature of dispersed phase-simplified model

\( \psi \) surfactant concentration

\( c, c_t \) the concentration of copper ions In aqueous phase at t time

\( c_p \) equilibrium concentration of Cu\( \text{II} \) + In aqueous phase

\( D, D_\alpha \) molecular diffusion coefficient, fractal diffusion coefficient, \( \text{m}^2/\text{s} \), \( D_\alpha \sim D \alpha \cdot S \alpha \cdot 1-\alpha \)

\( F \) relative surface of phase contacts, \( F = S/V \)

\( K_\alpha \) Revising reaction rate constant, \( K \alpha = K_\alpha \)

\( S \) the area of interphase

\( S_\alpha \) cross-sectional area of dispersed channel, \( 10^{-15} \leq S_\alpha \leq 10^{-17} \text{m}^2 \), here \( S_\alpha \approx 10-18 \text{m}^2 \)

\( V \) the volume of inorganic phase, equivalent to the volume of organic phase.

\( t \) time

\( P \) The pressure of inorganic phase,

\( i \) enthalpy

\( T \) Inorganic temperature, \( K \)

\( X \) mass transfer driving force of non-equilibrium thermodynamics

\( J \) mass transfer flow rate

\( h, h_0 \) thickness of IDZ or \( \sigma \) phase, layer thickness of the interphase at the equilibrium state without surfactant.

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The porosity, an internal structure parameter of the simplified IDZ model--\( \sigma \) phase layer, can be calculated based on formulas above. (Figure 5).

Figure 5 indicates that the porosity of \( \sigma \)-phase (interfacial fractal dimension) when applying 15V electrostatic field to the vertical direction of mass transfer in the external system is lower than that when applying the non-electric field to, which explains the inner reasons that the function of electric field induces the jump of nonlinear mass transfer in the experiment, and remedies the paradox of Fick's law quoted.
5. Conclusions

(1) Based on non-equilibrium thermodynamics and fractal dynamic, the simulation and calculation are carried out for non-linearity experiment phenomena in the mass transfer process of liquid-liquid interfacial system, which indicates that the disjoining pressure calculated through non-equilibrium thermodynamics mass transfer model and the thickness of interphase layer etc. can perfectly demonstrate the jump of mass transfer process induced by the external electric field. The tendency of the external electric field affecting interface microstructure can be observed from calculations of the IDZ fractal kinetics.

(2) The above simulations and calculations show that the equations of fractal mass transfer kinetics perfectly reflect the connotation of the simplified model of IDZ in the liquid-liquid system as well. It is not only theoretically important to understand the non-linear characteristics of mass transfer in interphase process from view of microcosmic point, but also useful to be applied in the process control of chemical reaction transfer production, moreover, helpful to develop cognitions to safety essential of chemical production based on further studying of the mechanism of nonlinearity in interface process.

Nomenclature

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