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## New kinetic model of multicomponent mass transfer and concentration waves in bi-functional matrix of nanocomposites

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### Аннотация

Theoretical investigation is presented with the purpose of the modeling of the multicomponent mass transfer in NanoComposites (NC) on the basis of the created NC Model. The NC are well known as the new materials with the bi-functional matrixes. The NC Model for the bi-functional matrixes of the NC includes the proposed key concept: two co-existed routes for the mass transfer in the NC matrix. These two routes are put together: (I) –chemical reactions onto the active nano-sites in the NC matrix, and (II)-multicomponent diffusion mass transfer. The routes (I&II) are co-existed simultaneously inside the bi-functional NC matrixes.

All results are presented in the terms of the additional concept ( $W^+$ ): multicomponent concentration waves propagating (and broadening) inside the NC matrix. The propagation of the concentration waves may be illustrated by the author's calculated animations obtained on the basis of computerized solution of the multicomponent mass balance equations. The animations show visually the propagating concentration waves inside the NC matrix of various shapes: spherical r-bead, cylindrical ro-fiber or planar L-membrane.

**Keywords:** Nano-Composites (NC), mass transfer, concentration waves, diffusion, multi-component kinetics, bi-functional matrix, active nano-sites.

Представлено теоретическое исследование с целью моделирования многокомпонентного массопереноса в НаноКомпозитах (НК) - новых материалах с бифункциональной матрицей.

Модель для многокомпонентного массопереноса в бифункциональной матрице НК включает предложенную ключевую концепцию: два сосуществующих маршрута (I – химические реакции на активных НК наночентрах-сайтах, и II - диффузионный массоперенос, I + II) внутри бифункциональных НК матриц.

Все результаты представляются в терминах дополнительной ( $W^+$ ) концепции: распространяющиеся концентрационные волны компонентов в НК матрице. Распространение концентрационных волн могут иллюстрироваться авторскими расчетными анимациями, показывающими визуальное распространение многокомпонентных концентрационных волн в НК матрицах различных форм: г-сфера, цилиндрическое го-волокно, или плоская L-мембрана.

**Ключевые слова:** нанокompозиты (НК), массоперенос, концентрационные волны, диффузия, многокомпонентная кинетика, бифункциональная матрица, активные наносайты

### Введение

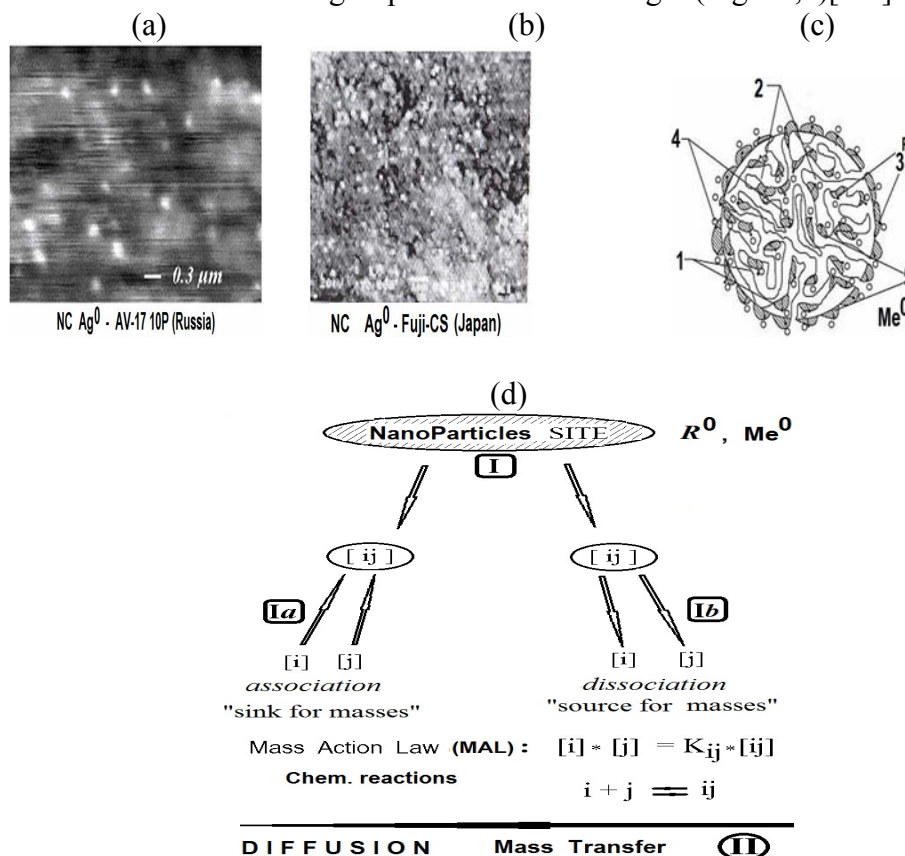
The created new theoretical Model [1-4] for the NanoComposites (NC) is assigned for the modern computerized investigations of the multicomponent mass transfer kinetics

in the bi-functional NC matrixes. The detailed description of the properties of the such new NC materials on the basis of the real examples for “the Metal-Ion Exchanger Nanocomposites” is published in the modern Russian monograph including the methods of the NC synthesis [5]. The NC contain a lot of the NanoParticles (NP) embedded in advance into the NC matrix-media during the NC synthesis. The details of the process of the synthesis of the NC which contains zero valent metal inside the ion exchange matrix are presented in the monograph. [5] The analogical information may be found in numerous references in [5]. The NC with the bi-functional matrix synthesized have a lot of advantages in comparison with the practice of application of the usual ion exchange materials [5].

The corresponding visual experimental micrograph with the micropictures of the NC structure including NanoParticles (NP) are presented (Figs. 1a,b) as the illustration of the NP agglomerates introduced into the NC matrix [5].

Figures 1a,b show the experimental micrography of the NC structure of the “Me<sup>0</sup> - ion exchangers” including the NP of zero valent metal (Me<sup>0</sup>, N5, dashed, Fig, 1c) inside the NC matrix.

Micrography of the NC, synthesized in the experiments (Figs, 1a,b) are obtained in the prof. T. Kravchenko group (Voronezh St. University) [5]. The experimental example are presented as illustrations of the NC media (Figs. 1a,b; Me<sup>0</sup>-NP, c – Me<sup>0</sup>, dashed). Nano-sites R<sup>0</sup>(or Me<sup>0</sup>), which play the role of the active centers of the bi-functional NC matrix, are localized near the fixed groups of the ion exchanger (Fig. 1c,d)[1-4].



Figures 1a-d. Schemes of mass transfer in bi-functional NC matrix (a,b - experiment), NC illustration (c): r-sphere, N5-Me<sup>0</sup>-NP agglomerates (dashed) [5], (d) – scheme of mass transformation, MAL onto the active nano-sites (R<sup>0</sup>, Me<sup>0</sup>): (Ia) – “association” stage (left), (Ib) – “dissociation” stage (right), (II) – multicomponent diffusion mass transfer along the NC pores (N2), (d) [2-4]

There is created the modern theoretical computerized multicomponent kinetic NC Model with the key concept: there are two co-existing routes (I +II) for the multicomponent mass transfer inside the bi-functional NC matrix [1-4]. These two co-routes in the NC reflect two simultaneously realizing processes: (I) – “*sorption-desorption*” of the *i*-components onto the active nano-sites of the NC matrix, and (II) – diffusion of the mixture *i*-components in the pores of the bi-functional NC matrix (Figs. 1a-c). Along with the diffusion mass transfer (II) the “sorption-desorption” process is realized via the “association-dissociation” mechanism (Ia,Ib, Fig. 1d) describing by the MAL relation (1) (see below)[2-4]. There is presented the scheme - illustration for the NC r-bead with the all accompanying elements of the process of the multicomponent mass transfer (Fig. 1d).

Figure 1d shows the scheme of the two co-existing routes (I +II) for the NC: I- active nanosites ( $R^0$ ) with the “sink” (Ia) and “source”(Ib) of the masses for the [ij]- “transformation” for the masses  $[ij] \leftrightarrow [i] + [j]$  (Ia, Ib). The accompanying diffusion process II in the NC matrix pores is presented also (Fig. 1d) [1-4].

The various *i*-components participate as in reactions (I), so in the multicomponent diffusion mass transfer (II) inside the bi-functional NC matrix during the kinetic process. The mechanism of the equilibrium “association-dissociation” reactions (MAL, Ia,Ib, Fig. 1d) brings to the retardation of the whole kinetic diffusion process.

Typical composition of the *i*-components may include: ions, complexes, neutral substances with zero charges, and in addition the immovable m-components ( ${}_mRi$ , with zero diffusivity,  $D_m = 0$ ) at the fixed  $R^0$  (or  $Me^0$ ) nano-sites (Fig. 1d) of the bi-functional NC matrix.

The created modern multicomponent Model has common points with the preceding approaches published previously at the end of the last century for the IEx kinetics [6–9]. However, the previous kinetic models have been applied to the IEx kinetics, accompanied by the chemical reactions only for the usual IEx resins (and only for the r-beads), but not for the new NC bi-functional materials, which are shown in Figs. 1a-d.

The created modern multicomponent NC Model [1–4] is used for the computer simulation of the multi-component mass transfer into the bi-functional NC matrix for the three various shapes: r-beads, cylindrical ro-fibers and planar L-membranes. There is used here the modern bi-functional NC “ $Me^0$ -Ion Exchanger”[4, 5], as the real example for the modern Model applications. For the generalization of the calculated examples (below) the active nano-sites herein after are labeled as the k-component:  ${}_kR^0$  (here number of any component is represented by the left index). So for any NC the  $R^0$  label means absolutely the same as  $Me^0$  for the example “ $Me^0$ -Ion Exchanger” in the Figs. 1c, 1d, ( $R^0$ , shaded).

The modern multicomponent NC Model [1–4] with the key conception: (I, II) – co-routes for the mass transfer, Fig. 1d) is represented by the adequate computerized description of the mass transfer in the bi-functional NC matrix of the novel materials. There are considered the two real factors of the multi-component mass transfer in the NC materials: multicomponent diffusion (II) ( $D_{i,j}$ ) of the *i, j*-components, together with the co-existing routes (I) for the equilibrium mass transformation (MAL, Fig. 1d) onto the active nano-sites  $R^0$ (Figs. 1c,d,  $R^0$ , dashed) through the mechanism of the “sinks & sources” (Fig. 1d) in the bi-functional (I, Reaction + II, Diffusion) NC matrix. The specific role of the Reaction (or Selectivity) factor (route Ia,b) concludes in the retardation of the whole diffusion process due to the equilibrium of the *association-dissociation* reaction (MAL) at the nano-sites ( $R^0$ ) of the NC (Fig. 1d).

It will be shown here the full similarity between the reaction (or selectivity) influence for the retardation of the diffusion kinetics in the bi-functional NC from one side and the sorption isotherms factor influence on the concentration waves propagation in the

approach of the theory of chromatography from the other side. Such similarity will be discussed in details in the Section: Discussion of Results (Table 1).

The multicomponent mass transfer kinetics in the bi-functional NC matrix represent the process, in which the selectivity (or reactions, i.e. equilibrium transformations of various components due to the factor **I**) the mass transport must undoubtedly be considered for the bi-functional NC materials.

Examples of the IEx kinetics and dynamics in the actual processes occurring via the mechanism of “sinks and sources” of the *i*-component masses are discussed in details [6–14]. Herewith, the effect of reactions on the kinetic behavior of the bi-functional NC system may be crucial: the kinetic process rate may be decreased by one or two orders of magnitude with the decisive dependence of the process on the solution concentration changes. Therefore, distinctive changes in the mechanism of the kinetic mass transport process may occur due to the reaction factor (**I**) influence.

Consideration of the active nano-sites influence in the bi-functional NC matrix (route I, Fig. 1*d*), at which changes of the mass for the components occur, is especially relevant in the case of the mass transport processes in the new NC materials with the bi-functional matrix [2–5].

### **Phenomenological approach for modeling of multicomponent mass transfer in bi-functional NC matrix**

Herewith the general phenomenological approach of the non-equilibrium thermodynamics has been used for the multi-component mass transfer in the NC matrix on the basis of the created Model [2-4]. The postulates for the various multicomponent Models for the IEx kinetics have been used during long-time period (around 50-60 years) starting from early prof. F. Helfferich publication [8] through his reviews concluding 90<sup>th</sup> years [9].

There is enumerated here (in short) the list of mathematical approaches in the description of the IEx kinetics: mass balance partial differential equations, quasi-homogeneous medium, isothermal process, electro-neutrality, fundamental Nernst–Planck relationship for the *i*-fluxes, constant diffusion coefficients ( $D_i$ ) for the *i*-components mixtures. As usual, the influence of the gradient of the electric field is expressed via the sum of the *j*-concentration gradients by using the absence of the electric current relationship [1-4, 6-9]. In result the *i*-flux of each *i*-ion-component is described by its own gradient with addition of the multicomponent superposition of the another *j*-concentrations gradients [1-4, 6-9]. Such superposition is called “diffusion potential” in the theory of irreversible thermodynamics.

For the bi-functional NC matrix the additional *i*-fluxes of the masses are formed due to the transformations of the  $i,j$  - components, which are expressed by MALs relations at the NP nano-sites  $R^0$  (Figure 1*d*, MAL).

These sinks and sources of the *i*-component masses are considered in the NC Model [1-4] by the corresponding *i*-fluxes of *i*-components, and bring the redistributions of the *i*-components masses for the various *i*- components participated. The effects of the mass transport for the created NC Model [1-4] by the “sinks-sources” mechanism at the nano-sites  $R^0$  (Figures 1*b,c*) are included in the material balance equations due to the introduction of the additional terms describing the decrease of the mass (with negative term for “sink”, 1*a*) or the increase of the another mass (with positive term for “source”, 1*b*), (Figure 1*d*).

For further advance of the NC Model the chemical reactions equilibrium uses the classical MALs relationships. In the computerized NC Model [1-4] they are presented in the generalized form:

$$\prod_i \{ [X_j]^{ms} [X_i]^{ns} \} = K_s, \quad s = 1, 2, \dots \quad (\text{MAL}_s), \quad (1)$$

where expression  $\prod_i (i \neq j)$  is the product of concentrations  $[X_i]^{ms}$  ( $i = 1, 2, \dots$ );  $ns$ ,  $ms$  (negative, or positive) - are stoichiometric coefficients of the chemical  $s$ -reaction;  $s$ -is the corresponding index;  $K_s$ - are the equilibrium constants in the MALs relationships (Eqn. 1), and (Figure 1d). In principle the stoichiometric coefficients ( $ms$ ,  $ns$ ) for the chemical reactions equilibrium (1) might be fractional [6,7]. During the computerized simulations all the  $ms$ ,  $ns$  values are assumed to be ( $\pm 1$ ). However in need all these values may easily be used in the NC Model as fractional or larger than unity.

The modern approach with all mentioned postulates and equations of the NC Model [1-4] has been realized by modern computer modeling. The set of the corresponding computer FORTRAN programs has been composed for the simulation of the various multicomponent mass transfer in the NC systems, describing the kinetic behavior inside the bi-functional NC matrix. The various shapes of the NC medium: r-beads, cylindrical ro-fibers, or planar L- membranes are included into the theoretical computer simulation. Thus, there are realized the computerized investigations of the influence of the equilibrium reactions parameters in co-operation with the various diffusion coefficients ( $D_i$ ) of the  $i$ -components on the kinetics inside the bi-functional NC matrix of the various three NC matrix shapes.

The basic properties in the development of the created generalized NC Model [1-4] accounting for the multicomponent character of the system are introduced. There are included the new properties of the bi-functional NC matrix based on the proposed key two routes concept (I & II) including "association-dissociation" mechanism onto nano-sites:  ${}_kR^0$  (Figure 1d). For further consideration let us simplify the generalized approach (Equation 1) to be closer to the multicomponent examples, which have been realized here by computers. The mathematical realization of the diffusion and relations for the chemical reactions inside the bi-functional NC matrix is based on the approach with the application of the simple form of MAL (Figure 1d) in the modern NC Model for the arbitrary  $i, j, ij$  - components concentrations:  $[i]$ ,  $[j]$ ,  $[ij]$ . The corresponding simple scheme, as for example for the simple reactions:  $i + j \leftrightarrow ij$  may be represented by the simple  $\text{MAL}_s$  relations for monovalent components:  $K_s \cdot [i] \times [j] = [ij]$  (Figure 1d).

The specific case is realized for the p-components, which are transformed into the complex:  ${}_m(R^0p)$ , ( $m^{\text{th}}$ - component) with zero diffusivity ( $D_m=0$ ). Meanwhile such p-components may participate in the "association- dissociation" transformation:  $ip + {}_kR^0 \leftrightarrow {}_m(R^0p)$  with the following change of the masses. It will be shown (Section Discussion of Results) that due to this  $i,p$ -components transformation at the nano-sites  ${}_kR^0$  (Figure 1d), the  ${}_kR^0$ - component concentration wave (Figures 2a-f, solid curves, 5) propagates in the bi-functional NC matrix (though  $D_{kR} = 0$ ).

It is desirable to pay attention that the obtained results of the computerized simulation on the basis of the created NC Model [2,3] are presented via the well known "multi-component concentration waves" ( $W^+$ ) concept [10-14].

Concentration waves arise and propagate along the distance (r-, ro-radius, or L-thickness) inside the NC matrix during the multicomponent mass transfer. The multicomponent waves with their propagation in the bi-functional NC matrix play the decisive role in the description of the multi-component NC kinetics of the mass transfer. Therefore this well known and widely used "wave" approach [10-14] is shortly reviewed in the next Section.

## Concept of concentration waves ( $W^+$ ) for multicomponent IEx mass transfer kinetics and dynamics

During the mass transfer sorption kinetics the concentration profiles-“waves” of the  $i$ -components are formed inside the porous media. Figures 2 represent a lot of computerized examples of the waves propagating during the multicomponent NC kinetics. The additional key concept ( $W^+$ ) of the “multicomponent waves” is widely used in the theoretical description for many scientific fields of the multicomponent transport for various kinetic and dynamic systems. The “multicomponent waves” concept has wide area for applications in such research fields, as percolation processes, mechanics of liquids, gas dynamics, theory of burning and even street traffic (see Refs. in [1-4]). The term “wave” ( $W^+$  concept) has been used in all these publications (see Refs. in [1-4]) including the mentioned excellent monograph [10] and the detailed reviews [11-13].

There are phenomenological concepts potentially common to all filtration processes, which can also be extended to a whole series of migration phenomena such as chromatography, sedimentation, electrophoresis and some others [10-14].

The fundamental monograph [10] (including additionally a lot of chromatographic publications by prof. F. Helfferich) is devoted to the all aspects of the travelling “concentration waves” conception. There is a lot of research papers adjoined, which are included into the special issue [11] dedicated to F. Helfferich (Festschrift) with the detailed consideration of the travelling “multicomponent concentration waves” ( $W^+$ ) concept, including some others related. A fairly detailed discussion of the wave concept, as well as many fundamental examples and definitions, are presented in a number of books and reviews (Refs. in [12,13]). In the presence of the effects of the non-ideality of the sorption medium the travelling concentration waves propagate with their broadening, including the results of their consequent interference [10-14].

The concept of the “multicomponent concentration waves” ( $W^+$ ) is widely used here to consider the results of the computer simulation of the concentration waves behavior in the NC kinetics. Naturally that this fundamental  $W^+$  concept is fruitfully used here for the description of the concentration waves behavior in the bi-functional NC matrix.

The quantitative description of the waves behavior is successfully described here by the well known two integral parameters used for the characterization of any  $k$ -distribution: “Center of Mass” ( $CM_k$ ) and “Dispersion” ( $Disp_k$ ). The “ $CM_k$ ” parameter describes the integral “Center” of  $k$ -wave (or  $kR^0$ -wave). The “ $Disp_k$ ” parameter describes “the integral width” of the  $k$ -wave distribution. Parameters “ $CM$ ” and “ $Disp$ ” are well known in the mathematical statistics as “average of distribution” and “dispersion” correspondingly. This two parameters are well known in mathematical statistics.

Such types of the descriptions are used below ( $CM_R$ ,  $Disp_R$ , Figs. 3a,b) for the estimation of the “completion Time”:  $T_{fin}$  of the kinetic process, and the “width” of the  $kR^0$ -concentration frontal  $k$ -wave in Figs. 2 ( $kR^0$ -wave, solids curves, 5). The concentration waves propagate across the various NC medium (L-membrane, ro-fiber, r-bead) from the boundary points ( $L_0$ ,  $ro_0$ ,  $r_0 = 1$ ) to the final “zero points”:  $L$ ,  $ro$ ,  $r = 0$  correspondingly (Figs. 2,3). The kinetic processes are finished at the completion moment  $T = T_{fin}$ , when the understandable relation  $CM_R + Disp_R = 1$  is realized. This moment  $T_{fin}$  corresponds to “the crossing” (in Figs. 3) of solid and dashed curves correspondingly. The more detailed description and discussion of the integral parameters are given below (Section Concentration  $i$ -waves behavior in modeling of multicomponent NC kinetics).

The description of the created NC Model [1-4] has been followed by the computerized simulation of the multicomponent system behavior in the bi-functional NC matrix via the numerical solution of the multicomponent mass balance partial differential

equations. All the parameters of the system in the computer simulations are dimensionless as it is better for any modeling, and for understanding, especially in Fundamentals. The obtained results of the computerized simulation for the multicomponent mass transfer in the NC are original and new [1-4].

The results of modeling are demonstrated and discussed in next Sections. They are illustrated by the set of the pictures (Figs. 2) representing the propagating concentration waves (especially the  ${}_5R^0$ -waves, which integrates the influences of all other waves).

Additional visual illustrations may be shown via the author's computerized presentations. The animations are framed by the real calculated multicomponent concentration "profiles-waves" for the successive time moments.

The propagations of the travelling concentration waves in the NC matrix via animations may be demonstrated visually. Such type of the computerized visual representations of the theoretical results with the dynamic and kinetic waves has been using by author repeatedly (including the sessions of "IEX 2004, 2008 and 2012" Conferences) [2,13,14].

### Concentration waves in multicomponent NC mass transfer kinetics

The described postulates of the mathematical Model for the NC kinetics were realized [1-4] for the all relationships including the multicomponent mass transfer kinetic partial differential equations, electro-neutrality relations, classical Nernst-Planck equations for the  $i$ -fluxes of the  $i$ -components, Mass Action Laws (MAL) for the chemical reactions equilibrium (Eqs.1), (Figure 1d).

All the systems describing the multicomponent kinetic behavior in the bi-functional NC matrix of the various shapes (**r**-bead, **ro**-fiber, **L**-membrane) were involved in the simulation with several author's FORTRAN computer programs for the such NC systems. The computer calculations were fulfilled for a number of variants with different values of the diffusion  $D_i$  coefficients and various  $K_S$  - constants of the MAL chemical reactions (Eqns. 1, Figure 1d). The results of the simulations for the multicomponent NC systems are presented below. All the computer calculations have been obtained by using the dimensionless values, including concentrations ( $X_i$ ); diffusion coefficients  $D_i$ ; constants of chemical association-dissociation reactions ( $K_S$ ). The mass transfer kinetics in the NC Model include the multicomponent concentration waves propagation along the dimensionless distance:  $r$ ,  $ro$ , or  $L$  in the course of the dimensionless time ( $T = D_0 t / r_0^2$ ). All the author's results of the computer simulation are obtained for the first time. The results of such calculations for the bi-functional NC matrix are presented below.

It should be marked here that the important partial case of the generalized NC Model for the some variants of the nonselective Ion Exchange (IEx) was also simulated [1-3]. The nonselective IEx corresponds to the absence of the nano-sites  $R^0$  (i.e. in this case: (I)-factor of the generalized NC Model is excluded). For the such partial (but important) case there were calculated some variants of the nonselective ternary ( $i=A,B,C$ ) IEx:  $RA_{resin} / (B^+ + C^+)_{solution}$ , where  $R$  are the fixed groups, and the  $i$ -components are equally charged ions [1-3]. These calculations describe the  $A^+, B^+, C^+$  - waves behavior with the various diffusivities -  $D_B, D_A > D_C$  including the  $F_i(T)$  kinetic curves for the usual, non-selective IEx matrix [1-3].

Only one case of the such type of the ternary  $i$ -concentration IEx system was considered previously in the paper [6]. There was calculated one variant of the three  $i$ -diffusivities mentioned ( $D_B > D_A > D_C$ ) for the spherical **r**-bead [6]. In the result of the calculation it was obtained the non-standard kinetic  $F_B^r(T)$  curve with the non-monotonic

behavior, i.e. with the kinetic maximum -  $F_B^{r, \max}$  for the most mobile B-ion with the largest  $D_B$  diffusivity. The results for the  $A, B, C$  -concentration waves behaviour were not presented, and the discussions of the reasons for the non-monotonous kinetic  $F_B^r(T)$ -curve were not given in [6].

Here the author's calculations of the usual ternary IEx on the basis of the partial case of the created NC Model bring for the **r**-bead matrix the non-monotonic kinetic curve  $F_B^r(T)$  behaviour (with the  $F_B^{r, \max}$  - maximum) for the relations  $D_B > D_A > D_C$  [1-3]. In addition some variants of the  $X_i$ -concentration waves-profiles were calculated for **r**-bead and **ro**-fiber.

For the other **ro**-fiber matrix the non-monotonic behavior of the kinetic  $F_B^{ro}(T)$ -curve (with the  $F_B^{ro, \max}$ ) is also calculated recently and these results will be published later.

At the same time it was calculated the kinetic curves with the usual monotonic behavior, (i.e. without the  $F_B^{L, \max}(T)$ ) for the **L**-membranes [1-3].

In author's publications [1-3] the preliminary explanation of the non-monotonic behavior of the kinetic  $F_B^{r, ro}(T)$  curves is given in terms of the propagating concentration  $X_i(T)$  - waves with some variants of the various diffusivities ( $D_A, D_B, D_C$ ) for the  $D_B, D_A \gg D_C$  inequality.

For many variants of the author's calculations the non-monotonic  $F_B^{r, ro}(T)$ -curves behavior is obtained recently for the various diffusion mobility  $D_i$  of the  $i$ -concentration  $A, B, C$ - waves. These results will be published later. The detailed explanations of the  $B$ -ion accumulation in the  $B$ -concentration wave with the non-monotonous  $F_B^{r, ro}(T)$  -curves behavior will be also presented.

For the relations  $D_B, D_A \gg D_C$  the  $B$ -accumulation in the  $B$ -concentration wave occurs due to the interference of the two incoming  $B, C$ -concentration waves. The author's computerized simulation shows the reason for this intensive  $B, C$ - waves interference – the *displacement effect* for the  $B$ -concentration wave. The influence of such displacement effect due to the interference of the two incoming  $B, C$ -concentration waves in the multicomponent kinetic mass transfer for the **r**-bead and **ro**-fiber was not known previously.

The accumulation in the fast  $B$ -wave is explained by the *displacement effect* due to the movement of the second invading  $C$ -concentration wave ( $D_B > D_C$ ), which moves to the  $B$  - concentration wave with the incursion via the front part of the  $C$ - wave. The details will be published.

Both characteristics of such type kinetic curves (the  $F_B^{r, ro, \max}$  - value and its position ( $T^m$ ) on the  $T$ -axes) depend on the relations for the  $D_i$  diffusivities,  $D_A \sim D_B \sim D_C$ . The physical sense of the  $B$ -concentration accumulation with the peak in the kinetic  $F_B^r(T)$ -curves for the **r**-bead should be explained by the displacement effect and by the steep decrease -  $dV_r$  of the **r**-volume for the diffusion into the **r**-sphere. The comparison with the  $dV_{ro}$  volume for the diffusion into the **ro**-fiber, doesn't show the steep decrease of  $dV_{ro}$ . Such changes of the  $dV_r, dV_{ro}$  volumes explain the difference in the intensity of the  $B$ -ion accumulation for the **r**-bead in comparison with accumulation for the **ro**-fiber. The details will be presented in the following publications.

One more result for the non-monotonous kinetic curve behavior in the ternary IEx system should be marked for the completeness of the information. For the **L**-membrane such behavior of the kinetic  $F_B^L(T)$  curve with the corresponding maximum -  $F_B^{L, \max}$  is obtained experimentally in the paper [15]. However this result is obtained for the **L**-membrane with the principal differences in comparison with the ternary IEx kinetics inside the **r, ro**-matrixes for the cases discussed above. In the case of the **L**-membrane the ternary IEx kinetics have been analyzed [15] for the absolutely another boundary



conditions. In the paper [15] the non-monotonous kinetic  $F_B^L(T)$  curve behavior was calculated in the ternary IEx for the diffusion of the two  $B,C$ -ions with the very short simultaneous action of the third  $A$ -ion on one side of the L-membrane. For the theoretical calculations [15] it was used the authors' phenomenological model (named as the "macroscopic" IEx model - MIE [15]) based on the usual differential equations for the ternary  $A,B,C$ - IEx kinetics. The  $A,B,C$ -concentration waves (see above) along the L-distance of the membrane may not be calculated in principle because of the "macroscopic character" of the authors' MIE model [15].

### Modeling of the multicomponent diffusion kinetics with the additional mass transformation (MAL) in the bi-functional NC matrix

Coming back to the NC systems, it should be marked, that the  $i$ -concentration waves approach to the quantitative estimation of the multicomponent mass transfer kinetics in the NC matrix is very fruitful. The additional method of the quantitative estimations of the  $i$ -concentration waves behavior includes the computerized calculations of the two integral parameters for the wave distributions: "Center of Mass - CM" and "Dispersion - Disp". The corresponding conclusions concerning co-influence of the reactions (I) and multicomponent diffusion coefficients (II) inside the bi-functional NC matrix on the  $kR^0$ -concentration wave behavior are obtained.

These integral  $CM_k(T)$ ,  $Disp_k(T)$  – parameters may be easily calculated during the computer calculations of the  $i$ -concentration waves during the simulation of the mass transfer process in the NC matrix. The dependence -  $CM_k(T)$  describes the  $k$ -wave velocity along the  $r, (r_0)$ - radius of the  $r$ -sphere ( $r_0$ -cylinder), or through the L-layer of the planar L-membrane. The  $Disp_k(T)$ -dependence (the dispersion) describes the change of the width of the frontal  $X_T$ -concentration wave in correspondence with the physical sense (Figs. 3a,b).

The illustrations of these postulates are presented in Figs. 2(a-f), and 3(a,b) for the profiles of the  $kR^0$ -wave with the position  $CM_k$  on the abscissa axes ( $CM_k$ -«triangles» on  $r, r_0$  or  $L$  – abscissa axes, Figs. 2(a-f)). The results of the computer calculations of the both dependences of the integral parameters-  $CM_k(T)$ ,  $Disp_k(T)$  for various shapes of the NC matrix ( $r, r_0$  or  $L$ ) are then presented in Figs. 3a,b. Here it is shown that these  $CM_k(T)$ ,  $Disp_k(T)$ -dependences describe quantitatively the  $kR^0$ - wave behavior, where  $kR^0$  is the  $k=5^{\text{th}}$  component with the concentration of the free nano-sites-  ${}_5R^0$ .

Such  $kR^0$  - wave (Figs. 2(a-f), solids,  $k=5$ ) is formed in the bi-functional NC matrix, due to the partial transformation (1B) of the  ${}_4H^+$ -component into the  ${}_5RH^+$  -component with the corresponding change of the  $[{}_kR^0]$  – concentration in the  $k$ -wave ( $k=5$ , Variant 1, Figs. 2(a-f)). The example of the description, and the transformation (1B) are presented in the following Section A for the Variant 1 with the two chemical reactions (1A), (1B). The list of the all components for the Variant 1 in the bi-functional NC matrix is presented below.

#### A. Kinetics of sorption of acid ( $H_2SO_4$ ) inside bi-functional NC Matrix with one Reaction onto the active nano-sites ( ${}_5R^0$ )

Variant 1. Mass transfer kinetics of  $H_2SO_4$  acid for 5 – component NC system. (Number of  $i$ - component is denoted by the index to the left of the symbol of the  $i$ - component with the corresponding diffusion coefficient  $D_i$ ):

${}_1SO_4^{2-}$  - two charged acid anions with diffusivity  $D_{1SO_4}=0.01$  in the NC pores (2, Рис. 1c);

${}_2RH^+$  - unmovable ( $D_{2RH^+}=0$ ) 2<sup>nd</sup>-component, formed by  ${}_5R^0$  nano-site with acid cations ( ${}_4H^+$ ) due to the *association* reaction (1B);

${}_3HSO_4^-$  - acid anions (formed by reaction (1A)) with diffusivity ( $D_3$ ) in the NC matrix pores;

${}_4H^+$  - cations of  $H_2SO_4$  acid with diffusivity ( $D_{4H^+}=0.03$ ) in the NC matrix pores;

${}_5R^0$  - zero valent nano-sites ( $D_{5R^0}=0$ , with the concentration  $[{}_5R^0]$ ), formed by NC agglomerates (Fig. 1d).

This 5-component NC system is characterized by: three diffusivities:  $D_{1SO_4}$ ;  $D_{3HSO_4}$ ;  $D_{4H^+}$  with reaction (1A) in the NC matrix pores, together with one “*association-dissociation*” reaction (1B) onto the active nano-sites -  ${}_5R^0$  correspondingly:



$$[{}_3HSO_4^-] = K_A [{}_4H^+] [{}_1SO_4^{2-}] \quad (\text{MAL}_A); \quad (1A)$$

onto active nano-sites  ${}_5R^0$ ,  ${}_2RH^+ \Leftrightarrow {}_5R^0 + {}_4H^+$ ,

$$[{}_2RH^+] = K_B [{}_5R^0] [{}_4H^+] \quad (\text{MAL}_B) \quad (1B)$$

The second relations of the reactions are described by  $\text{MAL}_S$  with the constants:  $K_A$ ,  $K_B$  (1A), (1B). The total quantity of the active nano-sites in the NC matrix is permanent. In result the relation (1C) for the  $[{}_5R^0]$ -concentration distribution (*Variant 1*) follows :

$$[{}_5R^0] + [{}_2RH^+] = 1 \rightarrow [{}_5R^0] + K_B [{}_5R^0] [{}_4H^+] = 1 \rightarrow [{}_5R^0] = 1 / (1 + K_B [{}_4H^+]) = 1 \quad (1C)$$

*Variant 1* describes sorption of  $H_2SO_4$  acid with the sulphate anions ( $\text{An}^- = {}_1SO_4^{2-}$ ), including концентрации  $[{}_iX]$  concentration of the all 5 component ( $i=1,2,\dots,5$ ; left indexes):  $[{}_1SO_4^{2-}]$ ,  $[{}_2RH^+]$ ,  $[{}_3HSO_4^-]$ ,  $[{}_4H^+]$ ,  $[{}_5R^0]$ . This diffusion kinetic process in the bi-functional NC matrix is accompanied by two MAL reactions: one in the NC pores (1A), and another reaction onto the NC nano-sites (1B). The parameters  $D_{1SO_4}$ ;  $D_{3HSO_4}$ ;  $D_{4H^+}$  - three diffusivities of  $i$ -components - 1,3,4. (naturally,  $D_2 = D_{5R^0}=0$ ).

All MAL relations (1A,1B) are represented here by the simple relationships:  $[i][j] = K_S [ij]$  (Fig.1d).

### Concentration i-waves behavior in modeling of multicomponent NC kinetics

The results of the computerized simulation are presented in this Section for the rather simple *Variant 1* with one “*association-dissociation*” reaction (1B) onto the  ${}_5R^0$  - nano-sites. It is obtained the description of the propagating concentration waves, including  ${}_5R^0$  - concentration waves (5 component NC system, Figs. 2,3).

Comparison of the  ${}_5R^0$ - waves (solids, 5, Figs. 2(a-f) shows that they propagate to the Center of r-bead (or ro-fiber, Figs. 2b,e) *faster* for the small  $K_B = 36$  value (a-c,up), than for the large  $K_B = 398$ (d-f, down):  $\text{CM}_R(c) < \text{CM}_R(f)$ . For the Dispersion the inequality is different in sense:  $\text{Disp}_R(c) > \text{Disp}_R(f)$ . In other words the  ${}_5R^0$ - wave propagates slower and with more sharp profile in Fig. 2f, ( $K_B=398$ ,down), in comparison with the same profile of the  ${}_5R^0$  - wave, but in Fig. 2c ( $K_B=36$ ,up).

Under the increasing of the  $K_B$  value from (a-c,up) to (d-f,down) in Figs. 2(a-f), the equilibrium of the (1B) reaction shifts to the left (see.1B). In this case (from Fig. 2(a-c, up) to Fig. 2 (d-f, down)), this shift of the equilibrium (1B) brings the retardation of the kinetic process. This is manifested in more slow movement of the  ${}_5R^0$ -wave. Figures 2(a-f) show the influence of the  $K_B$  value due to the (1B) reaction: the increase of the  $K_B$  value slows down the Time of the kinetic process -  $T_{\text{fin}}$ .

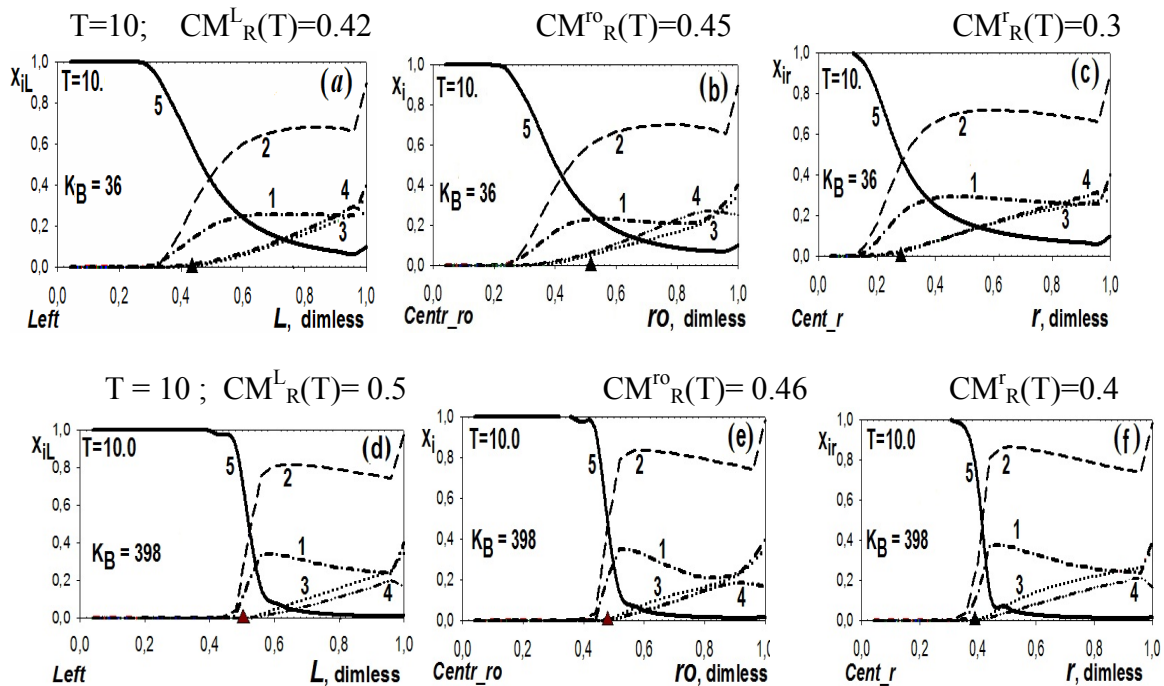


Fig. 2(a-f). Variant 1 (Анион  $\text{SO}_4^{2-}$ ). Comparison of the propagating  ${}_5R^0$  - waves (lines, 5) in the course of time (T) in NC matrix of various shape: L-membrane (left, a,d); ro-fiber (middle, b,e); r-bead (right, c,f). «Triangles» on the abscissa axes show the positions of  $\text{CM}_R$ . (Numbers of  $i$ -components are stated near the corresponding curves).  $D_{3\text{HSO}_4} = 0.0085 < D_{1\text{SO}_4} = 0.01 < D_{4\text{H}} = 0.03$ .  $K_B = 36$  (a-c, up);  $K_B = 398$  (d-f, down).  $T = 10$ .

Figures 2(a-f) illustrate the influence of the three various shapes of the NC matrix: r-sphere (right), ro-cylinder (middle) и L-membrane (left) on the  ${}_5R^0$  - waves behavior in the course of time (T) ( $T = 10$ ) for the same values of the  $K_B$  values:  $K_B = 36$  (a-c, up) or 398 (d-f, down).

The comparison of the propagating  ${}_5R^0$  - waves (2a-c, up) и (2d-f, down) shows that in the NC matrix of the r-bead the  ${}_5R^0$  - wave moves the most rapid in comparison with the NC matrixes of ro-fiber or L-membrane:  $\text{CM}_R^L(T)(a,d) > \text{CM}_R^{\text{ro}}(T)(b,e) > \text{CM}_R^r(T)(c,f)$  (compare the  $\text{CM}_R$  positions («triangles» on the abscissa axes) in Figs. 2(a-c), up; d-f, down).

The reason for this difference in the waves velocity for various shapes is geometric: in course of time T into the r-bead matrix diffusion takes place into the smaller volume:  $V_r = 4\pi r^3/3$  than in the ro-cylinder:  $V_{\text{ro}} = \pi(\text{ro})^2 h$  ( $r, \text{ro} < 1$ ). In the meantime in the planar L-membrane the volume for the diffusion is proportional to the rest of the thickness.

Figures 3a,b represent the total dependences in course of time for the integral parameters:  $\text{CM}_R(T)$  (solids), &  $\text{Disp}_R(T)$  (dashed), characterizing the  ${}_5R^0$  - wave (Variant 1) in the NC matrix of various shape: r-sphere, ro-cylinder, L-membrane.

Figures 3a,b show dependences for the estimation of the integral values:  $\text{CM}_R(T)$ , and  $\text{Disp}_R(T)$  for the mass transfer kinetics for all three shapes (r,ro,L) of the NC matrixes. It is clear, that the completion time for the kinetic process ( $T_{\text{fin}}$ ) corresponds to the criterion:  $(\text{CM} + \text{Disp})_R^{\text{r,ro,L}} = 1$ . The distance covered by the  ${}_5R^0$  - wave to the moment  $T_{\text{fin}}$  is equal to the characteristic size of the NC matrix:  $L_0$  (thick),  $\text{ro}_0$  (radius of cylinder) or  $r_0$  (radius of sphere). In other words the completion time -  $T_{\text{fin}}$  corresponds to the point of crossing of two curves:  $\text{CM}_R(T)$ , (solids), and  $\text{Disp}_R(T)$ , (dashed) (Figs. 3a,b) for each of three shapes of the NC matrix correspondingly. In correspondence with this criterion of

«crossing», it is evident from all Figs. 3, that for any variant of mass transfer the kinetic mass transfer the fastest one in the **r**-bead of the NC matrix, and the slowest in the **L**-membrane. The **ro**-fiber NC matrix is in the intermediate position in this row:  $T_{fin}^r < T_{fin}^{ro} < T_{fin}^L$ . These conclusions appear with evidence from Figs. 3, and 2.

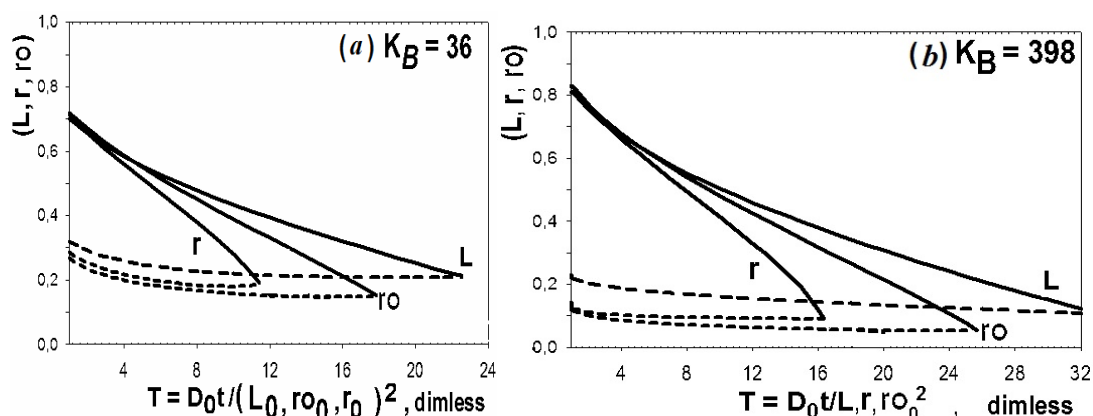


Fig. 3(a,b). Variant 1. Total dependences for the parameters:  $CM_R^{r,ro,L}(T)$ , (solids);  $Disp_R^{r,ro,L}(T)$ , (dashed) in course of time (T) for propagation of the  $5R^0$ - wave: L- membrane, ro-fiber, r-bead. Along ordinate axes: distance from matrix boundary ( $L_0, ro_0, r_0=1$ ) till the “zero” point ( $L, ro, r=0$ ).  $0 < L, r, ro < 1$ .  $D_{1SO4}=0.01$ ;  $D_{3HSO4}=0.0085$ ;  $D_{4H}=0.03$ .  $K_B=36(a)$ ;  $398(b)$ .

## Discussion of Results

The computerized simulation of the mass transfer kinetics in the NC matrix demonstrates rather comprehensive and clear analogy between the theory of nonlinear chromatography [10-12] and multi-component NC kinetics [1-4]. These analogies are shown in the Table 1 and concern the behavior of the multicomponent concentration waves in the bi-functional NC matrix. These comparison between theory of multicomponent chromatography and the mass transfer kinetics in the NC matrix discloses the driving forces for the multicomponent mass transfer kinetics in the NC matrix. The co-influence of the two co-existing (I)-Reaction or Selectivity, and (II)-multicomponent Diffusion factors in the bi-functional NC matrix determines the physical sense in the explanation of the reasons for the behavior of the propagating concentration waves (Fig. 2a-f). In respect to the theory of chromatography the same type of the co-influence is represented by the following factors: I-multicomponent sorption isotherms, and II – the set of broadening factors ( $HETP_i$ ) in columns (II). The factor II is characterized by the well known parameters –  $HETP_i$  in the theory of chromatography [10-14].

The analogy and the correlation between two processes: the NC kinetics (1) ~ the theory of chromatography (2) are obviously presented [1 (2<sup>nd</sup> string) ~ 2 (3<sup>d</sup> string)] in the Table 1.

The influence of the first factor (I – Reaction, Selectivity) is expressed by the  $K_S$  (MAL) values: the more is the  $K_B$  value (1B) – the less is the Dispersion ( $Disp_R$ ) of the  $5R^0$  concentration wave. In other words the width of the wave profile becomes narrower with the large  $K_B$  value (Figs. 3b, dashed). The comparison of the  $Disp_R$  (width) for the curves 5 in Figs. 2a-c (up, small  $K_B$ ) with Figs. 2d-f, (down, large  $K_B$ ) shows narrowing distinctly (compare the width of the corresponding curves 5 up and down). The same effect is shown via the comparison of Figs. 3a with Figs. 3b (dashed, corresponding r,ro,L -

curves). The influence of the second factor (II - Diffusion) gives, as usual, the widening of the concentration waves with the increase of the diffusivities.

Table 1.

(1) ~ (2): ANALOGY, MASS TRANSFER, WAVES ( $W^+$ )			DIFFERENCES, & FEATURES
(1) NC KINETICS MODEL ~		(2) THEORY of CROMATOGRAPHY (DYNAMICS)	PROPAGATING CONCENTRATION WAVES
(1) KINETICS, NC MODEL (Multicomponent Mass Transfer)	(1) EQUILIBRIUM REACTIONS (I) (Selectivity $K_S$ , MAL)	(1) NC MODEL (DISPERSION) for WAVES Multicomponent DIFFUSION ( $D_i$ , II)	(1) MOVEMENT of ALL WAVES Includes : $R, pR$ - Components, Though Diffusion $D_{R, pR} = 0$
(2) DYNAMICS, THEORY of CHROMATOGRAPHY (Multicomponent Mass Transfer)	(2) SORPTION EQUILIBRIUM (I) (Set of ISOTHERMS)	(2) THEORY of CROMATOGRAPHY (Multicomponent) BROADENING (DISPERSION) WAVES (HETP <sub>i</sub> Effect) (II)	(2) MOVEMENT of ALL WAVES (HETP <sub>i</sub> + SORPTION + MOBILE PHASE)

It should be emphasized here the non-trivial, specific effect for the  ${}_5R^0$  – wave in the NC kinetic system: there is no diffusivity for the  ${}_5R^0$ -component ( $D_{5R}=0$ ), nevertheless the propagation of the  ${}_5R^0$  - concentration wave takes place (Figs. 3a,b,  $CM_R$ -solids). The physical reason of such propagation is not the diffusivity ( $D_{5R}=0$ ) but the chemical reaction (1B) influence: the transformation for the masses of the  $i$ -components: eqn. (1A); eqn. (1B)  ${}_2RH^+ \leftrightarrow {}_5R^0 + {}_4H^+$ , and the diffusivities of the other  $i$ - components ( $D_{ISO4}$ ;  $D_{3HSO4}$ ;  $D_{4H}$ ) bring the resulting mass transfer for the  $[{}_5R^0]$  – concentration wave profile. This non-trivial, specific effect for the  ${}_5R^0$  – wave shows its integral character, which “includes” the influence of other  $i$ -concentration waves diffusing in the NC bi-functional matrix.

One more interesting result with the evidence of the above marked analogy (Table 1) can be seen from Figs. 3a,b. In this cases it takes place the typical behavior of the  $Disp_R$  in the course of Time (T, abscissa): the  $Disp_R$  value of  ${}_5R^0$ - wave tends asymptotically to the permanent value at the end of T- abscissa (Figs. 3a,b, see dashed curves behavior along the abscissa). This stabilization of the  $Disp_R$  value occurs due to the “compensation” of the broadening effect (II – “Diffusion”) by the stabilization effect of the “Reaction” factor (I). Here the broadening effect (II) is expressed by multicomponent diffusion of other  $i$ -components mentioned (though  $D_{5R}=0$ ). Significant to note that the integral character of the  ${}_5R^0$ - wave is also appeared at this stabilization process.

In the theory of chromatography the same effect of the compensation takes place for the concentration waves in column, when the favourable isotherm factor (I) used to compensate the unfavourable influence of the broadening HETP<sub>i</sub> factors (II) for the concentration waves in columns: favourable equilibrium (I) compensate the widening of the concentration wave.[10,12]

Thus the described analogy (Table 1) between the NC kinetics of the multicomponent mass transfer and theory of multicomponent chromatography is demonstrated obviously.

## Conclusion

The modern kinetic Model for the multicomponent mass transfer in the novel NC materials is created. The computerized simulations of the nonlinear IEx, NC systems on the basis of the created Model bring the new results describing the behavior of the multicomponent concentration waves in the bi-functional NC matrixes for the three various matrix shapes: r-bead, ro-fiber, L-membrane.

The results demonstrate rather comprehensive and clear analogy between theory of nonlinear chromatography and multicomponent mass transfer kinetics in the bi-functional NC matrix (Table 1). This analogy is used for the description of the multicomponent concentration waves behavior in the kinetic process in the bi-functional NC matrix. In the interpretation of the analogy there are shown the decisive influences of the equilibrium parameters and diffusion effects on the propagation of the concentration waves during the mass transfer inside the bi-functional NC matrix.

The “multicomponent concentration wave” concept ( $W^+$ ) in the study of the NC kinetics of mass transfer in the bi-functional NC matrix with the two co-existing factors: (I) Reactions on the active nano-sites, and (II) multicomponent Diffusion in the NC medium is effective. It brings the clear, and understandable treatment of the multicomponent mass transfer kinetics in the NC matrix. The original, new results demonstrate the behavior of broadening and interfering  $i$ -concentration waves in the bi-functional NC matrix during the kinetic multicomponent mass transfer process.

The quantitative estimations of the concentration waves behavior in the multicomponent NC systems are obtained by using the two integral parameters of the wave distributions: “Center of Mass - CM” and “Dispersion - Disp”. The corresponding conclusions concerning co-influence of the reactions (I) and multicomponent diffusion coefficients (II) inside the bi-functional NC matrix on the  $kR^0$  - concentration wave integral behavior are obtained.

All the obtained results are presented in terms of the additional key  $W^+$ -concept: propagating concentration waves in the bi-functional NC matrix. The used  $W^+$  concept for the description of the multicomponent NC mass transfer kinetics gives the clear interpretation of the computerized results. The obtained original, new results show the behavior of the broadening and interacting propagating concentration waves inside the bi-functional NC matrix during multicomponent mass transfer kinetics.

The corresponding computerized author’s animations are prepared for the visual demonstration of the calculated results of the simulation. The kinetic process regularities in the NC matrix illustrated by the animations (framed on the basis of the computerized new Model calculations) are perceived easily.

It should be emphasized the non-trivial, specific effect for the  $sR^0$  – wave integral behavior in the NC system: there is no diffusivity for the  $sR^0$ -component ( $D_{5R}=0$ ), nevertheless the propagation and broadening of the  $sR^0$  - concentration wave takes place.

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