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# Macroscopic model for multispecies ion-exchange kinetics

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## Abstract

A model for multispecies ion-exchange kinetics based on the Nernst–Planck equation is suggested. It is analyzed in comparison with the “locally-determinate” model described by Hwang and Helfferich [1]. The model makes possible simple computation. The conditions for the occurrence of unusual kinetic curves with a maximum are clarified. The proposed model is developed for different types of kinetic problems and verified by the experimental investigation of a kinetics in ternary systems.

*Keywords:* Multispecies ion exchange; Kinetics; Intraparticle diffusion; Macroscopic electric field

## 1. Introduction

An interest to multispecies ion-exchange kinetics is dictated by the following reasons. On the one hand, a behaviour of complicated ion-exchange systems cannot be adequately described by the models for two-ion systems. On the other hand, special features of the kinetics are seldom if ever used in actual ion-exchange practice and technology to create processes not only with greater intensity but with the components distribution between phases, more advantageous than equilibrium one.

Nevertheless, the multispecies ion-exchange kinetics is not sufficiently investigated yet because of difficulties in its modelling and experimental testing [1, 2]. The most rigorous model for intraparticle-diffusion controlled ion

exchange, based on the Nernst–Planck equation was developed by Y.-L. Hwang and F.G. Helfferich [1]. The more readily solved model to calculate the multispecies ion-exchange kinetics is suggested in the present study.

## 2. Premises and physical model

For the kinetic model to be set up one has to consider physical laws governing the movement and distribution of ions in the ion-exchanger phase.

### 2.1. Ion fluxes

The ion fluxes are operated by the factors: diffusion and electric field arising from the differences of ions mobilities. The flux for ions  $i$  can be described as follows:

$$J_i = D_i \text{grad } a_i + v_i a_i \quad (1)$$

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In accordance with the Einstein law the velocity of drift of the ions in the electric field can be expressed as follows:

$$v_i = b_i z_i F \cdot E = -\frac{F}{RT} D_i z_i \text{grad } \varphi \quad (2)$$

Equations 1 and 2 give the known form of the Nernst–Planck equation:

$$J_i = -D_i \left[ \text{grad } a_i + \frac{F}{RT} z_i a_i \text{grad } \varphi \right] \quad (3)$$

### 2.2. Material balances in the exchanger phase (ion exchange without chemical reactions)

The total quantity of given type substances is constant:

$$a_{i,t} + \text{div } J_i = 0 \quad (4)$$

### 2.3. Electroneutrality requirement to the intraparticle diffusion process

The sum of charges of counterions being under the thermodynamic equilibrium is equal to the sum of ion-exchanger fixed charges (functional groups charges):

$$\sum z_i a_i \approx \sum z_i a_{0i} = a_0 = \text{const} \quad (5)$$

(see Appendix, 1)

The left Eq. 5 is an approximation. The time it takes to establish any local equilibrium is by orders of magnitude less than the time for global thermodynamic equilibrium in the system (ion-exchange grain). Therefore, in the context of description of macroscopic process, Eq. 5 is close to the exact one.

At the same time it is imperfect compensation of the charges that gives rise to radial dipole moments in the grain and causes the centrally symmetric electric field, which tends to eliminate these dipoles. This statement is the main distinctive feature of the model proposed below from the “locally-determinate” model [1, 2] (LDM) in which the arising electric field is considered at the micro-level. The use of LDM leads to challenging mathematical problems related to

integration of nonlinear partial differential equations of second order. Our hypothesis for the macroscopic character of the electric field in an ion-exchange grain makes possible to the simplify mathematical formulation.

### 3. Macroscopic model of ion-exchange kinetics

Let us define the average concentration of ions  $i$  in the solid phase as follows:

$$\bar{a}_i = \frac{1}{V_0} \cdot \int_{V_0} a_i dV \quad (6)$$

According to the Gauss theorem and to Eqs. 5 and 6:

$$\frac{d\bar{a}_i}{dt} = -\frac{6}{d} \cdot (J_{0i} n) \quad (7)$$

Mass flux through this surface determined by Eq. 3 is:

$$J_{0i} = -D_i \left[ \text{grad}_0 a_i + \frac{F}{RT} z_i a_{0i} \text{grad}_0 \varphi \right]$$

Equations 3, 5 and 7 form the base for LDM, which was numerically solved in the papers [1, 2]. Mathematical expression for ionic fluxes without space derivatives can be formulated on the basis of the hypothesis mentioned above (electric and concentration fields are essentially macroscopic) and the fact represented in Eq. 7 (the function  $\bar{a}_i(t)$  is determined by the space derivatives at points of the ion-exchanger surface). In accordance with the hypothesis, a linear combination of concentration and potential gradients can be presented as functions of  $\bar{a}_i$  and  $\varphi$ . Assume, that such a function is linear and the following equality for  $J_{0i}$  works well:

$$\text{grad}_0 a_i + \left( \frac{F}{RT} \right) z_i a_{0i} \text{grad}_0 \varphi = -\frac{2\alpha n}{d} \left[ (a_{0i} - \bar{a}_i) + z_i \bar{a}_i \left( \frac{\alpha_1 F}{RT} \right) (\varphi_0 - \varphi) \right] \quad (\alpha, \alpha_1 = \text{const}) \quad (8)$$

The magnitudes  $a_{0i}$  and  $\varphi_0$  are taken for the grain boundary in LDM representation only. At the same time, these parameters characterize the

ion-exchange equilibrium for the whole grain in the framework of the macroscopic model (MM). For the intraparticle diffusion kinetics these statements are not in contradiction. Equations 3 and 8 can be rearranged as follows (see Appendix, 2):

$$\frac{d\bar{a}_i}{dt} - \frac{12\alpha}{d^2} \times D_i \left[ a_{0i} \bar{a}_i \left( 1 - \frac{z_i \sum D_i z_i (a_{0i} - \bar{a}_i)}{\sum D_i z_i^2 \bar{a}_i} \right) \right] \quad (9)$$

The constant  $\alpha = \pi^2/3$  can be determined from the asymptotics of LDM and MM for spherical grain at  $t \rightarrow \infty$ .

On the assumption that  $\varphi_0 - \varphi = 0$  in expression 8, the well-known E. Glueckauf kinetics approximation [3] can be derived. A principal limitation of the Glueckauf approach is that the parameters  $D_i$  are time dependent. In our model the diffusivities  $D_i$  are constant parameters, and the potential  $\varphi$  is time dependent.

#### 4. Types of kinetic problems

(1) The most simple formulation of kinetic problem was given earlier [1]; it can be represented in the following manner:

- given:  $z_i$ ,  $D_i$ ,  $a_{0i}/a_0$  and  $a_{i(t=0)}/a_0$  ( $i = 1, \dots, n$ );
- required: interrelation between  $\bar{a}_i/a_0$  and  $T = 4D_n t/d^2$ .

(2) The kinetic problem with the implicitly given parameters is more challenging, and this one frequently occurs in practice:

- given: the total ion-exchange capacity of the sorbent,  $a_0$  (meq/g); the average diameter of the grains,  $d$  (cm); porosity in the bed of the swelled exchanger,  $\varepsilon$ ; the volume of the bed ( $\text{cm}^3$ ) accounted for 1 g of dried mass,  $w$ ; the charges of functional groups and the ion-exchange equilibrium constants of different pairs of ions,  $K_{ij}$ ; the charges of ions,  $z_i$ ; their concentration in the external solution  $c_i$  ( $\text{mmol}/\text{cm}^3$ ); initial ions content of the sorbent,  $a_{i(t=0)}$ ;
- required: time dependence of  $z_i \bar{a}_i$ .

#### 5. Experimental

The following ion-exchange systems were used in this study: strong acidic cation-exchanger KU-2-8 “Khimreactiv”, Russia (styrene-divinylbenzene sulphonated resin which is analogous to the Dowex-50-8), in  $\text{Na}^+$ -form and solutions of mixtures of potassium chloride and strontium chloride with the concentrations 0.075–0.13 and 0.0024–0.089 mol/l, respectively. The root-mean-square grains diameter of specially selected fraction of the resin was  $0.064 \pm 0.013$  cm, the solutions used were prepared from reagents of Pure grade qualification.

The analyses of ion composition of the solutions were performed by the methods: atomic absorption in the flame of acetylene–air atomic emission in the flame of propane–air.

The experimental procedure, well-known as “shallow-bed” method [5] was used in the following manner: for a fixed time the working solutions were pumped with large enough flow rate (around  $25 \text{ cm}^3/\text{s}$ ) through the small portion of the cationic resin (0.1–0.2 g) placed in an experimental cell with the bed in thickness of one grain. Thereafter the process was rapidly interrupted by special three-channel cock and flushed out by distilled water. The contact time in each kinetic experiment was controlled with an error not greater than 0.5 s. After prior air drying and weighting the loaded probes of the cation-exchanger were treated by  $0.01 \text{ mmol}/\text{cm}^3$  solution of barium chloride at static conditions by the small successive portions of this solution up to the complete desorption of potassium and strontium. After that treatment the ions concentrations in the total collected volume of the solutions were analyzed and used to calculate the sorbents phases compositions at the fixed times of kinetic process and to plot the kinetic curves, as shown in Fig. 2.

#### 6. Results and discussion

The example of Problem 1:

- in the paper [1] a numerical solution on

the basis of LDM was presented for  $n = 3$ ,  $a_{3(t=0)} = a_0$ ;  $D_1 : D_2 : D_3 = 5 : 0.2 : 1$ ;  $z_1 = z_2 = z_3$ ;  $a_{01}/a_0 = 0.6$ ,  $a_{02}/a_0 = 0.4$ . We considered this problem from standpoint of MM. A comparison between results of both models presented in Fig. 1 demonstrates the acceptability of the premises made in the macroscopic model. An unusual kinetic effect is markedly seen in the curve for ions "1": a maximum with the coordinates (0.26;0.7). The investigation of this effect by MM resulted in the data presented in Table 1. Some conclusions concerning the maximum arising in kinetic curves can be made: a) a maximum (an overshoot of sorption uptake in comparison with an equilibrium magnitude) arises in the kinetic curve for the most mobile ion of competing ions; this conclusion is similar to that in the paper [1]; b) the diffusivity of a component being desorbed has to be greater than the diffusivity of at least one of competing components; c) the larger the differences between the

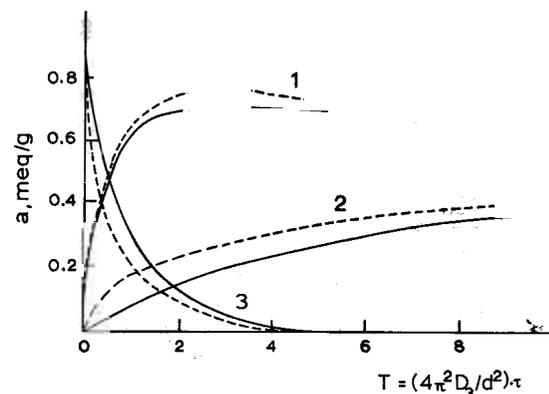


Fig. 1. Kinetic curves of most mobil competing ion (1), of another competing ion (2) and the curve of ion being desorbed (3). Ternary ion exchange simulated by the models: LDM (dotted lines) and MM (solid lines). Conditions:  $a_{3(t=0)} = a_0$ ;  $D_1 : D_2 : D_3 = 5 : 0.2 : 1$ ;  $z_1 = z_2 = z_3$ ;  $a_{01}/a_0 = 0.6$ ,  $a_{02}/a_0 = 0.4$ .

Table 1  
Overshoots on uptake-versus-time curves for the most mobile ion

Diffusivities ratio	Equilibrium uptake $Q_1$	Relative overshoot $\Delta Q_m/Q_1$
$D_1/D_3$ ( $D_1/D_3 = D_3/D_2$ )		
1	any	0
2	0.05	0.3
2	0.1	0.3
2	0.2	0.21
2	0.3	0.16
2	0.4	0.13
2	0.5	0.08
2	0.6	0.06
2	0.8	0.04
8	0.1	2.30
8	0.4	0.75
8	0.6	0.35
$D_1, D_2$ ( $D_1/D_3 \neq D_3/D_2, D_3 = 1$ )		
$D_1 \geq 1, D_2 = 1$	any	0
$D_1 = D_2 \leq 1$	any	0
$D_1 = 1, D_2 = 0.5$	0.1	0.11
$D_1 = 1, D_2 = 0.5$	0.2	0.10
$D_1 = 1, D_2 = 0.5$	0.5	0.04
$D_1 = 0.4, D_2 = 0.1$	0.2	0.86
$D_1 = 0.4, D_2 = 0.1$	0.5	0.37
$D_1 = 0.4, D_2 = 0.1$	0.8	0.11

diffusivities of competing components and between the diffusivities of the component being desorbed and the slowest competing component, the larger is the effect; d) the smaller the equilibrium concentration of the most mobile component in the ion-exchanger, the larger is the effect.

The examples of Problem 2 are given in Section 5:

– experimental kinetic curves for  $K^+$  in Fig. 2 show the maximums according to the theoretical predictions for the multi-ions systems. The calculated kinetic curves, as Fig. 2 shows, agree satisfactorily with the experimental ones. The calculations were performed by Eqs. A7–A9 with the parameters for special conditions of each experiment: characteristics and initial ions content of the sorbents, some physical characteristics and composition of the external solutions. Equation A9 also involves selectivity coefficients of ion exchange  $K_{ij}$  and equivalent conductivity of component in solutions  $\Lambda_i$ . In actual conditions one should take into account that these parameters are the functions of concentrations  $c_i$ . These data are presented in Table 2.

The empirical expression of the Onsager law type:

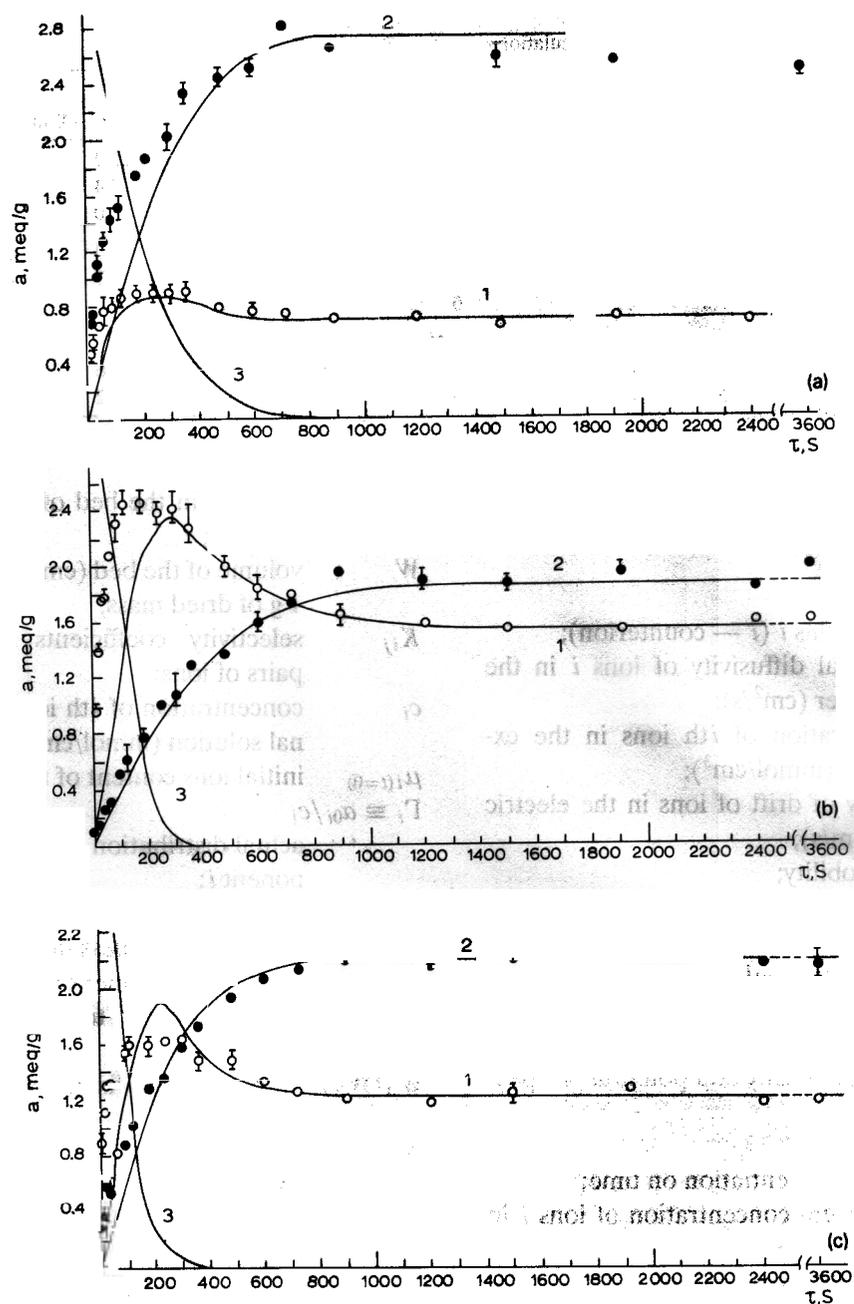


Fig. 2. Experimental points and calculated kinetic curves of  $K^+$  (1),  $Sr^{2+}$  (2) and  $Na^+$  (3) in ternary systems (see Table 2): (a) experiment No. 1; (b) experiment No. 2; (c) experiment No. 3.

$$\Lambda_i = \Lambda_{0i} - B \left( \sum z_i^2 c_i \right) \quad (10)$$

with  $B = 54.4$ ,  $r = 0.15$  and  $\Lambda_{0i}$  — the tabulated equivalent conductivity — was used to

calculate the actual values  $\Lambda_i$  of the internal solutions. Under these values of parameters, the experimental and calculated data are most close.

Table 2  
Parameters of the experimental systems used for calculations

Experiment no.	$K_{Sr/K}$ ( $\sqrt{g/cm^3}$ )	Ion	$c_i$ (mmol/cm <sup>3</sup> )	$z_i a_{0i}$ (meq/g)	$\Lambda_{0i}$ (cm <sup>2</sup> /Ohm/eq)	$\Lambda_i$ (cm <sup>2</sup> /Ohm/eq)	$D_i \times 10^6$ (cm <sup>2</sup> /s)
0.51		K	0.13	0.703	74	25.2	1.70
		Sr	0.089	2.737	56	7.4	0.255
		Na	0	0	52	3.0	0.808
.68		K	0.075	1.542	74	36.4	0.793
		Sr	0.0024	1.898	56	18.7	0.160
		Na	0	0	52	14.2	3.85
.62		K	0.103	1.231	74	33.4	1.18
		Sr	0.01	2.209	56	15.6	0.239
		Na	0	0	52	11.2	3.02

## Appendix

### 1. List of symbols

$J_i$	flux for ions $i$ ( $i$ — counterion);
$D_i$	individual diffusivity of ions $i$ in the exchanger (cm <sup>2</sup> /s);
$a_i$	concentration of $i$ th ions in the exchanger (mmol/cm <sup>3</sup> );
	velocity of drift of ions in the electric field (cm/s);
$b_i$	ions mobility;
	module of electric charge (in electron charges);
	the Faraday and gas constants, respectively;
$T$	temperature (K);
	electric intensity and potential, respectively;
	time (s);
$X_{,t}$	partial differentiation on time;
$a_{0i}$	equilibrium concentration of ions $i$ in the exchanger;
$a_0$	equivalent concentration of fixed groups;
$v, d$	volume (cm <sup>3</sup> ) and diameter (cm) of exchanger grain, respectively;
$n$	normal to the spherical surface of the grain;
"0"	index denoting the values taken at the surface;
$\alpha, \alpha_1$	constants;

$W$	porosity in the bed of the swelled exchanger;
	volume of the bed (cm <sup>3</sup> ) accounted for 1 g of dried mass;
$K_{ij}$	selectivity coefficients for different pairs of ions;
$c_i$	concentration of $i$ th ions in the external solution (mmol/cm <sup>3</sup> );
$\mu_i(t=0)$	initial ions content of the sorbent;
$\Gamma_i \equiv a_{0i}/c$	actual distribution coefficient for component $i$ ;
$\Gamma_{iT} \equiv a_{ei}/c_{ei}$	valid dimensionless distribution coefficient for component $i$ ;
"e"	index is assigned to locally equilibrium magnitudes;
$W_A(W_B)$	probability of fixed position (movement) of ion;
$\Lambda_i$	equivalent conductivity of $i$ th ions (cm <sup>2</sup> /Ohm/eq).

### A2. Mathematical part

1. When changes of electric field appearing in the process of electric charges motion are very small, the approximate expression takes place:

$$\sum J_i z_i - \sum J_f z_f \approx 0 \quad (A1)$$

where  $J_f$  and  $z_f$  are the fluxes and charges of co-ions, respectively. The Donnan effect makes difficult for free co-ions to transfer into the sor-

bent phase. Hence, the co-ions “f” in the sorbent are really the fixed ions of functional groups only (with  $D_f \equiv 0$ ). If so, Eq. 3 gives  $J_f \equiv 0$ , and then

$$\sum J_i z_i \approx 0 \tag{A2}$$

This equation and Eq. 4 lead to Eq. 5.

2. Equations 8 and 5 lead to the equality:

$$\text{grad}_{\varphi} \sum z_i^2 a_{0i} = \overline{\text{grad } \varphi} \sum z_i^2 \bar{a}_i \tag{A3}$$

$$\left( \overline{\text{grad } \varphi} = \frac{2\alpha\alpha_1 n(\varphi_0\varphi)}{d} \right)$$

A physical meaning of Eq. A3 is in the statement: the average electrostatic force (along the radius of a grain) acting on the ionic dipoles is equal to that on the grain boundary. So, the kinetics equation can be formulated as follows:

$$\frac{d\bar{a}_i}{dt} = \frac{12\alpha}{d^2} \times D_i \left[ a_{0i} - \bar{a}_i \left( 1 - z_i \alpha_1 \frac{F}{2RT} (\varphi_0 - \varphi) \right) \right] \tag{A4}$$

where the expression  $\alpha_1 \cdot (\varphi_0 - \varphi)$  is derived from the following condition, which is true with high accuracy (as Eq. 5):

$$\sum z_i d\bar{a}_i = 0 \tag{A5}$$

So:

$$\alpha_1 \cdot (\varphi_0 - \varphi) = -\frac{2RT}{F} \cdot \sum D_i z_i (a_{0i} - \bar{a}_i) \sum D_i z_i^2 \bar{a}_i \tag{A6}$$

3. The calculations of the parameters of this kinetic problem were made in the following manner: equilibrium parameters ( $a_{0i}$ ) were calculated in accordance with the mass-action law:

$$\Gamma_i^{1/z_i} = K_{ij} \cdot \Gamma_j^{1/z_j} \tag{A7}$$

where  $\Gamma_i \equiv a_{0i}/c_i$  is the actual distribution coefficient for component  $i$ . This parameter is related to the valid dimensionless distribution co-

efficient  $\Gamma_{iT}$  in the form

$$\Gamma_{iT} = \frac{\Gamma_i}{[W(1 - \varepsilon)]} \tag{A8}$$

The parameter  $\Gamma_{iT}$  forms a part of the expression for the intraparticle diffusivity of ions  $i$

$$D_i = \frac{RT \Lambda_i / (F^2 z_i)}{1 + \Gamma_{iT}^{1/z_i}} \tag{A9}$$

The deduction of this equation can be clarified by the model based on the assumption that ions only move in the solution impregnating the ion-exchange particle and they are fully motionless at bonded positions.

Interferences to ions motion by the exchanger matrix are neglected in this model (to sufficient accuracy this works well for polymeric ion exchangers [4]). Let us consider the following main reasons to deduce Eq. A9:

(a) The motion cycle is made up of two parts,  $A$  and  $B$ : the total time for ions translation from one point of the particle to another constitutes the residence time at fixed positions,  $A$  (fixed positions time), and the time of ions movement,  $B$ .

(b) Ratio between these times for a singly charged ion is equal to the ratio of concentrations of these ions in the associated phases; for linear isotherms this ratio is the valid distribution coefficient (having regard to phase volumes)  $\Gamma_{iT}$ , and this gives expression A9 for  $D_i$  at  $z_i = 1$ .

(c) The concept of probability of location in one position or another is more suitable for multiply charged ions. The ratio  $A/B$  is equal to the ratio of probabilities  $W_A/W_B$  (in this case  $W_A$  is probability for an ion to have at least one bond with matrix), but the ratio  $a_{ei}/c_{ei} = \Gamma_{iT}$  is equal to that between probabilities for ions to have bonds of one configuration or another,  $W_{eA}/W_{eB}$  (index “e” is assigned to locally equilibrium magnitudes). For example,  $W_{eA}$  for binary charged ions is probability to be concurrently bonded with two functional groups. The magnitude of this probability is equal to the square of probability to be bonded with at least one functional group:  $W_{eA} = W_A^2$  ( $W_{eB} = W_B^2$ ). Similarly, for  $z$ :  $W_{eA} = W_A^z$ .

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