A mechanism of separation of strong electrolytes by ion-exchangers, based on electro-kinetic exclusion of co-ions

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Abstract

An approach, describing the phenomenon of co-ions exclusion under violation of Donnann barrier in the ion-exchanger, is developed. This description is based on the difference between the composition of initial solution and electro-kinetic fluxes. The equations for equilibrium and kinetics of non-exchange process are deduced. It is shown that a certain transformation of counter-ions characteristics gives a way to describe the mass-transfer process with the use of the theory of the multicomponent ion exchange, i.e. the mass-transfer in non-exchanging process can be presented as equivalent to mass-transfer in ion-exchanging process. The quantitative parameters of the phenomenon depend on the characteristics of electrolyte, ion-exchanger and dynamic mode of contact of phases.

Keywords: acid retardation, exclusion of co-ions, Donnann effect, multi-species ion exchange kinetics

Развит подход, описывающий явление эксклюзии коионов при нарушении доннановского барьера в ионите, основанный на различии в составе раствора и электрокинетического потока смеси его компонентов. Выведены уравнения равновесия и кинетики необменного процесса. Показано, что при соответствующем преобразовании характеристик противоионов процесс массопереноса можно описать с помощью теории кинетики многокомпонентного ионного обмена, т.е. в определенном смысле массоперенос в необменном процессе эквивалентен массопереносу в ионообменном процессе. Количественные параметры явления зависят от характеристик электролита, ионита и динамического режима контакта фаз.

Ключевые слова: удерживание кислоты, эксклюзия коионов, эффект Доннана, кинетика многокомпонентного ионного обмена

Introduction

The properties of polymer ion exchangers in the field of *non-exchanging* processes in strong solutions, as well as these processes themselves, until now remain uninvestigated as a whole. However, the functional polymer-based process of separation of strong electrolyte mixes, shortly named as acid retardation process [1], in many cases are ecological and economical [2].

Several attempts to explain the acid retardation mechanism are based on the following ideas: 1. The interaction with polymer matrix is stronger for acid than for salt [3,4]; 2. The Donnann potential, that blocks up the surface for co-ions, can be passed over for less dissociated acid molecules more easily than for salt molecules [1]; 3. The

molecular-sieve effect of the polymer matrix, which leads to more availability of the polymer volume for smaller acid molecules [5].

The first hypothesis assumes different attraction (sorption) between various molecules and the polymer, which can be realized by either non-polar van-der-Waals forces or polar (but non-ionic) interactions, for instance, hydrogen bonds as the strongest ones. For strong electrolytes these both variants lead to low effects of concentrating near polymer chains, i.e. to negligible selectivity.

The second hypothesis assumes different repulsion of the co-ions under various screening from the inter-phase boundary. This mechanism of ion exclusion takes place for separation of mixes of weak acids or weak bases and does not effective for strong electrolytes.

The third assumption of the sieve effect would be useful under conditions of a regular micro-porous structure of the polymer, similar to the zeolite structure with the pore sizes less than 1 nm; however it is not quite right for polymeric ion-exchangers.

Each of these effects could be used as the matter of the phenomenon under investigation if special conditions of their participation are in accord with conditions of the real process of acid retardation.

The present paper proposes a new approach for explanation of the mechanism of the acid retardation process, which does not except elements of the named approaches, but it is based on the new idea – of electro-kinetic exclusion of co-ions.

Isotherm of non-exchanging equilibrium for strong electrolyte and ion-exchanger

Let us use the phase model of ion-exchanger postulating three zones of inner space: a van-der-Waals volume of polymer including also the volume of counter-ions; the volume referred to action zone of the field of fixed ions – the functional groups of polymer; and a free volume containing the fields of negligible magnitude so as they do not influent to behavior of ions. By mind of some researchers (N.B.Ferapontov et al), two parameters are important for this model: w_T is a fraction of the hollow space, i.e. the volume of ion-exchanger except its van-der-Waals volume, and w_F is a fraction of free volume. Consequently, a fraction of field of fixed charges is equal to $w_T - w_F$. Some authors (A.N.Krachak et al) assume different interaction between water and polymer in the each of zones; this also means different energy of ion bond thru the hydrate envelope. Here, we do not make so strong assumptions, we use the well known performance based on the Donnann effect.

The enter of co-ions (an ion of solution contacting with ion-exchanger, which has the same polarity as the fixed ion) into zone of the fixed ion field is closed. Usually, the functional groups form big clusters with the unify field for all; the field creates a general boundary around compact parts of the polymer. The Donnann effect arises in the case where fraction of the big clusters is large and, in generally, inner space of the ion-exchanger is unavailable for co-ions. At the same time, the free volume is available for co-ions. Fraction of this free volume is very small: this fact is confirmed by various characteristics of the ion-exchange processes, particularly, data on numbers of transfer for ion-exchange membranes [6] correspond to the fraction of the free volume not greater than 5-10% of total polymer volume. When the ionic strength is grounded, the field of the functional groups is more screened and does not unite – it becomes local and Donnann effect is missing. In that condition the whole hollow volume of ion-exchanger becomes available for outer electrolyte.

The convenience description of the moment of arising or missing the Donnann effect is realized in case if the polymer chain can be included into a regular lattice. For example, well known gel ion-exchangers can be placed within cubic lattice so that periods of polymer chain (monomers) are as diagonals of cubic cell edges. For the linear dimension of the period p, the constant of that lattice is $p/\sqrt{2}$. One more parameter is important for the ion-exchanger model: the average distance between functional groups (single-charged) b, which connect unambiguously with the ion-exchange capacity a_0 by the following expression: $a_0 = N_0^{-1}b^{-3}$, where N_0 is the Avogadro number. Counter-ions compensating fixed charges (and also single-charged) have average distance b, too. We can find value of the dipole arm for a couple of fixed ion and counter-ion by using the model of body-centered cubic lattice with fixed charges in the nodes and counter-ions in the center points: $b\sqrt{3}/2$.

The Donnann barrier is defined by the field of charged chains of polymer, [7]:

$$\phi(r) = \phi_0(r) - \frac{RT}{F} \ln\frac{a}{a_0}, \qquad (1)$$

where R, F are the gas and Faraday constants; T is temperature; ϕ_0 is the Donnann standard potential (when counter-ion concentration in polymer is equal $a = a_0$); for single cubic cell it is estimated as the dipole potential: $\phi_0(r) = \frac{\sqrt{3}}{2}\frac{be}{\varepsilon_e r^2}$, where ε_e is the dielectric permittivity of medium, $e = 4.8 \cdot 10^{-10}$ (CGSE) is the elementary charge.

The indicated above condition for the moment of co-ions breakthrough corresponds to absence of multiply of border potential in the scaling operation, i.e. the breakthrough arises for null value of potential on the distance of lattice step from a field source: $\phi(p/\sqrt{2}) = 0$. In accordance with (1) we obtain:

$$\ln\frac{a_{Dn}}{a_0} = \frac{F}{RT}\phi_0(p/\sqrt{2}) = \frac{\sqrt{3}N_0 e^2}{\varepsilon_e RT}\frac{b}{p^2}, \qquad (2)$$

where a_{Dn} is the critical concentration of counter-ions in attraction zone of polymer chain.

The first multiplier in expression (2) for T=298K and water dielectric permittivity ε_e=80 is equal 1.21 nm. The value of the second multiplier depends on ion-exchanger type. For instance, for anion-exchanger AV-17 (analogous of DOWEX-1) with cross-linking 8% ($p = 2.5$ nm, $b = 1$ nm) we obtain 0.16 nm^{-1}. The product in that case is equal $\ln\frac{a_{Dn}}{a_0} \approx 0.19$, i.e. $\frac{a_{Dn}}{a_0} \approx 1.21$, and for a_0=1.6 M we have a_{Dn}=1.9 M. Anyway, it is important the right part of (2) is positive, i.e. $a_{Dn} > a_0$.

So, for a sum concentration of solution participated in the acid retardation process, we obtain inequality: $c_0 > c_x \equiv a_{Dn} > a_0$.

The local concentration a_{Dn} (in caves of polymer) averaging on volume of an ion-exchanger grain gives two values: $\overline{a}_{Dn1} = w_F a_{Dn}$ and $\overline{a}_{Dn2} = w_T a_{Dn}$. The difference between hollow and free volumes of polymer leads to jump on the isotherm of equilibrium of solution and ion-exchanger, from $\overline{a}_{Dn1}$ to $\overline{a}_{Dn2}$. This is refracted on the theoretical dependence, where a simple filling of available volumes within polymer is assumed:

$$\overline{a} = \begin{cases} w_F c, \ 0 \le c < c_x \\ w_T c, \ c \ge c_x \end{cases}.$$ (3)

Statistical character of interaction of solution and polymer components excludes discontinuity of the dependence; therefore, the transfer between two branches of the plot has a view of thin line in Fig.1. For approximation one can use the function below:

$$y(x) = x \cdot \left\{ w_F + (w_T - w_F) \left[\frac{1}{2} + \frac{1}{\pi} \operatorname{arctg} A(x - c_x) \right] \right\},$$ (4)

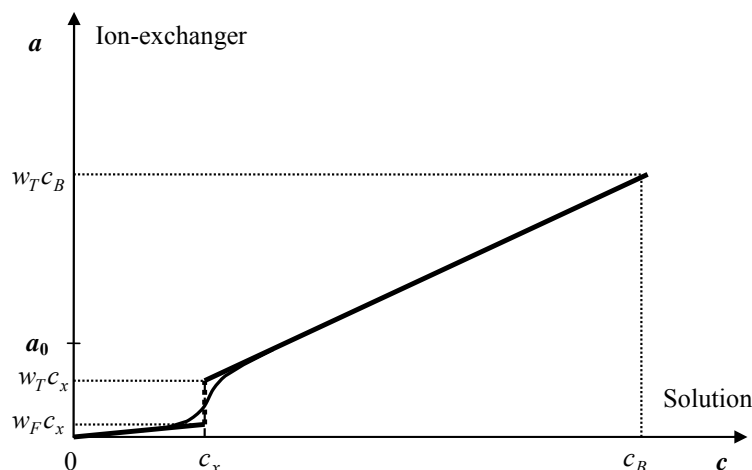where the function $\operatorname{arctg}[A(x - c_x)]$ is using for smoothing of jump in point c_x.

Fig. 1. Theoretical isotherm of distribution of strong electrolyte between solution and ion-exchanger phases. Thin line shows a possible smoothing of jump

The dynamical interpretation of the Donnann effect also is possible: in the process of equilibration of counter-ion concentrations within and out of polymer and grounding the first one up to ion-exchange capacity and further, the radial field arises in the polymer grain and allows for co-ions to go in a certain moment into inner volume of the polymer. For example, when the strong electrolyte solution is passed thru column with pure ion-exchanger the concentration of solution is grounding from null to initial value and can be passed the point c_x. In that moment the flux of ions into ion-exchanger increases quickly. As a result, the non-equilibrium state is arisen. That is the matter of the separation by the electro-kinetic exclusion mechanism.

Mechanism of electro-kinetic exclusion of co-ions

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.

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

$$\mathbf{J}_i = -D_i \operatorname{grad} a_i^* + \mathbf{v}_i a_i^*,$$ (5)

where D_i is diffusivity of the ion, a_i^* is molar concentration of the ion in solid phase (star notes the local value), $\mathbf{v}_i$ is velocity of ions migration under electric field action, which in accordance with the Einstein law is equal to

$$\mathbf{v}_i = b_i z_i e \mathbf{E} = -\frac{F}{RT} D_i z_i \mathbf{grad}\phi \tag{6}$$

where b_i is mobility of the ion; $\mathbf{E}$, ϕ are parameters of electric field. Equations (5) and (6) give the known form of the Nernst-Planck equation:

$$\mathbf{J}_i = -D_i \left(\mathbf{grad} a_i^* + \frac{F}{RT} z_i a_i^* \mathbf{grad}\phi \right) \tag{7}$$

<u>Material balances in the polymer phase.</u> The total quantity of given type substances is constant:

$$\frac{\partial a_i^*}{\partial t} + \operatorname{div} \mathbf{J}_i = 0 \tag{8}$$

<u>Electro-neutrality requirement.</u> If electric currents arising in an unstable process are small, the approximate expression takes place:

$$\sum \mathbf{J}_i z_i + \sum \mathbf{J}_m z_m \approx 0, \tag{9}$$

where $\mathbf{J}_m$ and z_m are accordingly fluxes and charges of counter-ions (here and below only co-ions we note by index i). Let us integrate of (9) with substitution of (8):

$$\sum a_i z_i - \sum a_m z_m \approx -a_0 = const, \tag{10}$$

(stars at symbols are omitted after integrating on volume). In the zone of functional group field for both cases of Donnann barrier (is it present or no) we obtain in accordance to (10):

$$\sum a_i z_i = \sum a_m z_m - a_0 = \begin{cases} 0; \ a_t < c_x \\ a_t; \ a_t \geq c_x \end{cases}, \tag{11}$$

where a_t is the current equivalent concentration of electrolyte in the polymer, $a_t \leq c_0 \equiv \sum c_i z_i$; a,c are molar concentrations of ions in the polymer (in the available zones) and in the solution (here are constant), accordingly; $c_0 = const$ is equivalent concentration of electrolyte in the solution. For the phenomenon under investigation the low expression of (11) is true:

$$\sum a_i z_i = a_t \tag{12}$$

In accordance with (11), the same value of a_t is equal to sum of equivalent concentrations of counter-ions without the concentrations participating in ion exchange.

<u>The eqn.12 can be formed as electro-neutrality law for ion exchange,</u> with use the following way. One can perform the counter-ions within polymer, exceeding the capacity of ion exchange, as ions (we named their 'conjugate co-ions') with the same mobility, but opposite charge and moving toward opposite direction; the concentration of conjugate co-ions (signed by tilde) supplements the counter-ion concentration up to constant: $\widetilde{a}_m = const - a_m$. Really, because in the mass-transfer equations (7,8) the concentrations participate in derivatives only, they are defined with accuracy to constant, however, choice of direction of moving and sign of charge must neutralize changes of signs of the derivatives. As a constant in given above transformation the value $a_{0m} + c_m$ is convenient:

$$\widetilde{a}_m = a_{0m} + c_m - a_m \tag{13}$$

In this case the process under investigation is performed as equivalent mono-polar exchange of conjugate co-ions, initially have been in polymer, to co-ions going from solution. Assignation by index i is expanded to conjugate co-ions, too, with concentration $a_{i(m)} = \widetilde{a}_m$. Instead of eqn.(12) we can write:

$$\sum a_i z_i = c_0 = const \tag{14}$$

For co-ions of the outer solution the identity $c_0 \equiv \sum c_i z_i$ takes place, therefore, for conjugate co-ions it follows $c_{i(m)} = \widetilde{c}_m \equiv 0$. Now, the equation deduced in paper [8] within frames of the macroscopic model (MM) for the kinetics of multi-component ion exchange (as well as the approach of local-determinate model, LDM, [9]), one can use to describe the phenomenon of non-exchange nature in the system 'ion-exchanger – strong electrolyte' under substitutions $a_0 \to c_0$ and $a_{0i} \to c_i$:

$$\frac{d a_i}{d t} = \frac{\pi^2}{6 r_g^2} D_i \left[c_i - a_i \left(1 - z_i \frac{\sum D_j z_j (c_j - a_j)}{\sum D_j z_j^2 a_j} \right) \right], \tag{15}$$

where r_g is the radius of a polymer grain.

The most simple task is following: a mix of two electrolytes consists of two co-ions ($i = 1,2$) and single counter-ion ($i = 3$); all components are single-charged $|z_1| = |z_2| = |z_3| = 1$; the co-ions are absent in the ion-exchanger at the start of the process $a_1(0) = a_2(0) = 0$, but at the same time the capacity is saturated by the counter-ion $a_m(0) = a_0$, i.e. in accordance with (13), $a_3(0) = c_0$. The task must contain also concentrations of the components in solution phase (constant values): c_1, c_2 and $c_m = c_0 = c_1 + c_2$, i.e. $c_3 = \widetilde{c}_m = 0$, — and their diffusivities D_1, D_2, D_3.

The first, a similar task for kinetics of multi-component ion exchange has been considered within the frames of LDM by Hwang and Helfferich in the paper [9]. For the most mobile ion the overshoot on uptake-versus-time curve is observed (Fig.2).
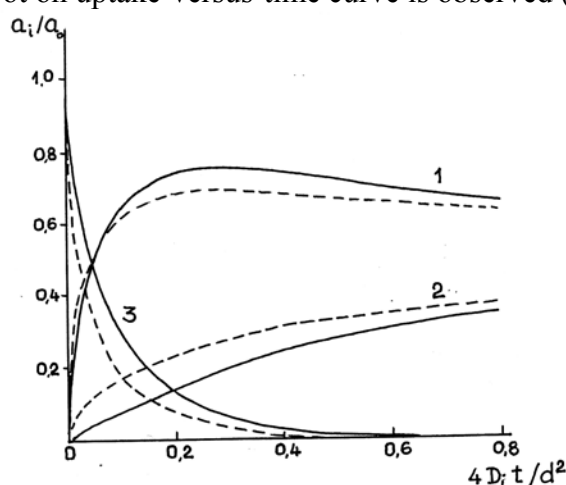

Fig. 2. Kinetic curves of the most mobile competing ion (1), another competing ion (2) and an ion being desorbed (3). Ternary ion exchange simulated by the models: LDM (dotted lines) and MM (solid lines).
Conditions: $a_{3(t=0)} = a_0$; $D_1 : D_2 : D_3 = 5:0.2:1$; $z_1 = z_2 = z_3$; $a_{01}/a_0 = 0.6$;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

Paper [8] considers solution of such tasks within the frames of theoretical approach, which is suggested there, named macroscopic model (MM) of ion-exchange kinetics. That simple theoretic instrument allows us to investigate conditions for arising of the effects of non-monotone kinetic curve in detail. The mathematical task under investigation has the

same view and the same features of solution, therefore, let us dwell on quality conclusions following from numerical computations.

Non-monotone behavior of polymer uptake is a short-time effect: its time is about of diffusion time of the most mobile co-ion to the centre of a grain:

$$\theta_1 = \zeta \frac{r_g^2}{D_h}, \tag{16}$$

where D_h is the diffusivity of the most mobile co-ion ('h') in the solution; $\zeta = \dfrac{c_0}{c_h + \sum c_i D_i / D_h} \sim 1$ is a corrected coefficient, that takes into account a presence of other co-ions (i) (for simplicity, here and below the symbols of charges are omitted, therefore, the concentration scale is used equivalent units).

The process of equilibrium establishing leading to equation of chemical potentials, in this case, corresponds to equation of concentrations in the different phases. Because of $a \neq c$, the exchange of co-ions is continued after electro-static balance establishing, too. This process characterizes the time of order:

$$\theta_2 = \frac{r_g^2}{\sum c_i D_i} (c_0 - c_h) \tag{17}$$

It is easy to create conditions, when $\theta_2 >> \theta_1$ and an effect of saturation of ion-exchanger by the most mobile co-ions takes place, because the penetration of co-ions goes in the proportion of their mobilities. Due to this law, the zone of more retention component in the eluting process is self cleaned. The law is expressed especially under presence in the mix of the water co-ions with anomaly mobility. So, for separation of salt and acid with common counter-ion in anion-exchanger, the exclusion of salt co-ions has to take place.

Computation of dynamical systems based on non-linear effects of multi-component ion-exchange kinetics, has been executed in the work [10] by N.A.Tikhonov, R.Kh.Khamizov et al. There, the conditions have been found for such a separation that takes place do not due to different selectivity of ion-exchanger, but due to their different mobility. Some quality conclusions are made below.

The maximum number of theoretical plates is deduced from kinetic character of the process as ratio:

$$N_m = \theta_2 / \theta_1 \tag{18}$$

One can estimate HETP by formula,

$$H = 2\theta_2 v ; \tag{19}$$

The effective length of column is estimated as

$$L_f = H N_m \tag{20}$$

We can obtain the expression of effective dead time for a double component system:

$$t_{0f} = \frac{L_f}{v} = \frac{2\theta_2^2}{\theta_1} \approx \frac{2 D_h R_g^2}{\zeta D_i^2} \approx \frac{2 c_h}{c_0} \frac{D_h R_g^2}{D_i^2} \tag{21}$$

For example, for the system with sodium and hydrogen co-ions of equal concentrations $R_g \approx 0.02$ см, $D_h \approx 10^{-4}$ см²/с, $D_i \approx 2 \cdot 10^{-5}$ см²/с, we obtain $t_{0f} \approx 100$ s (for diameter of grains 0.5-0.8 mm this value is greater to 2 - 2.5 times). So, when the productivity of system is given as the flow rate of mobile phase, one can find the volume of the column in the dynamical process.

Kinetic experiment on process mechanism examination

In accordance with the noted above theoretical interpretations of the process, the kinetic dependence for the most mobile component of the mixture is non-monotone, i.e. it must pass thru maximum (see Fig.2). The electro-conductivity of such mixture in the kinetic experiment in limited volume (when phase ratio is const) will decrease and become to constant level passing thru minimum, without fail. Otherwise, if the minimum is absent, we must confirm that our interpretations of the process are wrong. In this connection, the experiment described below has a very important mean.

As made above estimates say, the kinetic time for fraction of 0.5-0.7mm is about of 200-250 s. Taking less time order we design a setup and corresponding modes of experiment. The setup presents itself as a glass reactor (its volume 150-200 ml), magnetic stirrer, two electrodes connected with conductometric detector and registration device for plotting dependence of conductivity versus time.

In the initial time of experiment, the smelling ion-exchanger and the solution are mixed.

Fig.3 shows the kinetic curve, which is experimental dependence of conductivity versus time. Conditions: solution: 50 ml of 3.1 M $NaNO_3$ +3.1 M HNO_3; ion-exchanger: 50 ml of AV-17, smelling in water, NO_3-form. In the interval 60-250 s, we can see the minimum on the curve (for the point 140 s), which is corresponded to the estimates made.
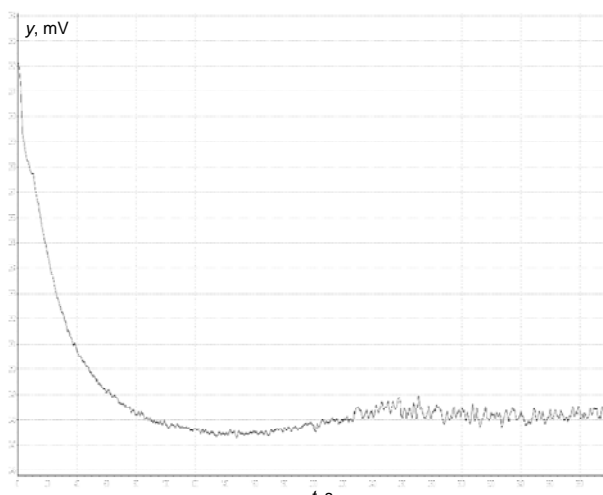

Fig. 3. Experimental kinetic curve, given as the dependence
of electroconductivity *vs* time. Conditions: solution: 50 ml of 3.1 M $NaNO_3$ +3.1 M HNO_3;
ion-exchanger: 50 ml of AV-17, smelling in water, NO_3-form

So, the acid retardation mechanism can be based on two effects: the Donnann effect, establishing the equilibrium in the system, and electro-migration of ions, determining the kinetics. When the strong electrolyte solution is passed through column with pure and equilibrated ion-exchanger the concentration of solution is grounding from null to initial value and can pass the point of the jump (c_x). In that moment the flux of ions into ion-exchanger increases quickly. As a result, the non-equilibrium state arises. That is the matter of the separation by the electro-kinetic exclusion mechanism. Its description is based on the difference between the compositions of initial solution and electro-kinetic fluxes.

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