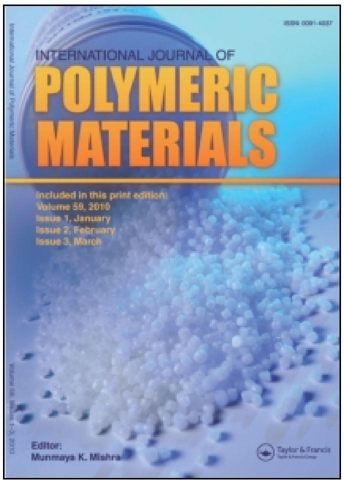

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Phenomenological Equations of the Baromembrane Transfer of Strong Electrolyte Solutions

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Differential phenomenological equations of mass transfer of strong electrolyte solutions for baromembrane process are developed and discussed.

Keywords: Baromembrane process; mass transfer; strong electrolyte solutions; phenomenological equations

INTRODUCTION

The equation of flow, based on the phenomenology of thermodynamics of the irreversible processes governs the transport of the molecular as well as of the ion components of the solution. The chemical potential of the molecular components is the function of the pressure and activity, while the potential of the ions – also a function of the electric potential. Using the Gibbs-Durham equation and the condition of the electro neutrality of the environment and the total change flow, the equation of the connection between the flows is obtained and the functional dependence of the electric potential

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gradient from the other variables of the statuary system is established. The reverse substitution of this dependence into the determinative equation allowed us to present the ions flow as the function of the pressure and the composition of the solution. It is shown that in general case of the poly component on electrolytes solution it is impossible to establish the correspondence between flows of the ions and electrolytes. The particular equation of the single electrolyte flow [with the common ion and one electrolyte] in the solution with the molecular components is suggested.

THEORY AND DISCUSSION

The membrane technology is most widely used for the purification of aqueous solutions of salts in the processes of reverse osmosis. Because of the difference of ions mobility at their transfer through the membrane the solutions before and after the membrane have the excess charge of the opposite polarity. The jump of the electric potential, which takes place, evens the flows of the opposite charges and its stationary value is the function of the other parameters of the process. As we know none of the general models of the baromembrane process [1] shows this functional connection based on the equations of transfer of strong electrolytes.

Lets consider the polycomponent solution, which consists of the molecular not dissociating components and ions (of the cations K_i and anions A_j) which are formed by dissociation of strong electrolytes according to the scheme:

$$Kv_kAv_a = v_kK^{(z_k)} + v_aA^{(z_a)} \tag{1}$$

in which z_k and z_a – charges of the cation and anion expressed in units of the electron charge; v_k and v_a – their stoichiometric coefficients in this electrolyte. They are linked by the relation ship

$$v_kz_k + v_az_a = 0 \tag{2}$$

For the molecular as well as for ionic compounds of the solution we use the equation of the flow, based on the phenomenology of the thermodynamics of irreversible process (T=const.).

$$J_s = -(L_s/RT)c_s\nabla\mu_s \tag{3}$$

Here: J_s and L_s – flow and coefficient of transfer, and c_s and μ_s – molar-volume concentration and chemical potential of the s-component of the solution; $\nabla = \partial/\partial x$, where x – coordinate of the transfer at perpendicular to the surface of the membrane.

At constant temperature the chemical potential of the molecular components of the solution is the function of their activities a_s and of the pressure P while in case of the ion components-also of the electrical potential ψ. Consequently, for the molecular (index m) and the ion components of the solution the phenomenological Eq. (3) assumes the following forms;

$$J_m = -L_m c_m(v_m\nabla P + RT\nabla\ln a_m)/RT \tag{4}$$

$$J_{ki} = -L_{ki}c_{ki}(v_{ki}\nabla P + RT\nabla\ln a_{ki} + z_{ki}F\nabla\psi)/RT \tag{5}$$

$$J_{aj} = -L_{aj}c_{aj}(v_{aj}\nabla P + RT\nabla\ln a_{aj} + z_{aj}F\nabla\psi)/RT \tag{6}$$

where v – partial-molar volume of the corresponding component of the solution, F – Faradays constant.

Using the Gibbs-Durham Eq. (7) the condition of electro-neutrality (8) and the relation between molar-volume concentrations (9) from (4–6) we obtain the equation of the connection between the flows (10)

$$\sum_m c_m\nabla\ln a_m + \sum_i c_{ki}\nabla\ln a_{ki} + \sum_j c_{aj}\nabla\ln a_{aj} = 0 \tag{7}$$

$$\sum_i c_{ki}z_{ki} + \sum_j c_{aj}z_{aj} = 0 \tag{8}$$

$$\sum_m c_m v_m + \sum_i c_{ki}v_{ki} + \sum_j c_{aj}v_{aj} = 1 \tag{9}$$

$$\sum_m J_m/L_m + \sum_i J_{ki}/L_{ki} + \sum_j J_{aj}/L_{aj} = -\nabla P/RT \qquad (10)$$

In the stationary system ($\partial c/\partial t = -\nabla J = 0$, $J = \text{const.}$) the equation of the connection (10) is easily transformed in to its integral form

$$\sum_m J_m/L'_m + \sum_i J_{ki}/L'_{ki} + \sum_j J_{aj}/L'_{aj} = -\Delta P/RT \qquad (11)$$

Here $\Delta P = P'' - P'$ – the difference of the pressures in solutions before (P') and after (P'') the membrane; $L' = L/\delta_m$ where δ_m – effective thickness of the membrane or of its working layer.

In stationary system the ions flows must be static. Therefore in addition to (10), one more equation of connection, coming from the condition of electro-neutrality of the summary charge flow must be included.

$$\sum_i J_{ki}\, z_{ki} + \sum_j J_{aj}\, z_{aj} = 0 \qquad (12)$$

Using (5) and (6) in (12) we establish the functional dependence of the gradient of electric potential from other variables of the system

$$-F\nabla\psi = \frac{\sum_i L_{ki}\, z_{ki}\, c_{ki}(v_{ki}\nabla P/RT + \nabla \ln a_{ki}) + \sum_j L_{aj}\, z_{aj}\, c_{aj}(v_{aj}\nabla P/RT + \nabla \ln a_{aj})}{\sum_i L_{ki}\, z^2_{ki} c_{ki} + \sum_j L_{aj}\, z^2_{aj} c_{aj}} \qquad (13)$$

At $\nabla P = 0$ (13) presents the gradient of diffusion potential on the border of two solutions. The reverse substitution (13) in (5) and (6) allows us to present the flow as the function of the pressure and composition of the solution. For example for s-cation we have

$$J_{ks} = L_{ks}\, c_{ks}(X_{ks}\nabla P/RT + Y_{ks})/Y, \qquad (14)$$

$$X_{ks} = \sum_i L_{ki}\, z_{ki}\, c_{ki}(z_{ki}\, v_{ks} - z_{ks}\, v_{ki}) + \sum_j L_{aj}\, z_{aj}\, c_{aj}(z_{aj}\, v_{ks} - z_{ks}\, v_{aj}), \qquad (15)$$

$$Y_{ks} = \sum_i L_{ki}\, z_{ki}\, c_{ki}(z_{ki}\nabla \ln a_{ks} - z_{ks}\nabla \ln a_{ki}) + \sum_j L_{aj}\, z_{aj}\, c_{aj}(z_{aj}\nabla \ln a_{ks} - z_{ks}\nabla \ln a_{aj}), \tag{16}$$

$$Y = \sum_i L_{ki}\, z_{ki}^2 c_{ki} + \sum_j L_{aj}\, z_{aj}^2 c_{aj}. \tag{17}$$

According to (14–17) the flow of ion in destination from the molecular flow component of the solution (see Eq. (4)) depends not only from its own parameters of the ion, but also from their relationship with all other parameters (X_{ks}, Y_{ks}) and of the total characteristics of the solution (Y).

In polycomponent electrolyte solution the connection between the concentrations of c_i ions and the concentrations of c_s electrolytes $c_i = \Sigma_s \upsilon_{is} c_s$ and running out from it connection between their flows $J_i = \Sigma_s \upsilon_{is} J_s$ is not reciprocally synonymous. Therefore, knowing from (14–17) the flows of ions we may not simultaneously determine the flows of the electrolytes. Finally in one component electrolyte solution the correspondent connections are reciprocally synonymous $c = c_k/\upsilon_k = c_a/\upsilon_a$, $J = J_k/\upsilon_k = J_a/\upsilon_a$. Using them and omitting the summarizing of ion indices in (14–17), we obtain the equation of the flow of electrolyte in the solution:

$$J = -Lc(v\nabla P + RT\nabla \ln a) \tag{18}$$

in which $a = a_k^{\upsilon_k} a^{\upsilon_k}$ – activity, and $v = \upsilon_k v_k + \upsilon_a v_a$ – partial molar volume of electrolyte.

Thus, only in this particular case the equation of the flow of strong electrolyte acquires the same simple form as the Eq. (4) of the flow of molecular components of the solution, expressed for the electrolyte by (19)

$$L = L_k L_a/(\upsilon_k L_a + \upsilon_a L_k) \tag{19}$$

References

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