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Heat and mass transfer in saturated porous media with ice inclusions

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Abstract

This paper continues the theoretical exploration of the heat and mass transfer in a biporous medium with the coupled phase transformations. A more complicated system is considered, such as porous medium-ice-aqueous solution. General statements been formulated for a simple medium [4], remain in force for the given system: the heat and mass fluxes each depend linearly on all thermodynamical forces, the transport coefficients satisfy the Onsager reciprocal relations; the coupled phase transformations intensify significantly the cross effects.

The presence of contaminants in water imparts the osmotic properties to the biporous medium and decreases the rate of the heat and mass transfer in the system. The dissolved matter takes effect beginning with the concentration of $\sim$0.001 mol l^{-1}. At the high concentration of the aqueous solution ($>$0.1 mol l^{-1}) the cross effects become negligible small and the medium loses its unique capacities.

Keywords: Porous media; Aqueous solution; Ice; Phase transition; Coupled phenomena

1. Introduction

The integral part of a porous medium is free space, which is imagined as the pore set in the solid body [1]. The freezing point of liquid in a pore decreases with dropping the size of the confined space. A pore size distribution makes possible for the phase transformation in an interval of the negative temperature. A quantity of the liquid phase diminishes progressively with decreasing the temperature, and simultaneously ice content increases [2].

In that system the transport processes have a peculiarity. Not only are heat and liquid transferred in the system, but also solid (ice) takes part in the transport processes. Ice motion in a porous medium is realized due to regelation [3], which involves the coupled phase transitions of melting and freezing, whose locations are spatial separated. A necessary condition for the movement of the solid is a hydraulic connection between the freezing region and the melting one. The coupled phase transition may significantly intensify the cross effects [4]. The porous medium considered in that paper was saturated by pure water. In actual practice the dissolved matter not infrequently contaminates the water. The influence of that factor on the heat and mass transfer in the porous medium with ice inclusions constitutes the subject matter.

We should examine a steady state of the heat and mass transfer in the biporous medium that is saturated by aqueous solution and contains the ice inclusions. The free space of the porous materials, as a rule, has irregular configuration. That complicates significantly a rigorous studying of the transfer processes. And so in the scientific practice the heterogeneous media with the periodical structure are used fairly often [5]. That simplifies a problem definition and reduces the one to studying of the transfer processes in an elementary cell.

2. Problem statement

Consider a porous medium with the bimodal pore distribution (biporous medium, Fig. 1). Large pores (E_1) are equal spherical cavities, diameters of which are significantly greater than the size of the pores in fine pored medium (E_2). The centres of the cavities are located at the rectangular

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Nomenclature

b	height of the cell [m], Fig. 2
C	transport coefficient
c_s	solution concentration [mol m^{-3}]
c_{s0}	average solution concentration [mol m^{-3}], Eq. (35)
D_n	diffusion coefficient [m^2 s^{-1}]
J_q	heat flow at the base of the cell [W m^{-2}]
J_s	molar flow of dissolved matter across the base of the cell [mol m^{-2} s^{-1}]
J_V	volume flow across the base of the cell [m s^{-1}]
J_w	molar flow of water across the base of the cell [mol m^{-2} s^{-1}]
$\mathbf{j}_q$	heat flux [W m^{-2}]
$\mathbf{j}_s$	molar flux of dissolved matter [mol m^{-2} s^{-1}]
$\mathbf{j}_V$	volume flux [m s^{-1}]
$\mathbf{j}_w$	molar water flux [mol m^{-2} s^{-1}]
K_h	hydroconductivity coefficient of fine-pored medium E_2 [m^3 s kg^{-1}]
$\mathbf{n}$	unit vector
P_i	ice pressure component normal to an ice–water interface [Pa]
p	water pressure [Pa]
R	radius of ice inclusion [m]
R_g	gas constant, $R_g = 8.31$ J K^{-1} mol^{-1}
S_a	area of base [m^2], Fig. 2
T	temperature [K]
V_i	molar volume of ice [m^3 mol^{-1}]
V_s	partial molar volume of dissolved matter [m^3 mol^{-1}]
V_w	partial molar volume of water in solution [m^3 mol^{-1}]
$\mathbf{v}_i$	velocity of ice [m s^{-1}]
X	thermodynamical force

Greek symbols

α	dimensionless parameter of the cell, $\pi R^2/S_a$
β	dimensionless parameter of the cell, $2R/b$
κ	latent heat of fusion [J mol^{-1}]
λ_1	thermal conductivity of ice [W m^{-1} K^{-1}]
λ_2	thermal conductivity of fine-pored medium [W m^{-1} K^{-1}]
μ	chemical potential [J mol^{-1}]

Subscripts

i	ice
q	heat
R	surface of inclusion
s	dissolved matter
w	water

Other symbols

∇	vector gradient operator
∇_b	difference gradient operator, Eq. (20)

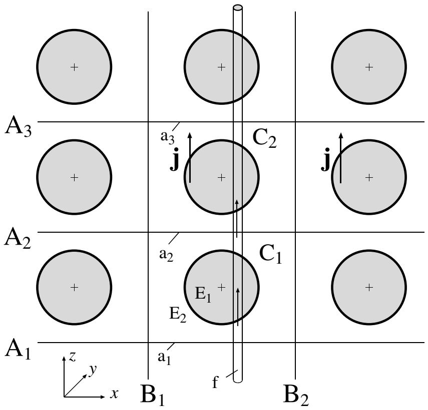

Fig. 1. A fragment of the model porous medium. E_1 – ice inclusion, E_2 – fine pored medium.

lattice points. The thermodynamical conditions provide maintenance of ice in the cavities and forbid the ice from penetrating in the fine pored medium. Gas is absent, liquid is incompressible, solids (ice and framework of porous medium) are rigid. The fine pored medium is permeable for the fluid, which is the aqueous solution. A dissolved matter and a liquid water do not penetrate into ice. The ice moves relative to the mineral framework. The surface of the framework is inactive for chemical, ion-exchange, and other reactions. The elements of the heterogeneous medium considered (E_1 and E_2, Fig. 1) are isotropic each taken separately.

The problem of the steady-state heat and mass transfer in the porous medium as whole reduces to defining the heat and mass (water and dissolved matter) flows through the elementary cell, on the bases of which the thermodynamical values of the temperature, the liquid pressure and the solution concentration are given. The lateral faces of the cell are impermeable for heat and matter. All conductivity coefficients will be accepted as constants. Fix the Cartesian co-ordinate system to the mineral frame of the element E_2.

Heat transport in the elements of E_1 and E_2 obeys a Fourier conduction type law:

$$\mathbf{j}_q = -\lambda_i \nabla T, \quad i = 1, 2 \tag{1}$$

where the index i denotes the element E_i.

Assume that the convective transfer of energy may be neglected in comparison to the conductive one. The conversation of energy and Fourier's law give Laplace's equation for defining the temperature in the cell's elements:

$$\Delta T = 0 \tag{2}$$

with the boundary conditions as follows:

at the faces of the cell

$$T|_{z=-b/2} = T_1, \quad T|_{z=b/2} = T_2, \quad \frac{\partial T}{\partial n_b} = 0 \tag{3}$$

where $\frac{\partial}{\partial n_b}$ is the normal derivative directed to the lateral area of the cell;

at the surface of the ice inclusion

$$T|_{r=R-0} = T|_{r=R+0} \text{ (continuity of temperature)} \tag{4}$$

$$-\lambda_1 \frac{\partial T}{\partial r}\bigg|_{r=R-0} - \left(-\lambda_2 \frac{\partial T}{\partial r}\bigg|_{r=R+0}\right) = \frac{\kappa v_i \cos\theta}{V_i} \text{ (heat balance)} \tag{5}$$

where (r, θ) – radius and angle in spherical co-ordinate system (Fig. 2).

The liquid (aqueous solution) flows only in fine pored medium E_2 and is subjected to Darcy's law:

$$\mathbf{j}_V = -K_h \nabla p \tag{6}$$

where K_h is hydroconductivity coefficient of the element E_2.

The volume flux is expressed in terms of molar fluxes [6]:

$$\mathbf{j}_V = V_w \mathbf{j}_w + V_s \mathbf{j}_s, \tag{7}$$

The continuity of mass and Darcy's law lead to Laplace's equation for liquid pressure:

$$\Delta p = 0 \tag{8}$$

with the boundary conditions *at the faces of the cell*

$$p|_{z=-b/2} = p_1, \quad p|_{z=b/2} = p_2, \quad \frac{\partial p}{\partial n_b} = 0 \tag{9}$$

Eq. (7) and two conditions at the inclusion surface as follows:

Impermeability of ice for an impurity

$$j_{sr}(R, \theta) = 0 \tag{10}$$

and continuity of water

$$j_{wr}(R, \theta) = v_i \cos\theta / V_i \tag{11}$$

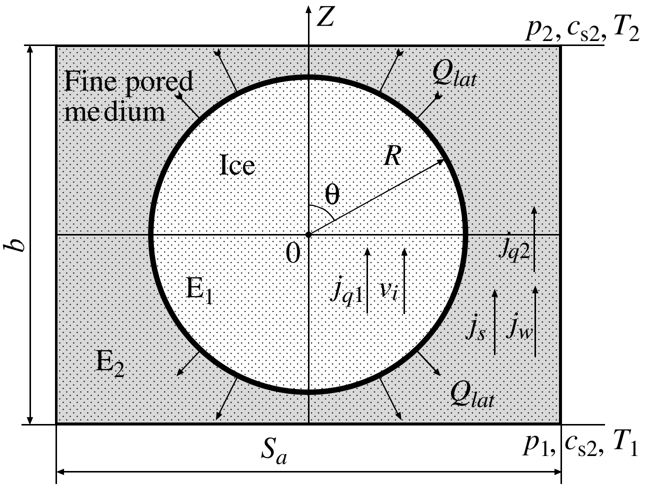

Fig. 2. Scheme of fluxes in an elementary cell. Q_{lat} is heat production at the phase transition surface.

where the index r denotes the radial component in the spherical co-ordinate, allow to connect the volume flow $j_{Vr}(R, \theta)$ with the ice velocity v_i: $j_{Vr}(R, \theta) = V_w v_i \cos\theta / V_i$. This equation and Darcy's law lead to a relation *at the surface of the ice inclusion*

$$-K_h \frac{\partial p}{\partial r}\bigg|_{r=R+0} = \frac{V_w}{V_i} v_i \cos\theta \tag{12}$$

The movement of the substance dissolved in water realizes by two following ways: convective transport and diffusion. A Fick law gives a relation for the dissolved matter flux $\mathbf{j}_s$:

$$\mathbf{j}_s = c_s \mathbf{j}_V - D_n \nabla c_s \tag{13}$$

Fick's law (13) and the continuity of mass lead to a Fick equation for defining the concentration c_s in the element E_2:

$$\Delta c_s - \nabla \cdot (c_s \mathbf{j}_V / D_n) = 0 \tag{14}$$

with the boundary condition *at the faces of the cell*

$$c_s|_{z=-b/2} = c_{s1}, \quad c_s|_{z=b/2} = c_{s2}, \quad \frac{\partial c_s}{\partial n_b} = 0 \tag{15}$$

Combining the rejection relation (10), the Fick law (13), the definition (7) and the water balance Eq. (11) gives the boundary condition *at the surface of the ice inclusion*

$$\left(\frac{\partial c_s}{\partial r} - \frac{V_w v_i \cos\theta}{V_i D_n} c_s\right)\bigg|_{r=R+0} = 0 \tag{16}$$

The equation set (2)–(5), (8)–(9), (12) and (14)–(16) allows to define the distribution of the temperature, the pressure and the concentration in space and, as a result, to find the heat and mass fluxes through the bases of the cell if only an ice velocity is known.

In a steady state the ice velocity is constant in time and therefore a sum of forces, those act on the inclusion is equal to zero. The forces of two types applied to the ice – bulk and surface. The bulk forces are initiated by external force fields (for example, gravitational). The total bulk force $\mathbf{F}_{ex}$ must be balanced by the surface ones.

Two peculiarities: ice and mineral are disjoined by liquid layer that eliminates an immediate contact between solids (1) and the tangential surface force is negligible small in comparison to the normal one (2), allow to write the mechanical balance of the ice inclusion as follows [4]:

$$\mathbf{F}_{ex} - \int_{S_R} P_{iR} \mathbf{n} \, dS = 0 \tag{17}$$

where $\mathbf{n}$ is a unit vector perpendicular to dS, P_{iR} is the ice pressure component normal to an interface.

Assume a postulate of local thermodynamical equilibrium to be valid. The condition for two phases to be in equilibrium with respect to any species is that the chemical potential of that species should have the same value in the two phases [7]. Applying that rule for ice and water near a mineral surface gives

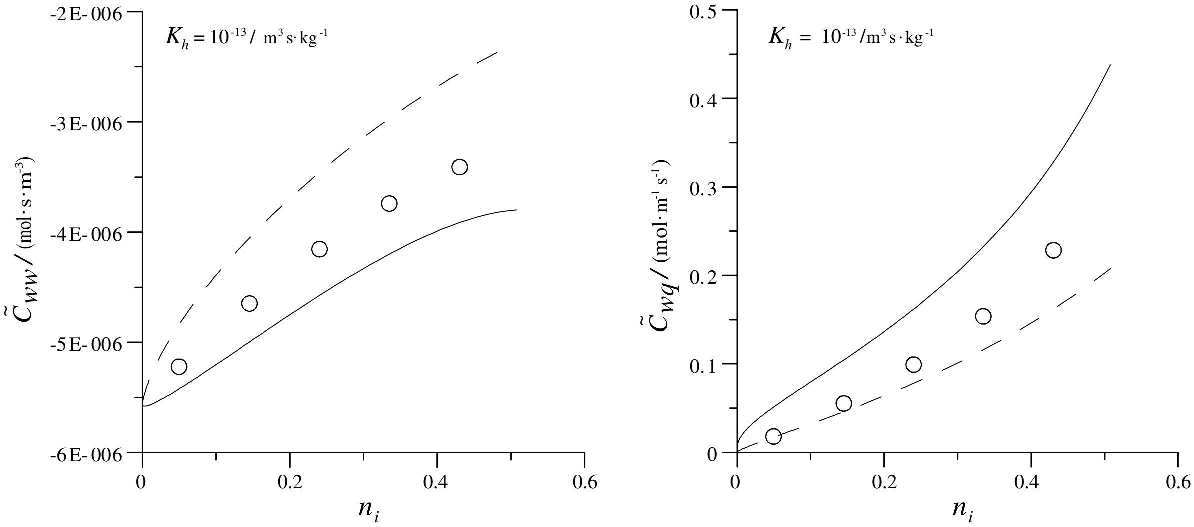

Fig. 3. Standard transport coefficients versus volumetric part of ice n_i. Lines are constructed from analytical formulas for two cell with infinite (solid lines) and zero (dot lines) horizontal conductivity. Symbols are the numerical calculation with an accuracy of ~5%.

$$\mu_i(T_R, P_{iR}) = \mu_w(T_R, p_R, c_{sR}) \tag{18}$$

where μ_i, μ_w are chemical potentials of pure ice and water in solution.

The expansion in series near the phase transition point of bulk pure water and ice at atmospheric pressure results in the following relationship:

$$V_i(P_{iR} - p_0) - V_w(p_R - p_0) = -\frac{\kappa(T_R - T_0)}{T_0} - \gamma_w c_{sR} \tag{19}$$

where $T_0 = 273.15$ K; $p_0 = 0.1$ MPa; $\gamma_w = -\frac{\partial \mu_w}{\partial c_s}$ (for ideal solution $\gamma_w = R_g T V_w$).

The relation set (3)–(5), (9), (12), (15) and (16) is the boundary condition for the heat and mass transfer problem that is presented by equations for the temperature (2), the liquid pressure (8) and the concentration (14).

In this paper the problem will be solved by the anisotropic conductivity method [4], that allows finding the solution in an analytical form. The method is based on the replacement of the isotropic elements by the anisotropic ones.

In the direction of the imposed gradients parallel to the streamwise, the conductivity coefficients of the elements are maintained to be real, and in the direction perpendicular to selected, the conductivities are taken to be equal zero or infinity. Therefore the problem will be solved for two cells, the transport coefficients of which gives the extreme points of intervals. The transport coefficients of the cell with the isotropic elements fall into those intervals. The representative plots of some coefficients for the cell, fine-pored medium of which to be saturated by pure water [4] are shown in Fig. 3.

3. Heat transfer and filtration

A problem consists in defining the heat and liquid flows across the bases of the cell (Fig. 2) at the boundary conditions (3)–(5), (9) and (12). A distinctive feature of the system involved is the ice–water phase transition that generates the heat and liquid sources. A solution of this problem repeats, in many respects, the solution of the analogical problem for the porous medium with ice and pure water [4]. Therefore only the final results will be presented as follows: the fluxes through the cell's bases and the temperature and pressure values at the inclusion surface.

3.1. Infinite horizontal conductivity

$$J_q = \lambda_2 \left\{ -\frac{\kappa v_i}{V_i \Delta\lambda_{21}} - \left[\nabla_b T - \frac{\kappa v_i}{V_i \Delta\lambda_{21}} \right] \cdot \frac{f_1}{\beta + f_1(1-\beta)} \right\} \tag{20}$$

$$T_R(\theta) = \begin{cases} \dfrac{\kappa v_i}{V_i \Delta\lambda_{21}} R\cos\theta + \left(\nabla_b T - \dfrac{\kappa v_i}{V_i \Delta\lambda_{21}} \right) \\ \quad \times \dfrac{R}{\beta + f_1(1-\beta)} \dfrac{\ln\left|\dfrac{1+\varepsilon_t\cos\theta}{1-\varepsilon_t\cos\theta}\right|}{\ln\left|\dfrac{1+\varepsilon_t}{1-\varepsilon_t}\right|} + T_m, \ \Delta\lambda_{21} < 0 \\ \dfrac{\kappa v_i}{V_i \Delta\lambda_{21}} R\cos\theta + \left(\nabla_b T - \dfrac{\kappa v_i}{V_i \Delta\lambda_{21}} \right) \\ \quad \times \dfrac{R}{\beta + f_1(1-\beta)} \cdot \dfrac{\operatorname{arctg}(\varepsilon_t \cos\theta)}{\operatorname{arctg}\varepsilon_t} + T_m, \ \Delta\lambda_{21} > 0 \end{cases} \tag{21}$$

$$J_V = \frac{V_w v_i}{V_i} - \left(K_h \nabla_b p + \frac{V_w v_i}{V_i} \right) \frac{f_2}{\beta + f_2(1-\beta)} \tag{22}$$

$$p_R = -\frac{V_w v_i}{V_i K_h} R\cos\theta + \left(\nabla_b p + \frac{V_w v_i}{V_i K_h} \right) \frac{R}{\beta + f_2(1-\beta)} \cdot \frac{\operatorname{arctg}(\varepsilon_p \cos\theta)}{\operatorname{arctg}\varepsilon_p} + p_m \tag{23}$$

where $\nabla_b T = \frac{T_2 - T_1}{b}$; $\nabla_b p = \frac{p_2 - p_1}{b}$; $T_m = \frac{T_1 + T_2}{2}$; $p_m = \frac{p_1 + p_2}{2}$; $\Delta\lambda_{21} = \lambda_2 - \lambda_1$ and β, ε_t, ε_p, f_1, f_2 are dimensionless parameters:

$$f_1 = \begin{cases} \dfrac{2\varepsilon_t}{(1-\varepsilon_t^2)\ln\left|\dfrac{1+\varepsilon_t}{1-\varepsilon_t}\right|}, & \Delta\lambda_{21} < 0 \\ \dfrac{\varepsilon_t}{(1+\varepsilon_t^2)\operatorname{arctg}\varepsilon_t}, & \Delta\lambda_{21} > 0 \end{cases},$$

$$f_2 = \frac{\varepsilon_p}{(1+\varepsilon_p^2)\operatorname{arctg}\varepsilon_p}, \quad \varepsilon_t = \frac{R}{e_t}; \quad \varepsilon_p = \frac{R}{e_p};$$

$$e_t^2 = \frac{\lambda_2 S_a - \Delta\lambda_{21}\pi R^2}{\pi|\Delta\lambda_{21}|}; \quad e_p^2 = \frac{S_a - \pi R^2}{\pi}$$

3.2. Zero horizontal conductivity

$$J_q = -\lambda_2 I_3 \nabla_b T - \frac{\lambda_2 \kappa\alpha\beta}{\lambda_1 V_i} v_i I_1 \tag{24}$$

$$T_R(\theta) = \frac{\lambda_2}{\lambda_1}\frac{R\cos\theta}{1+\varepsilon_0|\cos\theta|}\left(\nabla_b T - \frac{\kappa}{V_i}\frac{(1-\beta|\cos\theta|)}{\lambda_2}v_i\right) + T_m \tag{25}$$

$$J_V = \frac{V_w}{V_i}\alpha v_i - (1-\alpha)K_h \nabla_b p \tag{26}$$

$$p_R(\theta) = \begin{cases} p_2 + \frac{V_w R}{V_i \beta K_h}(1-\beta\cos\theta)v_i, & 0 \leqslant \theta < \pi/2 \\ p_1 - \frac{V_w R}{V_i \beta K_h}(1+\beta\cos\theta)v_i, & \pi/2 \leqslant \theta \leqslant \pi \end{cases} \tag{27}$$

where α, ε_0, I_1, I_3 are dimensionless parameters:

$$\varepsilon_0 = \beta\left(\frac{\lambda_2}{\lambda_1} - 1\right), \quad I_1 = \frac{1}{\varepsilon_0} - \frac{2}{\varepsilon_0^2} + \frac{2}{\varepsilon_0^3}\ln(1+\varepsilon_0),$$

$$I_3 = (1-\alpha) + \frac{2\alpha}{\varepsilon_0^2}[\varepsilon_0 - \ln(1+\varepsilon_0)]$$

4. Diffusion

The statement of the problem presented in Section 1 implies finding a dissolved matter distribution in the cell. That is needed to define the fluxes of dissolved substance through the bases of the cell at the boundary conditions (15) and (16).

We shall accept a sequence of the simplifying suppositions. The dissolved matter is transported only in the fine pored medium E_2 because the impurities are rejected by ice completely. The transfer of the dissolved matter in the region E_2 obeys Fick's law (13). The relations will be obtained in the linear approximation relative to the fluxes and the gradients of thermodynamical values (temperature, pressure and concentration); i.e. the system is near the equilibrium state.

The diffusion problem will be solved by the anisotropic conductivity method for two cells with the infinite and zero horizontal conductivities.

4.1. Infinite horizontal conductivity

The term *infinite conductivity* relates to both filtration and diffusion. The solution concentration does not depend on horizontal co-ordinates (x and y) due to the accepted supposition. In the direction of the Z-axis a diffusion coefficient equals a real value D_n. In the interior of the cell the production sources of the dissolved matter is absent, therefore the steady-state total flow of the dissolved substance Q_s through any horizontal section is fixed:

$$Q_s = J_s S_a = \text{const} \tag{28}$$

where J_s is the dissolved matter flux through the bases of the cell.

In the region of $z \in [-b/2, -R]$ and $[R, b/2]$ the medium is homogeneous (Fig. 4). The volume flux j_V and the molar flux of the dissolved matter j_s in direction of Z-axis are the constants and equal the fluxes across the cell's bases J_V and J_s, respectively. The solution concentration c_s depends only on z-co-ordinate. A relation between the matter flows and the concentration at sections $z = \pm R$, $\pm b$ may be found from Fick's equation (14). In the linear approximation relative to the value of J_V the flow J_s is following

$$J_s = \frac{c_{s1} + c'_{s1}}{2}\cdot J_V - D_n \frac{c'_{s1} - c_{s1}}{b/2 - R} \tag{29}$$

$$J_s = \frac{c_{s2} + c'_{s2}}{2}\cdot J_V - D_n \frac{c_{s2} - c'_{s2}}{b/2 - R} \tag{30}$$

In the region of $z \in [-R, R]$ the dissolved matter moves only in the fine pored medium E_2, therefore the mass balance is presented as follows:

$$j_s(z)\cdot S_2(z) = Q_s \tag{31}$$

where j_s is z-component of the dissolved matter molar flux, S_2 is area of the element E_2 at the horizontal section z: $S_2(z) = S_a - \pi(R^2 - z^2)$. Substituting j_s in (31) from Fick's law (13) gives an equation for defining of a function of $c_s(z)$:

$$\frac{dc_s(z)}{dz} - \frac{j_V(z)}{D_n}c_s(z) = -\frac{Q_s}{D_n S_2(z)} \tag{32}$$

A dependence of $j_V(z)$ must be found from the solution of the filtration problem. In the section of $z = \pm R$ the

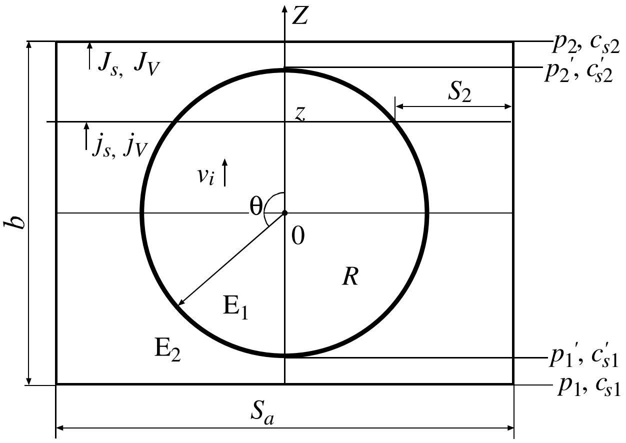

Fig. 4. Scheme of mass fluxes through the selected layer at infinite horizontal conductivity.

continuity conditions for the concentration are realized: $c_s(-R) = c'_{s1}$ and $c_s(R) = c'_{s2}$. Taking into account the first condition the solution of the differential equation (32) is presented as follow [8]:

$$c_s(z) = e^{-F(z)}\left[c'_{s1} - \frac{Q_s}{D_n}\int_{-R}^{z}\frac{e^{F(\zeta)}}{S_2(\zeta)}d\zeta\right] \tag{33}$$

where $F(z) = -\frac{1}{D_n}\int_{-R}^{z} j_V(\zeta)d\zeta$.

Linearizing Eq. (33) relative to the fluxes of J_s and j_V and using the second condition for concentration ($c_s(R) = c'_{s2}$) and Eqs. (28)–(30) gives an expression for the flux J_s of the dissolved matter across the cell's bases:

$$J_s = \frac{f_2}{\beta + (1-\beta)f_2}[-D_n\nabla_b c_s - c_{s0}K_h\nabla_b p] \tag{34}$$

and a concentration distribution at the ice inclusion surface:

$$c_{sR}(\theta) = \frac{V_w}{V_i}\frac{c_{s0}v_i}{D_n}R\cos\theta + \left[\nabla_b c_s - \frac{V_w}{V_i}\frac{c_{s0}v_i}{D_n}\right]\frac{R}{\beta + f_2(1-\beta)} \cdot \frac{\operatorname{arctg}(\varepsilon_p\cos\theta)}{\operatorname{arctg}\varepsilon_p} + K_s \tag{35}$$

where $\nabla_b c_s = \frac{c_{s2}-c_{s1}}{b}$, $c_{s0} = \frac{c_{s1}+c_{s2}}{2}$, K_s are constants.

The distinctive feature of Eq. (34) is that the dissolved matter flow through the cell is defined only by the concentration and pressure gradients and does not depends on the ice velocity.

4.2. Zero horizontal conductivity

The sreamlines of the water and the dissolved matter are parallel to Z-axis due to the accepted anisotropy. Since the ice is impermeable for impurities, the dissolved matter may be transported only in the homogeneous region $r > R$ (Fig. 5, element E_2). In the linear approximation the dissolved matter flux J_{s2} in this region is presented as follows:

$$J_{s2} = -D_n\frac{c_{s2}-c_{s1}}{b} + c_{s0}J_{V2} = -(D_n\nabla_b c_s + c_{s0}K_h\nabla_b p)$$

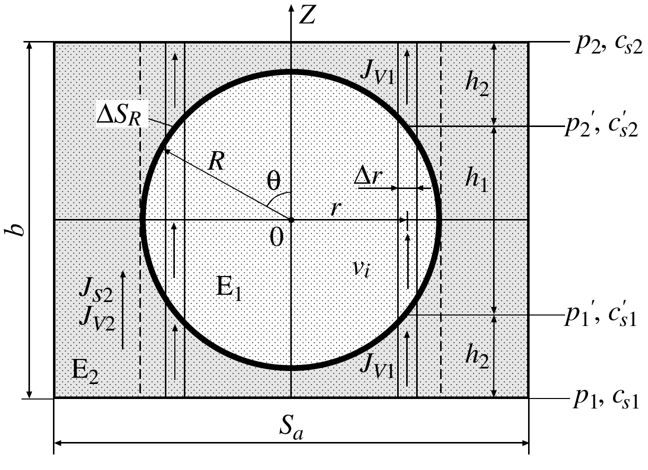

Fig. 5. Scheme of mass fluxes through the selected layer at zero horizontal conductivity.

And an average value of the flux J_s through the cell equals

$$J_s = -(1-\alpha)(D_n\nabla_b c_s + c_{s0}K_h\nabla_b p) \tag{36}$$

Define the concentration of the dissolved matter near the inclusion surface. Since the impurities are rejected by ice, z-component of the dissolved matter flux in the region $r < R$ is equal to zero. In the linear approximation the diffusion law (13) may be written in the difference form:

$$-D_n\frac{c'_{s1} - c_{s1}}{h_2} + c_{s0}J_{V1} = 0 \tag{37}$$

$$-D_n\frac{c_{s2} - c'_{s2}}{h_2} + c_{s0}J_{V1} = 0 \tag{38}$$

where J_{V1} is the volume flow of the solution in the region $r < R$.

Combining the relation of the water balance (11), the rejection condition (10) and the definition (7) give an expression for a value of J_{V1}:

$$J_{V1} = V_w v_i / V_i \tag{39}$$

The values of c'_{s1} and c'_{s2} in Eqs. (37) and (38) for given r define the concentration c_{sR} at the inclusion surface. Substituting J_{V1} from (39) in (37) and (38) gives

$$c_{sR}(\theta) = \begin{cases} c_{s2} - \frac{V_w c_{s0} R}{V_i \beta D_n}(1 - \beta\cos\theta)v_i, & 0 \leqslant \theta < \pi/2 \\ c_{s1} + \frac{V_w c_{s0} R}{V_i \beta D_n}(1 + \beta\cos\theta)v_i, & \pi/2 \leqslant \theta \leqslant \pi \end{cases} \tag{40}$$

5. Ice velocity and transport coefficients

For finding the ice velocity it is needed to use two independent conditions: the mechanical equilibrium of the inclusion (17) and the local thermodynamical equilibrium (19).

Assume that the external force is negligible small ($\mathbf{F}_{ex} = 0$). Since the values of T_R, p_R, c_{sR} and hence the pressure P_{iR} (22) are axially symmetrical (see (21), (23), (25), (27), (35) and (40)), the integral (17) is converted in the following expression:

$$\frac{V_w}{V_i}\Theta_0(p_R) - \frac{\kappa}{T_0 V_i}\Theta_0(T_R) - \frac{\gamma_w}{V_i}\Theta_0(c_{sR}) = 0 \tag{41}$$

where Θ_0 is a linear functional: $\Theta_0(f) = \int_0^{\pi} f(\theta)\cos\theta\sin\theta\, d\theta$.

5.1. Infinite horizontal conductivity

The term *infinite conductivity* relates to heat transfer, filtration and diffusion. Substituting Eqs. (21), (23) and (35) in Eq. (41) gives an ice velocity as a linear function of the temperature, pressure and concentration gradients

$$v_i = -\omega_{p1}\nabla_b p - \omega_{t1}\nabla_b T - \omega_{s1}\nabla_b c_s \tag{42}$$

where

$$\omega_{\mathrm{p}1}=\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\frac{f_{\mathrm{p}}}{\mathrm{den}_1};\quad \omega_{\mathrm{t}1}=-\frac{\kappa}{T_0V_{\mathrm{i}}}\frac{f_{\mathrm{t}}}{\mathrm{den}_1};\quad \omega_{\mathrm{s}1}=-\frac{\gamma_{\mathrm{w}}}{V_{\mathrm{i}}}\frac{f_{\mathrm{p}}}{\mathrm{den}_1},$$

$$f_{\mathrm{t}}=\begin{cases}\frac{(1-f_1)}{[\beta+(1-\beta)f_1]}\cdot\frac{(\varepsilon_{\mathrm{t}}^2-1)}{\varepsilon_{\mathrm{t}}^2}, & \Delta\lambda_{21}<0\\ \frac{(1-f_1)}{[\beta+(1-\beta)f_1]}\cdot\frac{(\varepsilon_{\mathrm{t}}^2+1)}{\varepsilon_{\mathrm{t}}^2}, & \Delta\lambda_{21}>0\end{cases},$$

$$f_{\mathrm{p}}=\frac{(1-f_2)(1+\varepsilon_{\mathrm{p}}^2)}{[\beta+(1-\beta)f_2]\varepsilon_{\mathrm{p}}^2}$$

$$\mathrm{den}_1=\left(\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\right)^2\left(f_{\mathrm{p}}-\frac{2}{3}\right)\frac{1}{K_{\mathrm{h}}}+\left(\frac{\kappa}{V_{\mathrm{i}}}\right)^2\frac{(f_{\mathrm{t}}-2/3)}{T_0\Delta\lambda_{21}}+\frac{\gamma_{\mathrm{w}}V_{\mathrm{w}}c_{\mathrm{s}0}}{V_{\mathrm{i}}^2D_n}\left(f_{\mathrm{p}}-\frac{2}{3}\right)$$

Substituting then Eq. (42) in Eqs. (20) and (22) having in view Eq. (34), gives the fluxes as the linear functions of the imposed gradients

$$J_V=C_{\mathrm{pp}}\nabla_bp+C_{\mathrm{ps}}\nabla_bc_{\mathrm{s}}+C_{\mathrm{pq}}\nabla_bT/T \tag{43}$$

$$J_{\mathrm{s}}=C_{\mathrm{sp}}\nabla_bp+C_{\mathrm{ss}}\nabla_bc_{\mathrm{s}}+C_{\mathrm{sq}}\nabla_bT/T \tag{44}$$

$$J_{\mathrm{q}}=C_{\mathrm{qp}}\nabla_bp+C_{\mathrm{qs}}\nabla_bc_{\mathrm{s}}+C_{\mathrm{qq}}\nabla_bT/T \tag{45}$$

with transport coefficients as follows

$$\begin{aligned}&C_{\mathrm{pp}}=-\left[K_{\mathrm{h}}f_{\mathrm{w}}+\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{p}1}\right],\quad C_{\mathrm{ps}}=-\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{s}1},\\ &C_{\mathrm{pq}}=-\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\alpha\beta f_{\mathrm{p}}\omega_{\mathrm{t}1}T_0,\\ &C_{\mathrm{sp}}=-c_{\mathrm{s}0}K_{\mathrm{h}}f_{\mathrm{w}},\qquad C_{\mathrm{ss}}=-D_{\mathrm{n}}f_{\mathrm{w}},\quad C_{\mathrm{sq}}=0,\\ &C_{\mathrm{qp}}=\frac{\kappa}{V_{\mathrm{i}}}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{p}1},\quad C_{\mathrm{qs}}=\frac{\kappa}{V_{\mathrm{i}}}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{s}1},\\ &C_{\mathrm{qq}}=\left(\frac{\kappa}{V_{\mathrm{i}}}\cdot\alpha\beta f_{\mathrm{t}}\omega_{\mathrm{t}1}-\lambda_2f_{\mathrm{q}}\right)T_0\end{aligned} \tag{46}$$

Compared to the simple sample, such as porous medium-ice-pure water [4], the system considered has an additional thermodynamical degree of freedom. As a result, a number of the transport coefficients increases and becomes equal to 9. But the coefficients are not independent and satisfy some relations which will be obtained below.

Introduce the standard values of the fluxes $(J_{\mathrm{w}},J_{\mathrm{s}},J_{\mathrm{q}})$ and the corresponding thermodynamical forces $(X_{\mathrm{w}}, X_{\mathrm{s}},X_{\mathrm{q}})$, as is customary in irreversible thermodynamics [6]:

$$X_{\mathrm{w}}=V_{\mathrm{w}}\nabla_bp-\gamma_{\mathrm{w}}\nabla_bc_{\mathrm{s}},\quad X_{\mathrm{s}}=V_{\mathrm{s}}\nabla_bp+\frac{c_{\mathrm{w}}}{c_{\mathrm{s}}}\gamma_{\mathrm{w}}\nabla_bc_{\mathrm{s}},$$

$$X_q=\frac{\nabla_bT}{T},\ J_V=V_{\mathrm{w}}J_{\mathrm{w}}+V_{\mathrm{s}}J_{\mathrm{s}}$$

where c_{w} is molar concentration of water, J_{w} is molar flux of water through the bases of the cell. Writing Eqs. (43)–(45) in the terms of the standard values and assuming the symmetry of the standard cross coefficient gives the three relations:

$$\begin{aligned}&c_{\mathrm{s}}\left[\frac{1}{V_{\mathrm{w}}}(C_{\mathrm{pp}}-V_{\mathrm{s}}C_{\mathrm{sp}})+\frac{1}{\gamma_{\mathrm{w}}}(C_{\mathrm{ps}}-V_{\mathrm{s}}C_{\mathrm{ss}})\right]\\ &\quad=c_{\mathrm{w}}C_{\mathrm{sp}}-\frac{c_{\mathrm{s}}V_{\mathrm{s}}}{\gamma_{\mathrm{w}}}C_{\mathrm{ss}};\quad \frac{1}{V_{\mathrm{w}}}(C_{\mathrm{pq}}-V_{\mathrm{s}}C_{\mathrm{sq}})\\ &\quad=c_{\mathrm{w}}C_{\mathrm{qp}}-\frac{c_{\mathrm{s}}V_{\mathrm{s}}}{\gamma_{\mathrm{w}}}C_{\mathrm{qs}};\quad C_{\mathrm{sq}}=c_{\mathrm{s}}\left(C_{\mathrm{qp}}+\frac{V_{\mathrm{w}}}{\gamma_{\mathrm{w}}}C_{\mathrm{qs}}\right)\end{aligned}$$

which are verified by direct substituting the known C-coefficients (46). By that the standard transport coefficients are proved to be symmetrical for the system considered and therefore Onsager's reciprocal postulate occurs to be valid.

5.2. Zero horizontal conductivity

At the inclusion surface Eqs. (25), (27) and (40) define the values of the temperature, the liquid pressure and the concentration. Substituting those functions in Eq. (41) and algebraic transforming gives an ice velocity:

$$v_{\mathrm{i}}=-\omega_{\mathrm{p}0}\nabla_bp-\omega_{\mathrm{t}0}\nabla_bT-\omega_{\mathrm{s}0}\nabla_bc_{\mathrm{s}} \tag{47}$$

where

$$\omega_{\mathrm{p}0}=\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\frac{1}{\mathrm{den}_0};\quad \omega_{\mathrm{t}0}=-\frac{\kappa\lambda_2}{T_0V_{\mathrm{i}}\lambda_1}\frac{\beta I_1}{\mathrm{den}_0};\quad \omega_{\mathrm{s}0}=-\frac{\gamma_{\mathrm{w}}}{V_{\mathrm{i}}}\frac{1}{\mathrm{den}_0},$$

$$\begin{aligned}\mathrm{den}_0=&\left(\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\right)^2\left(1-\frac{2}{3}\beta\right)\frac{1}{K_{\mathrm{h}}}+\left(\frac{\kappa}{V_{\mathrm{i}}}\right)^2\frac{\beta(I_1-\beta I_2)}{T_0\lambda_1}\\ &+\frac{\gamma_{\mathrm{w}}V_{\mathrm{w}}c_{\mathrm{s}0}\beta}{V_{\mathrm{i}}^2D_n}\left(1-\frac{2}{3}\beta\right),\end{aligned}$$

$$I_2=\frac{2}{3\varepsilon_0}-\frac{1}{\varepsilon_0^2}+\frac{2}{\varepsilon_0^3}-\frac{2}{\varepsilon_0^4}\ln(1+\varepsilon_0)$$

Subsequent substituting (47) in (24) and (26) gives in combination with (36) the equation set for the fluxes in the form (43)–(45) with the transport coefficients as follows:

$$\begin{aligned}&C_{\mathrm{pp}}^0=-\left[(1-\alpha)K_{\mathrm{h}}+\alpha\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\omega_{\mathrm{p}0}\right],\quad C_{\mathrm{ps}}^0=-\alpha\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}\omega_{\mathrm{s}0},\\ &C_{\mathrm{pq}}^0=-\alpha\frac{V_{\mathrm{w}}}{V_{\mathrm{i}}}T_0\omega_{\mathrm{t}0},\\ &C_{\mathrm{sp}}^0=-(1-\alpha)c_{\mathrm{s}0}K_{\mathrm{h}},\quad C_{\mathrm{ss}}^0=-(1-\alpha)D_n,\quad C_{\mathrm{sq}}^0=0,\\ &C_{\mathrm{qp}}^0=\frac{\lambda_2\kappa}{\lambda_1V_{\mathrm{i}}}\alpha\beta\cdot I_1\omega_{\mathrm{p}0},\quad C_{\mathrm{qs}}^0=\frac{\lambda_2\kappa}{\lambda_1V_{\mathrm{i}}}\alpha\beta\cdot I_1\omega_{\mathrm{s}0},\\ &C_{\mathrm{qq}}^0=\left(\frac{\lambda_2\kappa}{\lambda_1V_{\mathrm{i}}}\alpha\beta\cdot I_1\omega_{\mathrm{t}0}-\lambda_2I_3\right)T_0\end{aligned} \tag{48}$$

which ensure the symmetry of the standard transport coefficients.

The additional relations for C-coefficients follow from the physical properties of the system. When the ice velocity is equal to zero then a flux of heat or volume depends only on the "direct" gradient (temperature or pressure; see (20), (22), (24) and (26)). The type and the quantity of those relations are defined, in general, by the structure of porous medium and the form of the input transfer equations. The detailed studying of this problem is beyond the purpose of this paper. Notice only that the additional equation for the system to be considered are following: $C_{\mathrm{sq}}=0$ (see (46) and (48)).

6. Properties of the porous medium with inclusions

In this part the calculation results are presented for heat transfer and osmosis in the special biporous materials (see Fig. 1).

6.1. Effective thermal conductivity

A value of the heat flux through the medium depends on the temperature gradient as well as the pressure and concentration gradients (45). Consider open and closed systems.

In the open system the pressure and concentration drop will be assigned equal to zero ($p_1 = p_2$, $c_{s1} = c_{s2}$). The heat transport may be accompanied by the mass flows. An equation for the thermal conductivity effective coefficient $\tilde{\lambda}_0$ follows from Eq. (45):

$$\tilde{\lambda}_0 = -C_{qq}/T_0 \tag{49}$$

In the closed system the mass fluxes through the boundary are equal to zero ($J_V = 0$, $J_s = 0$). The additional relations between the gradients follow from Eqs. (43) and (44):

$$C_{pp}\nabla_b p + C_{ps}\nabla_b c_s + C_{pq}X_q = 0 \tag{50}$$

$$C_{sp}\nabla_b p + C_{ss}\nabla_b c_s + C_{sq}X_q = 0 \tag{51}$$

The effective coefficient of thermal conductivity $\tilde{\lambda}_C$ is found from the equation set (45), (50) and (51):

$$\tilde{\lambda}_C = -\frac{C_{qq} + C_{qp}A_{pq} + C_{qs}A_{sq}}{T_0} \tag{52}$$

where $A_{pq} = \frac{C_{sq}C_{ps} - C_{pq}C_{ss}}{C_{ss}C_{pp} - C_{sp}C_{ps}}$; $A_{sq} = \frac{C_{pq}C_{sp} - C_{sq}C_{pp}}{C_{ss}C_{pp} - C_{ps}C_{sp}}$.

All the numerical calculations were produced for the cubic cell, the elements of which hold the thermal conductivity coefficients as follow: $\lambda_1 = 2.2\ \mathrm{W\,m^{-1}\,K^{-1}}$, $\lambda_2 = 1.54\ \mathrm{W\,m^{-1}\,K^{-1}}$.

In the biporous medium with the ice inclusions the matter dissolved in the water influences on the thermal conductivity of the system beginning with concentration $\sim 0.001\ \mathrm{mol\,l^{-1}}$ (Fig. 6).

The thermal conductivity of the open system is greater than the one for the closed one. This distinction may be significant at the high conductivity of the medium (curves 1 and 2, Fig. 6).

An extreme value of concentration, at which ice movement does not influence on thermal conductivity, depends on the type of the system. In the closed system that value is about $0.01\ \mathrm{mol\,l^{-1}}$, and in the open one an extreme concentration is on the one order greater ($0.1\ \mathrm{mol\,l^{-1}}$).

6.2. Osmosis

The osmotic effect is studied mostly in closed system and is disclosed in a pressure difference of solutions, which are separated by a porous membrane and have the different concentration. A value of the effect is defined by an osmotic coefficient K_{os} that is equal to one for the ideal semipermeable membrane. A relation between the pressure difference and the concentration difference is presented as follows:

$$\Delta p = K_{os}R_g T\Delta c_s \tag{53}$$

The value of the osmotic effect is defined at isothermal conditions ($X_q = 0$) and at the absence of the volume flow ($J_V = 0$). Transforming Eq. (43) having in view (53) gives an expression for the osmotic coefficient:

$$K_{os} = -\frac{C_{ps}}{C_{pp}R_g T_0}$$

All calculation was produced for ideal solution (see (19)). The value of K_{os} for the cells with the zero and infinite horizontal conductivities is very close (Fig. 7). The osmotic coefficient increases with decreasing the hydroconductivity of porous medium and the solution concentration; i.e. the low-permeable and low-contaminated medium is almost ideal semipermeable membrane. For example, at $K_h < 10^{-14}\ \mathrm{m^3\,s\,kg^{-1}}$ and $c_s < 0.01\ \mathrm{mol\,l^{-1}}$ the coefficient of K_{os} is greater than 0.8. It must be emphasized that the sample

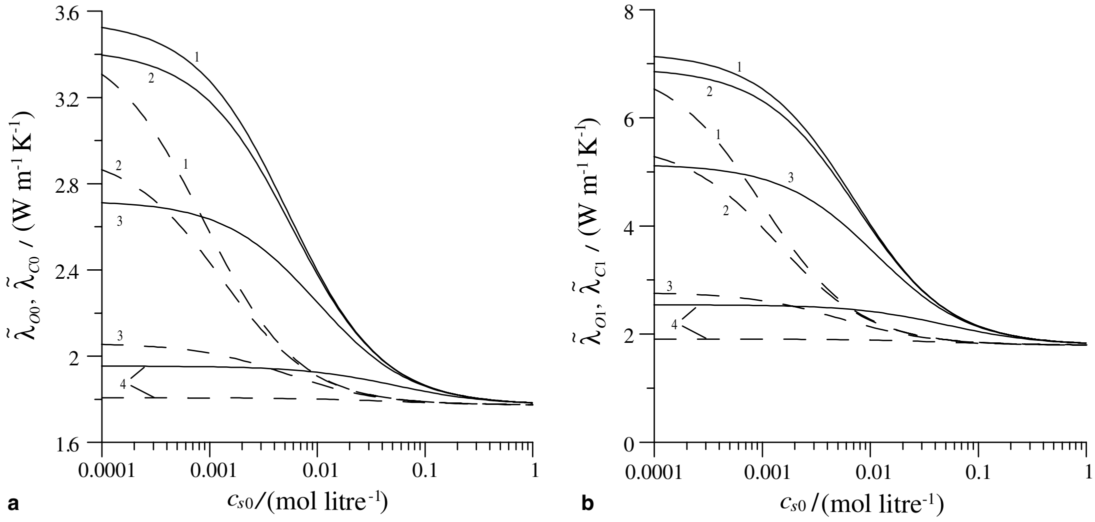

Fig. 6. Thermal conductivity effective coefficient of a cubic cell in the conditions of the open (solid lines) and closed (dot lines) system versus the average solution concentration c_{s0} at the different hydroconductivity coefficients of fine pored medium (E_2) K_h [m^{3}s kg^{-1}]: (1) -10^{-12}; (2) -10^{-13}; (3) -10^{-14}; (4) -10^{-15} with zero (a) and infinite (b) horizontal conductivity. Volumetric ice content equals 0.4, $D_n = 10^{-10}\ \mathrm{m^2\,s^{-1}}$.

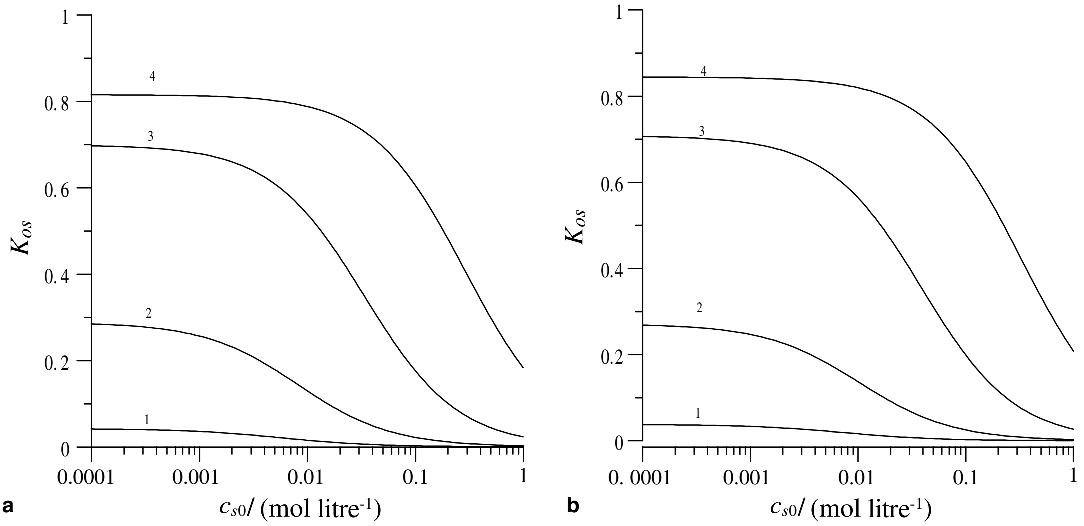

Fig. 7. Osmotic coefficient of cubic cell versus the average solution concentration c_{s0} at different hydroconductivity coefficients of fine pored medium (E_2) K_h [m^{3}s kg^{-1}]: (1) -10^{-12}; (2) -10^{-13}; (3) -10^{-14}; (4) -10^{-15} with zero (a) and infinite (b) horizontal conductivity. Volumetric ice content equals 0.4, $D_n = 10^{-10}$ m^2 s^{-1}.

begins to take on the osmotic properties as soon as appearing the ice into the medium.

7. Conclusions

A biporous media with coupled phase transformations possess the special properties due to the great value of the latent heat of fusion, the impermeability of ice for liquid substance and the complete rejection of impurities by ice.

The presence of foreign matters in liquid phase change a character of heat and mass processes in the system. The unique properties of the medium with the coupled phase transformations vanish at the high concentration of the solution.

Based on results of two papers (presented and [4]), a supposition may be made that the Onsager reciprocal relations hold for the heterogeneous system with phase transformations if only two conditions are realized as follow: in homogeneous parts of the system the Onsager reciprocal relations between the (linear) transport coefficients are valid and the local thermodynamical equilibrium remains in force all over the system.

The interesting properties of the porous media considered bring up the question: Is the regelation phenomena the unique property of ice only? The basic equations of the theory do not forbid a regelation for other matters. There are indirect indications of such possibility [9,10]. The special experimental investigations are needed to provide the clear answer. The more so as the peculiar properties of the biporous media with coupled phase transformations may be used for the development of the new methods in the heterogeneous catalysis technology and the metallurgy.

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