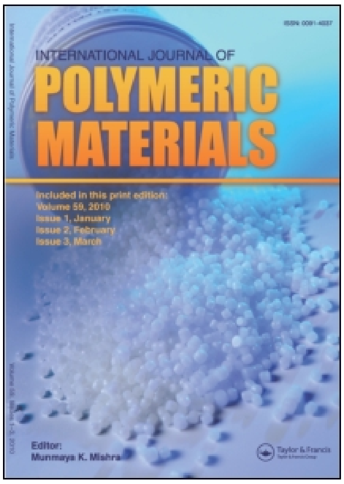

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Parameters of the Mass-Transfer Through the Reverse Osmosis Polysulphonamid Membrane of the Binary Aquatic Solutions of Salts

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Experimental data of mass transfer through the reverse osmosis polysulfonmide membrane of binary aqueous solutions of salts are compared with the predictions of phenomenological equations of mass transfer.

Keywords: Baromembrane process; polysulphonamide membrane; reverse osmosis; mass transfer; component flow; binary aquatic solutions; salts; concentration polarization; phenomenological equations

INTRODUCTION

The results of the experiments and their interpretation using the equation of mass transfer through the membrane and the limit diffusion layer, are presented, the equation is based on the phenomenology of the thermodynamics of the reverse processes are presented. It is shown, that the equation of the bond between the flows statistically agree with experimental data. The obtained values of the

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coefficients of transfer of water in the solutions of salts $Fe(NO_3)_3$ and $Ni(NO_3)_2$ are practically the same, although the coefficients of transfer of these salts differ almost in 7 times. After the estimation of the coefficient of diffusion of water in the solution on integral equations of the mass transfer, taking into account the concentration polarization, the calculated dependencies of the molar flows of water and salts from pressure at different concentrations of salts are obtained. Their qualitative and quantitative agreement with the experimental data is observed.

THEORY AND DISCUSSION

Purification of water solutions from the heavy metals ions and their utilization is the expensive stage of many chemical enterprises. Baromembrane processes of separation may not serve as the alternative to the existing technologies, but may solve the problem, reducing the technological expenses. The increased attention to this problem is well reflected in the scientific literature although in most cases the experimental data are considered only from the point of view of the technological indicators of the baromembrane process. In this work the results of the experiments are discussed from the position of equations of mass transfer through the membrane and the limit diffusion layer, which is based on the phenomenology of the thermodynamics of the irreversible processes.

Experimental data presented on Figure 1 as the molar flows of water (J_{1m}) and salt (J_{2m}) at pressure change ΔP at different concentrations of the salt in the initial solution.

If the concentration polarization exists, the equation of bond between the flows of components in the membrane (J_{im}) and in the limit diffusion layer (J_{is}) for binary solution in the integral form is

$$J_{1s}/D'_1 + J_{2s}/D'_2 = -\Delta P_s/RT, \qquad (1)$$

$$J_{1m}/L'_1 + J_{2m}/L'_2 = -\Delta P_m/RT. \qquad (2)$$

Here $\Delta P_s = P^\circ - P'$ and $\Delta\ P_m = P'' - P^\circ$ – of pressure changes in limit diffusion layer, and membrane (P', P° and P'' – pressure in volume of

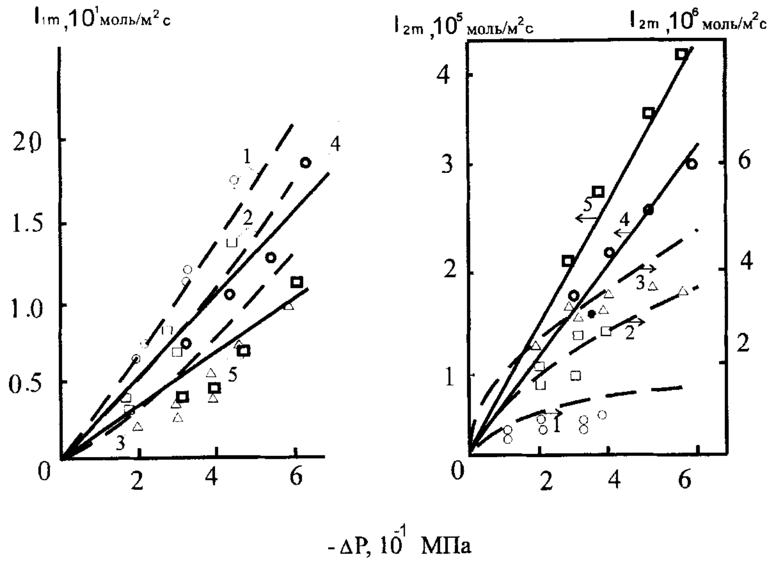

FIGURE 1 Experimental (points) and calculated using Eqs. (6–8) (solid and dashed lines) dependencies of molar flows of water J_{1m} and salt J_{2m} through membrane from difference of pressure under various concentrations of salt in initial solution $Fe(NO_3)_3$:1, 2, 3–0.32, 0.7, 1.07% mass; $Ni(NO_3)_2$: 4, 5 –0.5, 1.0% mass.

the initial solution, in the initial solution at the boundary with the membrane and in the final solution); $D_i' = D_i/\delta_s$ and $L_i' = L_i/\delta_m$ – effective in other words related to the thickness of the limit diffusion layer (δ_s) and the working layer of the membrane (δ_m), the coefficients of diffusion in the solution and of the mass transfer correspondingly.

Molar flows J_{is} and J_{im} may be expressed through volume flow J_v, common for the limit diffusion layer and membrane

$$J_{is} = J_v \Delta c_i, \quad J_{im} = J_v c_i'' \tag{3}$$

where $\Delta c_i = c_i'' - c_i'$ – the difference of the molar-volume concentrations of the component in the volumes of the final (c_i'') and initial (c_i') solutions. Introducing the total change of the pressure $\Delta P = \Delta P_s + \Delta P_m = P'' - P'$, we obtain from (1)–(3) the united equation of bond between the flows;

$$J_v(\Delta c_1/D_1' + \Delta c_2/D_2' + c_1''/L_1' + c_2''//L_2') = -\Delta P/RT \tag{4}$$

While the volume fraction of the component is determined we express $\phi_i = c_i v_i$ and accepting, that the partial-molar volume v_i in the narrow diapason of the composition change of the solution is practically constant, (that is $v_i = \text{const.}$), we give the Eq. (4) the form the multifunctional linear equation of the regression

$$Y = a_0 + a_1 X_1 + a_2 X_2, \tag{5}$$

where the function $Y = -\Delta P / J_v RT$, variable $X_1 = \phi_2''$, $X_2 = \phi_2'' - \phi_1'$, and constant $a_0 = (L_1' v_1)^{-1}$, $a_1 = (L_2' v_2)^{-1} - a_0$, $a_2 = (D_2' v_2)^{-1} - (D_1' v_1)^{-1}$. The calculations of solutions densities of allowed us to estimate the partial-molar volumes of the components. These calculations were carried out assuming; $v_1 = v(H_2O) = 1.8 \cdot 10^{-5}$, $v_2 = v(Fe(NO_3)_3) = 7.5 \cdot 10^{-5}$, $v_2 = v(Ni(NO_3)_2) = 4.75 \cdot 10^{-5} m^3/mol$.

The results of the statistical experimental data processing using the Eq. (5) are presented in Table I. The correlation of the experimental and calculated values of the function Y – on Figure 2. These data show that the Eq. (5) agrees with the experimental data. We emphasize that the obtained values of the coefficient of transfer of water in the salt solutions of $Fe(NO_3)_3$ and $Ni(NO_3)_2$ are practically the same, although the coefficients of transfer of these salts are widely different (7 times).

Meanwhile the data of the table show that the component a_2X_2 in Eq. (5); gives a small contribution to Y, but coefficient a_2 is determined with a large relative error and by this its top value in 95 % confidence interval is positive, while the lowest one is negative. This allows us to accept $a_2 \approx 0$ or $D_1' \; v_1 \approx D_2' \; v_2$, that according to the Eq. (1) means $\Delta P_s \approx 0$ consequently $\Delta P_m \approx \Delta P$. Indeed the processing of the experimental data using Eq. (5) without the component a_2X_2 which represents the contribution of the concentration polarization in the total change of pressure ΔP, leads practically to the same results, as those presented in the table.

By fulfillment of the condition $D_1' v_1 \approx D_2' v_2$, or $\Delta P_s \approx 0$, $\Delta P_m \approx \Delta P$, and also $v_2 \Delta P / RT \ll 1$, and using the approach of the solutios ($v_2 \phi_1 \gg v_1 \phi_2$, $v_i = \text{const}$, $\gamma_i = \text{const}$, where γ_i –coefficient of activity in connection between the activity of the component and its molar fraction) the integral equations of the mass transfer of the components

TABLE I The results of the statistical processing experimental data on the Eq. (5)

Solution	*Number of dimensions*	*Constants*	*Estimation of constants*	*Standard error*	*Estimation of constants for 95% probability range*		*Transfer coefficients m/sec*	
					Lower boundary	*upper boundary*	*water* $L_1 \cdot 10^3$	*salt* $L_2 \cdot 10^8$
H_2O	19	a_0	$4.6 \cdot 10^7$	$1.5 \cdot 10^7$	$1.5 \cdot 10^7$	$7.7 \cdot 10^7$		
$Fe(NO_3)_3$		a_1	$3.1 \cdot 10^{11}$	$2.7 \cdot 10^{10}$	$2.5 \cdot 10^{11}$	$3.7 \cdot 10^{11}$	1.2	4.3
		a_2	$-1.1 \cdot 10^{10}$	$7.9 \cdot 10^9$	$-2.8 \cdot 10^{10}$	$5.7 \cdot 10^9$		
H_2O		a_0	$3.4 \cdot 10^7$	$3.0 \cdot 10^6$	$2.6 \cdot 10^7$	$4.2 \cdot 10^7$		
$Ni(NO_3)_2$	8	a_1	$8.8 \cdot 10^{10}$	$2.7 \cdot 10^9$	$8.1 \cdot 10^{10}$	$9.5 \cdot 10^{10}$	1.6	23.9
		a_2	$2.1 \cdot 10^9$	$3.4 \cdot 10^9$	$-6.6 \cdot 10^9$	$1.1 \cdot 10^{10}$		

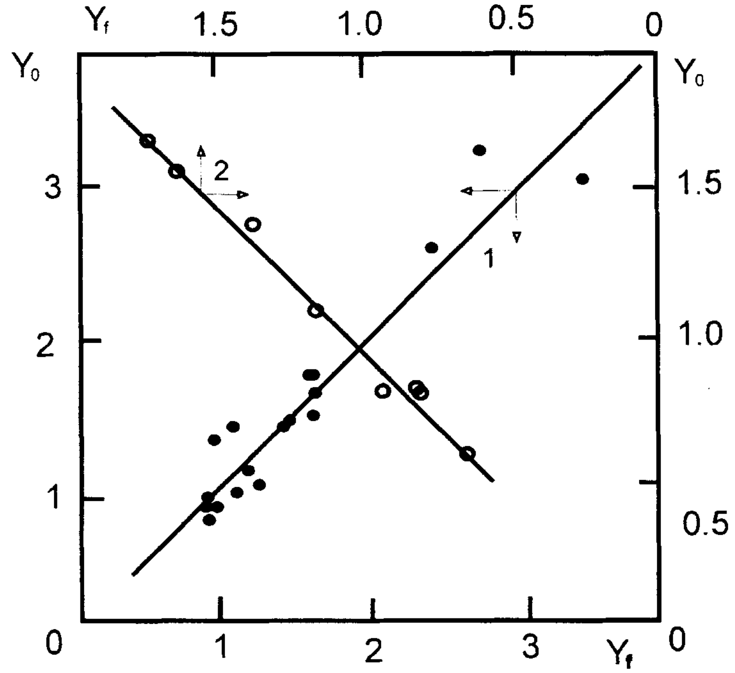

FIGURE 2 Correlation between experimental (Y_0) and calculated (Y_f) using Eq. (5) function values of $Y = -(\Delta P/I_v RT)\cdot 10^{-8}$ for aqueous solutions of ferrum nitrate (regression line 1, correlation coefficient 0.92) and nickle (regression line 1, correlation coefficient 0.99).

of binary solution through membrane and the limit diffusion layer can be represented as

$$\phi_1'' = \phi_1^\circ(1 - J_v\phi_1''\nu_2/L_1'\nu_1)/(1 + \nu_2\phi_1^\circ\Delta P/RT), \qquad (6)$$

$$\phi_1^\circ = \phi_1'(1 - J_v\Delta\phi_1\nu_2/D_1'\nu_1) \approx \phi_1'(1 - J_v\Delta\phi_1/D_2') \qquad (7)$$

where $\phi_1^\circ = c_1^\circ\nu_1$ – volume fraction of the 1-component in the initial solution on the boundary with the membrane.

Adding (6) and (7) with the equation of bond (2) in

$$J_v(\phi_1''/L_1'\nu_1 + \phi_2/L_2'\nu_2) = -\Delta P/RT \qquad (8)$$

we obtain the system of the algebraic equations for calculations ϕ_i°, ϕ_i'', J_v, and also $J_{im}(3)$, on given $\phi_i', \Delta P, D_i', L_i'$. Since, however the D_i' – values are unknown initially the system of the Eqs. (6)–(8) was used for estimation of D_i' from experimental data. For this purpose the functional $F = \sum (z_{jo} - z_{jp})^2$ was minimized in which z_{jo} and z_{jp} are the experimental and calculated values using Eqs. (6)–(8). The values of parameter of minimization in J-th experiment the sum $g_1 J_1 + g_2 J_2$ was considered in which the weight coefficients g_i at J_i were determined by relation $g_i = n / (\sum J_{ij}^2)^{0.5}$ where n is the number of measurements. By this the following values of the effective coefficient of diffusion of water D_i' were obtained: in the solution of the salt of iron – $6.2 \cdot 10^{-6}$, in the solution of nickel – $1.0 \cdot 10^{-6}$ m/sec. The difference between these values as between the values L_1', which are presented in the Table I, falls in the range of experimental error. Let us compare also the obtained values D_1' with empirically established dependence [1].

$$D_1' = 0.285(D_1/r)(\mathrm{Re}_w)^{0.55}\mathrm{Sc}^{0.35} \tag{9}$$

in which $\mathrm{Re}_w = \omega r^2/\upsilon$ – the centrifugal. Reinolds criterion, $\mathrm{Sc} = \upsilon/D_1$ – Shmidts number ω – angle velocity of rotation, r – radius of the membrane, υ – kinematics viscosity. Having in our case $\omega = 3$ rad/sec., $r = 2.85 \cdot 10^{-2}$m, and accepting for water $\upsilon = 10^{-6}\mathrm{m}^2/$ sec., $D_1 = 10^{-9}\mathrm{m}^2/$sec. we obtain from (9) $D_1 = 8.4 \cdot 10^{-6}$, that consider close to D_1' values obtained by us.

They were used for the calculation of the molar flows of water (J_{im}) and of salt (J_{rm}) using Eqs. (6)–(8). Results of the calculations are presented at Figures 1 and 2 by solid and dashed lines. Comparing the experimental and calculated dependencies of the molar flows. J_i from the change of the pressure ΔP at different concentration of salt, we find a satisfactory quantitative and qualitative agreement.

In conclusion, the results of this work show that, the suggested equations of the baromembrane mass-transfer, which are based on the phenomenology of the thermodynamic irreversible processes, conform to the experimental data.

This allows us to calculate the physical parameters of process. Especially convenient for determination of the coefficient of transfer are the equations of bond between the (4) or (8). They are simpler and at the same more accurate, than the integral equations of mass transfer (6) and (7).

References

[1] Colton, C. K., Friedman, S., Wilson, D. E. and Les, R. S. (1972). *J. Clin. Inv.*, **51**(10), pp. 2472–2480.