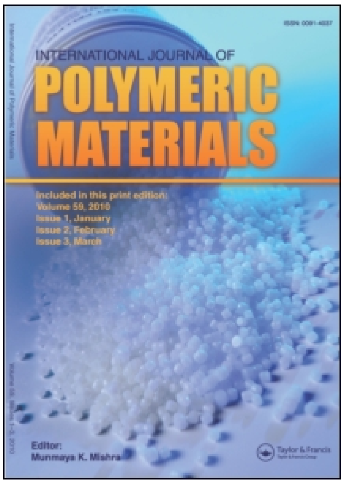

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Medvedevskikh, Yu. G. , Bilinskiy, O. J. , Berlin, A. A. , Turovskiy, A. A. and Zaikov, G. E.(1998) 'Integral Equations of Mass-Transfer of the Components of Binary Solution Through the Membrane', International Journal of Polymeric Materials, 41: 1, 123 — 130

To link to this Article: DOI: 10.1080/00914039808034860

URL: http://dx.doi.org/10.1080/00914039808034860

Intern. J. Polymeric Mater., 1998, Vol. 41, pp. 123-130
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the Gordon and Breach Science
Publishers imprint.
Printed in India.

Integral Equations of Mass-Transfer of the Components of Binary Solution Through the Membrane

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(Received 8 July 1997)

Integral equations of the mass-transfer of binary solution for a baromembrane process are developed and discussed.

Keywords: Baromembrane process; mass transfer; binary solutions; phenomenological equations

INTRODUCTION

For binary solution the initial differential equation of the flow, based on the phenomenology of the thermodynamics of irreversible processes, and its integrated form imply that the partial – molar volumes and the activity coefficients of the components are not dependent from the composition of the solution. All the integral equations present the same picture of the baromembrane process, which agrees with the experiment. The results of the calculations on general integral equation in the entire range of the binary solution composition at pressures up to 100 MPa are presented. They show, that in the pressure

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range from 10 to 100 MPa the satisfactory efficiency of the baromembrane process is maintained in the entire interval of the binary solution composition.

THEORY AND DISCUSSION

The integration of the differential equations of the mass transfer through the membrane is an independent problem, which has the practical and theoretical importance. Many studies are devoted to this problem. One approach assumes the linear change of the pressure and concentration of the components along the coordinate of the transfer perpendicular to the surface of the membrane. The second approach is based on the theory of the diluted solutions, in which the flow of the solvent (the fast component) is the same as the volume flow.

As the initial differential equation of the molar flow J_i of the component of the solution through the membrane we accept the expression.

$$J_i = -(L_i/RT)c_i(v_i\nabla P + RT\nabla \ln a_i), \quad i = 1,2, \tag{1}$$

in which the operator $\nabla = \partial/\partial x$ is responsible for the flow is one dimensional perpendicular to the surface of the membrane; P – pressure, T and R – temperature and universal gas constant; L_i – transfer coefficient; c_i, v_i and a_i – molar-volume concentration, partial-molar volume and activity of the i component of the solution, which is prolonged into the membrane and occupying its free volume. That's why the limit conditions for (1) are at $x = 0$; $c_i = c'_i$; $P = P'$; at $x = \delta_m$ (δ_m – the effective thickness of the membrane) $c_i = c''_i$, $P = P''$; where prime (′) indicates the parameters of the initial (to membrane) solution, the double prime (″) the final parameters (after the membrane).

Since δ_m is unknown we use the relative coordinate of the transfer $y = x/\delta_m$. Thus, the Eq. (1) keeps its form

$$J_i = -(L'_i/RT)c_i(v_i\nabla P + RT\nabla \ln a_i), \quad i = 1,2, \tag{2}$$

but here $L'_i = L_i/\delta_m$ – the normalized transfer coefficient, and $\nabla = \partial/\partial y$. Limit conditions are have the form: by $y = 0$ $c_i = c'_i$, $P = P'$; by $y = 1$ $c_i = c''_i$, $P = P''$.

According to the equation the Gibes-Durham the flows of the components of the binary solution are connected with the relation

$$J/L_1' + J_2/L_2'' = -\nabla P/RT \tag{3}$$

For the stationary system J_i are the integrals of the process, from (3) follows the equation $\nabla P = \text{const.}$ The integration which takes into account the limit conditions, we obtain

$$\nabla P = P'' - P' = \Delta P \tag{4}$$

According to (4) the Eq. (3) may be given the integral form, without simplifying assumptions

$$J_1/L_1' + J_2/L_2'' = -\Delta P/RT \tag{5}$$

However while integrating (2) the simplifying assumptions are necessary because the analytical form of the functions $v_i = v_i(c_i)$, $a_i = a_i(c_i)$ is in the general case unknown. For keeping of the integration of (2) correct it is sufficient to recognize, that the partial-molar volumes of the components and their activities coefficients γ_i, (which are determined by the connection $a_i = \gamma_i N_i$, where N_i – molar fraction of the component), are independent from the solution composition.

$$v_i = \text{const.}; \quad \gamma_i = \text{const.} \tag{6}$$

Without the interpretation of the constants (6) is valid for the ideal as well as for the diluted solutions. From the condition $\gamma_i = \text{const.}$ follows $\nabla \ln a_i = \nabla \ln N_i$. Taking into account this relation, and also (4) and (6), and introducing the variable $\phi_i = c_i v_i$ – volume fraction of the component of the solution, the Eq. (2) assumes the form:

$$J_i = -L_i'(\Delta P \phi_i/RT + \nabla \phi_i/(\phi_1 v_2 + \phi_2 v_1)), \quad i = 1, 2 \tag{7}$$

Before obtaining the general solution of (7) we receive two particular they may have the independent application, but due to particularities, (7) they don't come directly from the general solution.

The first particular solution of (7) is obtained by introducing the condition

$$v_1 = v_2 = v \tag{8}$$

which, as an approach, is acceptable for some practical cases. From the theoretical point of view this is interesting because it allows us to compare the mobility factors $L_i v_i$ of the components in membrane by emphasizing the role of the transfer coefficients.

With the condition (8) the Eq. (7) assumes the standard form of the linear differential equation of the first, order

$$\nabla\phi_i + (v\Delta P/RT)\phi_i = J_i v/L_i', \quad i = 1,2 \tag{9}$$

solution of which for the limit conditions is

$$\phi_i' = e^{-v\Delta P/RT}(J_i RT(1 - e^{-v\Delta P/RT})/L_i'\Delta P + \phi_i'), \quad i = 1,2, \tag{10}$$

At small changes of pressure approximately up to 2 – 3 MPa for $v \cong v(H_2O) = 1.8 \cdot 10^{-5} m^3/mole$) it may be accepted $v\Delta P/RT \ll 1$, that simplifies (10) into (11), where $\Delta\phi_i' = \phi_i'' - \phi_i'$:

$$J_i = -L_i'(\Delta P\phi_i''/RT + \Delta\phi_i/v), \quad i = 1,2 \tag{11}$$

The second particular solution (7) is obtained assuming

$$\phi_1 v_2 \gg \phi_2 v_1 \tag{12}$$

The condition (12) holds in the range of the diluted solutions ($\phi_2 \ll \phi_1$) at not very much different v_1 and v_2, and also for the relatively concentrated solutions, if additionally $v_2 > v_1$. For aqueous solutions this is the typical situation.

Taking into account (12) the Eq. (7) with substitution $\phi_1^{-1} - z$ becomes

$$\nabla_z - (J_1 v_2/L_1')z = v_2\Delta P/RT \tag{13}$$

For given limit conditions the solution of (13) is

$$\phi_1'' = \phi_1' e^{-J_1 v_2/L_1'}(L_1'\Delta P\phi_1/J_1 RT(1 - e^{-J_1 v_2/L_1'}) + 1)^{-1} \tag{14}$$

The condition $v_2\Delta P/RT \ll 1$, according to the relationship (5), provides also the unequality $J_1 v_2/L_1' \ll 1$. By implementing this in (14) we obtain:

$$J_i = -L_i'(\Delta P\phi_i''/RT + \Delta\phi_i/v_2\phi_1'), \quad i = 1,2 \tag{15}$$

The general solution of (7) is obtained by introducing the variable.

$$u = (\phi_1 v_2 + \phi_2 v_1)^{-1} \tag{16}$$

which makes sense only at $v_2 \neq v_1$. With this variable the Eq. (7) is normalized to the standard form

$$\nabla u + mu = \Delta P/RT \tag{17}$$

$$m = v_i\Delta P/RT - J_i/L_i'(v_j - v_i) \tag{18}$$

In view of condition (5), the latter is independent of index *i*. The solution of (18) is the expression

$$u'' = e^{-m}(\Delta P(e^m - 1)/mRT + u'), \tag{19}$$

in which $u' = (\phi_1' v_2 + \phi_2' v_1)$ and $u'' = (\phi_1'' v_2 + \phi_2'' v_1)$ are the limit values u at $y = 0$ and $y = 1$ correspondingly.

The Eqs. (19) and (10) are true formally in all range of the binary solution composition and at any pressures; they complement each other, because (10) is true only at $v_1 = v_2$, and (19) at this condition looses its sense. For the diluted solutions it is more convenient to use (14) and (15).

All the obtained solutions contain integral equations with two unknown values. For finding of all four unknown values J_1, J_2, ϕ_1'' and ϕ_2'' the integral equations must be solved with the equation of the condition (6) and taking into account the relationship $\phi_1 + \phi_2 = 1$ or with $\phi_1'' = J_1 v_1/(J_1 v_1 + J_2 v_2)$.

We carried out numerous calculations using the obtained integral equations of flows. These integral equations create the main picture of the – baromembrane process, which agrees with experimental data. We consider the following rule the most important.

With the increase of the pressure the efficiency of the baromembrane process increases. However, at usually used pressures (up to 5–7

MPa), the satisfactory efficiency of the baromembrane process appears only in the range of dilute solutions. Therefore, it is natural to investigate the possibilities of extending the range of the composition of the binary solution by increasing the working pressure. As a theoretical estimate of this possibility we carried out the calculations based on Eq. (19) in the entire range of the binary solution compositions at pressures up to 100 MPa. The results of these calculations are presented in Figures (1–3) assuming: $L'_1 = 10^{-5}$, $L'_2 = 2 \cdot 10^{-8}$ (m/sec), $v_1 = 2 \cdot 10^{-5}$, $v_2 = 10^{-4}$ (m^3/mole). As we see, at pressures up to 5 MPa the efficiency of the process is low even in the range of the small concentrations of the slow component. However in the range of the pressures from 10 to 100 MPa the satisfactory efficiency of the baromembrane process is kept in the entire range of the composition of the binary solution. The conclusion may, therefore, be made that

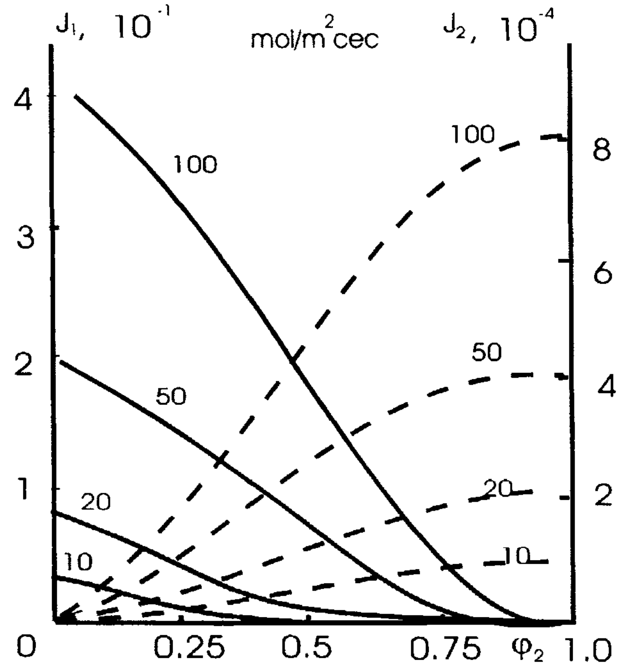

FIGURE 1 Calculated on Eq. (19) dependents of molar flows of quick (J_1) and slow (J_2) components (correspondingly solid and dash lines) from composition of the initial solution at different pressures (numbers at the curves in MPa).

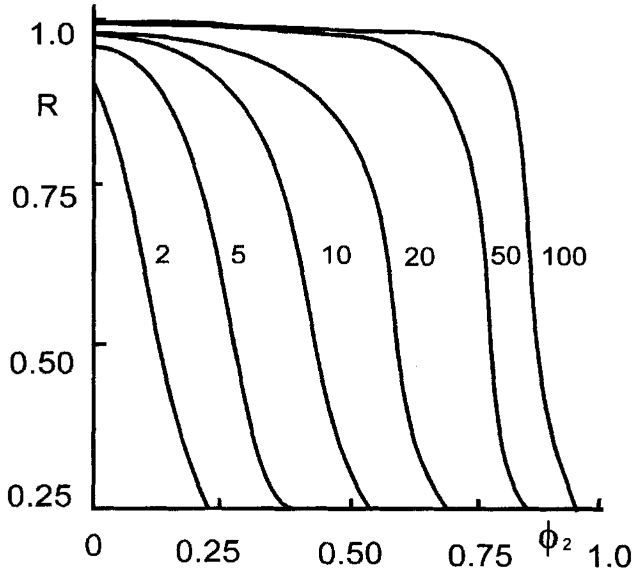

FIGURE 2 Calculated on Eq. (19) dependence of the coefficient of delay $R = 1 - \phi_2''/\phi_1''$ of the slow component from the composition of the initial solution at different pressures (numbers at curves in MPa).

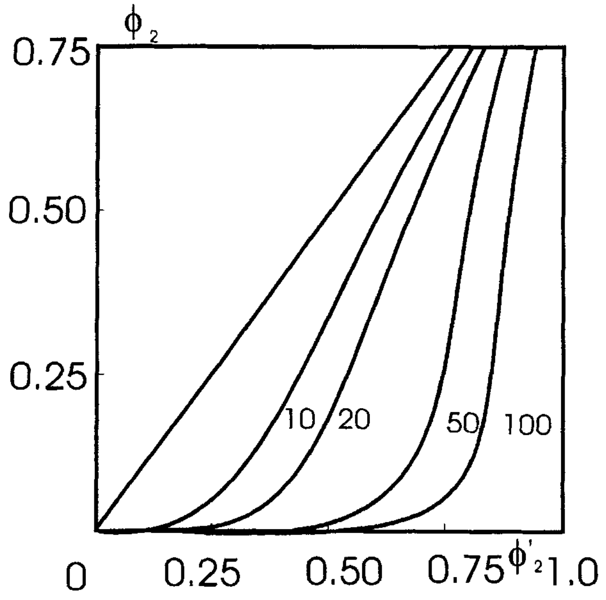

FIGURE 3 Calculated on Eq. (19) dependencies of the composition of the permeate from composition of the initial solution at different pressures (numbers at curves in MPa). Straight line corresponds to the equality of the composition of the final and initial solution: $\phi_2'' = \phi_1''$.

the baromembranes have a superior performance when operating at working pressures in the range from 10 to 100 MPa.

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