HYBRID SOLUTIONS FOR THE ANALYSIS OF MASS TRANSFER IN HOLLOW-FIBER MEMBRANES

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Abstract. A computational simulation was done in order to analyze the influence of the variable solute distribution coefficient on a process of mass separation in modules of hollow-fiber membranes. Due to the functional variation of this coefficient, a nonlinear boundary condition at interface solute-membrane is found, this way an analytical solution for the mass diffusion equation is not possible, therefore, the Generalized Integral Transform Technique (GITT) is then used to obtain a hybrid analytical-numerical solution for this physical problem. The use of the GITT approach in such analysis leads to a coupled system of first order ordinary differential equations in the axial variable. The resulting transformed ODE system is then numerically solved by Gear's method for stiff problems. Numerical results are presented for the average solute concentration along the dimensionless axial length with different values of the governing parameters (Sherwood number and dimensionless slope of the distribution coefficient), permitting to verify their effects on the mass transfer separation. A comparison is also performed with previously reported results in the literature to evidence a critical evaluation of the technique performance.

Keywords: mass transfer separation, hollow-fiber membrane modules, variable solute distribution coefficient, integral transforms.

1. INTRODUCTION

The development of membrane separation processes and their industrial applications are considered relatively recent, especially taking into account that phenomena involving membranes have been studied for over a century (Habert et al., 2006). Recently, it has increased the interest in the use of supported liquid membranes as selective barrier separation (Urtiaga et al., 1992). The membranes extractant contain a substance or a carrier, which facilitates the process of selective permeation by the use of facilitated transport mechanisms (Gherrou and Kerdjoudi, 2002).

A promising technique for separation by liquid membrane is the use of micro-porous hollow-fibers modules as part of contact between the liquid-liquid phases (Prakorn et al., 2004). The basic principle of mass separation in hollow-fiber supported liquid membranes (HFSLM) is the immobilization of organic extractant in the pores of a hydrophobic membrane (Loiacono et al., 1986, Sheng et al., 2004).

The transport of solute through a membrane is that becomes limiting the mass transfer rates in selective mass separation devices. An important physical parameter to analyze the transport of solutes through a membrane is the Sherwood number, which is defined as the ratio of the resistances of solute mass transfer in the fluid to the solute mass transfer in the membrane. Urtiaga et al. (1992) reported that membranes used in selective mass extraction processes have a relatively small Sherwood number, which makes lower solute mass transfer rates, and that in liquid membranes, a relatively high Sherwood number is obtained, when it is employed appropriate liquid with higher distribution coefficient for the solute.

The mathematical model for mass transport in modules of hollow-fiber membranes is discussed in this work, and it is assumed that the hollow-fibers are small enough to lead the steady laminar flow of the fluid containing the solute in the fully developed region and Fickian diffusion in the perpendicular direction to the flow (See Fig. 1). Here, it is also discussed the problem of a variable solute distribution coefficient as a function of the solute concentration, and its effect on the mass transfer rate in modules of hollow-fiber supported liquid membranes. The removal of the solute in the fluid that permeates through the membrane is done by Fickian diffusion, which reacts with an exhaustion solution (stripping) at the membrane external wall. The exhaustion solution that circulates outside of the membrane removes the solute in the fluid that permeates through the membrane under chemical reaction. The chemical reaction that occurs between the solute and the exhaustion solution at the external wall of the hollow-fiber is instantaneous and makes the solute concentration in the stripping phase to be equal to zero. A diagram of the separation mechanism is shown in Fig. 2 according to the considerations taken into account in the model.
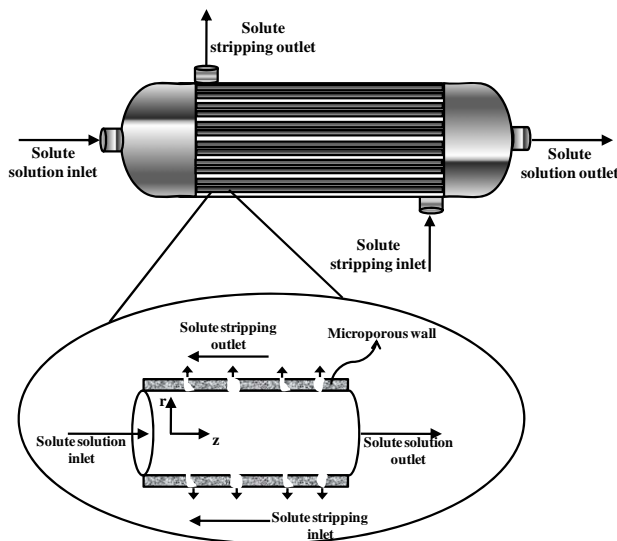
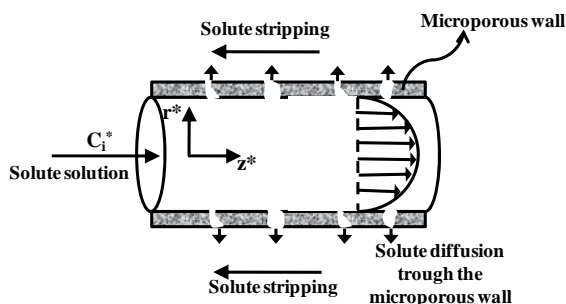Figure 1. Hollow-fiber module with tube side solute-solution flow.

Figure 2. Diagram of the mass transfer mechanism in a module of hollow-fiber membranes.

Therefore, the present work is aimed at developing a computational code capable of simulating the process of solute extraction using hollow-fiber supported liquid membranes, and the influence of the variable solute distribution coefficient on a process of mass separation is closer analyzed. For this purposes, the GITT approach is then employed to solve the equation of species conservation related to such solute extraction. Numerical results are produced for the average solute concentration distribution along the dimensionless axial variable, which are discussed in the light of the influence of relevant parameters in the extraction process, such as, Sherwood number and dimensionless slope of the distribution coefficient. Comparisons with previously reported results in the literature by Urtiaga et al. (1992) for typical situations are also performed permitting to evaluate the technique performance.

2. MATHEMATICAL FORMULATION OF THE PHYSICAL PROBLEM

The equilibrium distribution coefficient H is defined as the equilibrium distribution ratio of the solute concentration in the liquid membrane to the concentration in the fluid side (Urtiaga et al., 1992). According to Urtiaga et al. (1990) and Urtiaga (1991), it is assumed that exists a linear dependency of the distribution coefficient on the solute concentration in the aqueous phase in the following dimensionless form:

$$H = h_0(1 + \gamma C); \quad \gamma = \frac{C_i^* h^*}{h_0} \tag{1,2}$$

where h_0 is the value of the distribution coefficient for infinite dilute solutions; γ is the dimensionless slope and takes into account the dependency of the solute distribution coefficient on the solute concentration ($\gamma = 0$ for a constant distribution coefficient); C_i^* is the solute concentration in the hollow-fiber inlet (mol/m^3); and h^* is the slope of the distribution coefficient (m^3/mol).

The mathematical modeling for this physical problem is based on the equation of species conservation related to the solute extraction in the fluid phase, which together with the appropriate inlet and boundary conditions in dimensionless form are written as (Urtiaga et al., 1992):

$$2(1-r^2)\frac{\partial C}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right), \quad \text{in } 0<r<1, \ z>0 \tag{3}$$

$$C(r,0) = 1, \quad 0 \le r \le 1 \tag{4}$$

$$\frac{\partial C(0,z)}{\partial r} = 0 \ ; \quad \frac{\partial C(1,z)}{\partial r} + Sh_w C(1,z) = -\gamma Sh_w C^2(1,z), \quad z>0 \tag{5,6}$$

The following dimensionless groups were employed in Eqs. (3) to (6) above

$$r = \frac{r^*}{R}, \quad z = \frac{z^*D}{u_{av}R^2}, \quad C = \frac{C^*}{C_i^*}, \quad Sh_w = \frac{k_m s R h_0}{D}, \quad s = \frac{R_0 - R}{R\ln(R_0/R)} \tag{7}$$

where C is the dimensionless solute concentration, r and z are the dimensionless radial and axial coordinates, and Sh_W is the Sherwood number. Also, C^* is the solute concentration (mol/m³), r^* is the radial coordinate (m), R and R_0 are the inner and outer radii of the hollow-fiber, respectively (m), z^* is the axial coordinate (m), D is the solute diffusivity in the fluid phase (m²/s), u_{av} is the average fluid velocity (m/s), k_m is the membrane permeability coefficient (m/s), and s is the hollow-fiber shape factor.

Equation (6) represents a nonlinear boundary condition at interface solute-membrane, because the functional variation of the distribution coefficient, so that an analytical solution for the equation of species conservation is not possible, therefore, the Generalized Integral Transform Technique (GITT) is then used to obtain a hybrid analytical-numerical solution for this physical problem.

2.1. Solution methodology

The next step is to find a solution for the potential C(r,z), and for this purpose, it is followed the ideas in the GITT approach (Cotta, 1993), so that it has to be selected an appropriate auxiliary eigenvalue problem, which shall provide the basis for the eigenfunction expansion. Therefore, the following eigenvalue problem is proposed:

$$\frac{d}{dr}\left(r\frac{d\psi_i}{dr}\right) + 2r(1-r^2)\mu_i^2\psi_i = 0, \quad \text{in } 0<r<1 \tag{8}$$

$$\frac{d\psi_i(0)}{dr} = 0 \ ; \quad \frac{d\psi_i(1)}{dr} + Sh_w\psi_i(1) = 0 \tag{9,10}$$

where μ_i and $\psi_i(r)$ are the eigenvalues and the eigenfunctions, respectively. The problem defined by Eqs. (8) to (10) is solved by the so-called Sign-Count Method or by the GITT approach itself (Mikhailov and Özisik, 1984; Cotta, 1993), which offer safe and automatic accurate computation as many eigenvalues and eigenfunctions as desired. Such eigenvalue problem enjoys the following orthogonality property:

$$\int_0^1 W(r)\psi_i(r)\psi_j(r)dr = \begin{cases} 0, & i \ne j \ ; \\ N_i, & i=j \end{cases} \quad N_i = \int_0^1 W(r)\psi_i^2(r)dr; \quad W(r) = 2r(1-r^2) \tag{11-13}$$

The auxiliary eigenvalue problem given by Eqs. (8) to (10) allows the definition of the following integral transform pair for the potential C(r,z):

$$\overline{C}_i(z) = \int_0^1 W(r)\tilde{\psi}_i(r)C(r,z)dr , \quad \text{transform} \tag{14}$$

$$C(r,z) = \sum_{i=1}^{\infty} \tilde{\psi}_i(r)\overline{C}_i(z) , \quad \text{inverse} \tag{15}$$

where $\tilde{\psi}_i(r) = \psi_i(r)/N_i^{1/2}$ are the normalized eigenfunctions, and N_i is the normalization integral.

The next step is thus to accomplish the integral transformation of the original partial differential equation and the inlet and boundary conditions given by Eqs. (3) to (6). For this purpose, such equations are multiplied by the normalized eigenfunctions, integrated over the domain [0,1] in r, and the inverse formula given by Eq. (15) is employed. After the appropriate manipulations, the following coupled ordinary differential system results, for the calculation of the transformed potentials $\overline{C}_i(z)$:

$$\frac{d\overline{C}_i(z)}{dz} + \mu_i^2 \overline{C}_i(z) = -\gamma Sh_w \tilde{\psi}_i(1) \left[\sum_{j=1}^{\infty} \tilde{\psi}_j(1)\overline{C}_j(z) \right]^2 \tag{16}$$

$$\overline{C}_i(0) = \overline{f}_i = \int_0^1 W(r)\tilde{\psi}_i(r)dr \tag{17}$$

The system of coupled ordinary differential equations given by Eqs. (16) and (17) constitutes a nonlinear initial value problem of infinite equations, which has to be truncated in a sufficiently high number of terms N, in order to compute the transformed potentials $\overline{C}_i(z)$. In the solution of such system, due to its stiff characteristic, appropriate subroutines must be employed, such as the subroutine DIVPAG from the IMSL Library (1991). This subroutine provides the important feature of automatically controlling the relative error in the solution of the ordinary differential equations system, allowing the user to establish a priori error targets for the transformed potentials. Once the system given by Eqs. (16) and (17) is solved for such transformed potentials, the inverse formula, Eq. (15), is recalled to provide the concentration field.

Afterwards, physical quantities of practical interest such as the average solute concentration is defined as

$$C_{av}(z) = \frac{\int_0^1 W(r)C(r,z)dr}{\int_0^1 W(r)dr} = 2\int_0^1 W(r)C(r,z)dr \tag{18}$$

Also, through the application of the inverse formula given by Eq. (15) into Eq. (18), one obtains the following expression for the average solute concentration:

$$C_{av}(z) = 2\sum_{i=1}^{\infty} \overline{f}_i \overline{C}_i(z) \tag{19}$$

3. RESULTS AND DISCUSSION

Numerical results for the $C_{av}(z)$ concentration distribution were obtained along the axial coordinate evolution. For this purpose, a computational code was developed in FORTRAN 90/95 programming language and implemented on an INTEL CORE (TM) 2 DUO 2.13 GHz computer. The routine DIVPAG from the IMSL Library (1991) was used to numerically handle the system of ordinary differential equations given by Eqs. (16) and (17), with a relative error target of 10^{-8} prescribed by the user. Different values of the governing parameters (Sh_w and γ) were employed in the computational simulations, whose results are shown in terms of convergence behavior in table forms and graphically compared with those of Urtiaga et al. (1992).

Table 1 presents the results of the dimensionless average solute concentration $C_{av}(z)$ with Sherwood number equal to 10, dimensionless slope for the variable distribution coefficient, $\gamma=0.1$, at the dimensionless axial lengths, z=0.01, 0.1, 0.2, 0.5, 1.0 and 2.0. As can be observed, it was a convergence of four significant digits using a truncation order of N=1000 terms in the summations. Similarly, Tab. 2 brings a convergence behavior for $C_{av}(z)$ with $Sh_w=10$ and $\gamma=1$, and for this case a truncation order N, within the range of 500 to 600 terms in the summations, a fully convergence of four digits is reached. It is also verified that for this case, the results for $C_{av}(z)$ are lower than for the case $Sh_w=0.1$ and $\gamma=10$, this way evidencing the strong influence of the Sherwood number. The consistency of the results shown in Tabs. 1 and 2 is a direct validation of the computational codes developed in the present work.

Table 1. Convergence behavior of the average solute concentration along the axial length for Sh_w=0.1 and γ=10.

z	$C_{av}(z)$									
	Sh_w=0.1 and γ=10									
	N=100	N=200	N=300	N=400	N=500	N=600	N=700	N=800	N=900	N=1000
0.01	0.9833	0.9834	0.9834	0.9835	0.9835	0.9835	0.9835	0.9835	0.9835	0.9835
0.1	0.8762	0.8768	0.8770	0.8771	0.8772	0.8773	0.8773	0.8773	0.8774	0.8774
0.2	0.7851	0.7859	0.7863	0.7865	0.7866	0.7867	0.7867	0.7868	0.7868	0.7869
0.5	0.5881	0.5891	0.5896	0.5898	0.5900	0.5901	0.5901	0.5902	0.5903	0.5903
1.0	0.3950	0.3960	0.3963	0.3966	0.3967	0.3968	0.3969	0.3969	0.3970	0.3970
2.0	0.2165	0.2171	0.2173	0.2175	0.2175	0.2176	0.2176	0.2177	0.2177	0.2177

Table 2. Convergence behavior of the average solute concentration along the axial length for Sh_w=10 and γ=1.

z	$C_{av}(z)$						
	Sh_w=10 and γ=1						
	N=100	N=200	N=300	N=400	N=500	N=600	N=700
0.01	0.9224	0.9225	0.9226	0.9226	0.9227	0.9227	0.9227
0.1	0.6360	0.6361	0.6362	0.6362	0.6363	0.6363	0.6363
0.2	0.4556	0.4557	0.4558	0.4558	0.4558	0.4558	0.4558
0.5	0.1749	0.1749	0.1749	0.1749	0.1749	0.1749	0.1749
1.0	0.0358	0.0358	0.0358	0.0358	0.0358	0.0358	0.0358
2.0	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015

Figure 3 shows the influence of change in the distribution coefficient on the dimensionless average concentration $C_{av}(z)$ along the axial length for the Sherwood number equal to 0.1 and different values of the parameter γ. It is observed that with increasing axial length z the solute average concentration diminishes for all values of the parameter γ analyzed. However, a reduction in $C_{av}(z)$ is less intensified for negative values of γ, indicating that the extraction process becomes more efficient for positive values of such parameter.
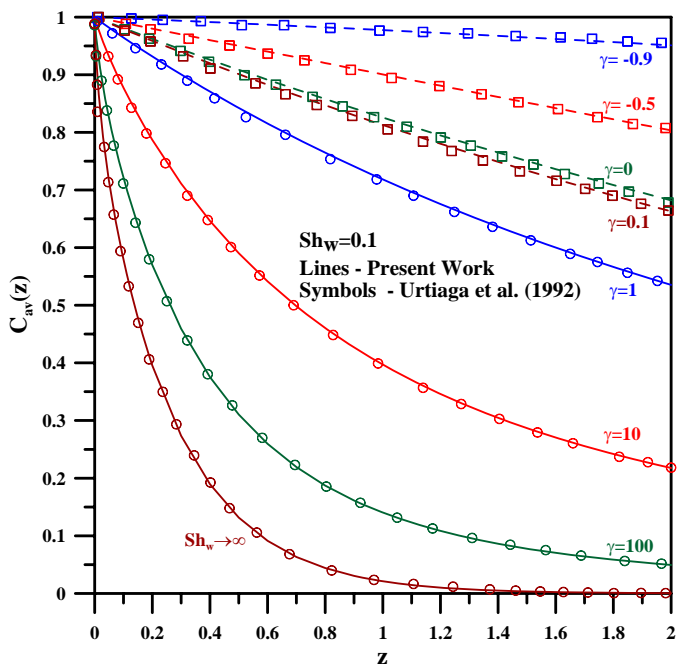

Figure 3. Comparison of the average solute concentration along the dimensionless axial length for Sh_w=0.1 and different values of the γ parameter.

Similar analysis is made in Fig. 4 for the case of $Sh_w=1$ and different values of the γ parameter. In this case the effect of the slope of the distribution coefficient γ on the mass separation is small compared to the case with Sherwood equal to 0.1. In both cases, for $\gamma=0.1$, the variation of the dimensionless average solute concentration is very close to the case of a constant distribution coefficient $\gamma=0$. However, for $\gamma=1$, it is verified an increase in the performance of the solute mass extraction in relation to $\gamma=0$. The $C_{av}(z)$ distribution is higher in positions closer to the hollow-fiber inlet than for positions far from the inlet (higher axial lengths), consequently the distribution coefficient is lower leading to less efficient solute mass extraction for small axial lengths. In higher positions, the concentration $C_{av}(z)$ diminishes, therefore, increasing values of the distribution coefficient and, as a consequence, the solute separation is intensified. It is clear from Figs. 3 and 4 that the solute mass extraction is more efficient for the case of $Sh_w=1$, due to the decrease in the mass transfer resistance of the solute in the fluid.
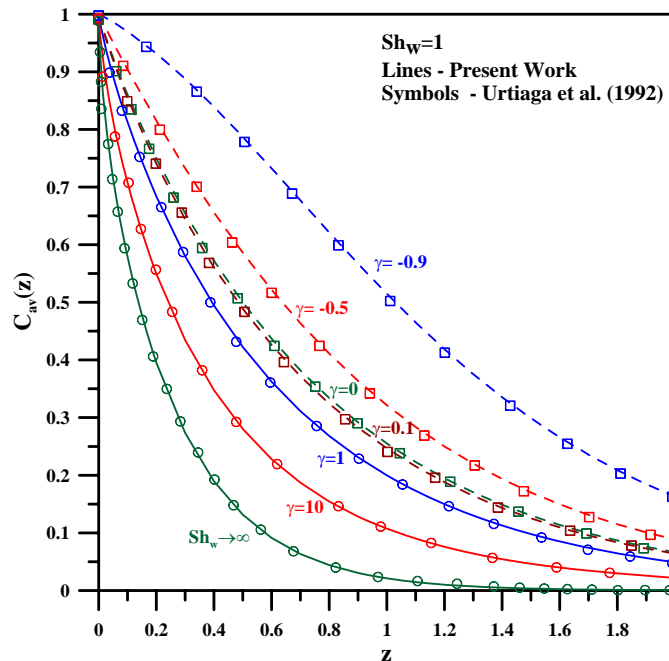

Figure 4. Comparison of the average solute concentration along the dimensionless axial length for $Sh_w=1$ and different values of the γ parameter.

Finally, Fig. 5 shows the analysis for the case of $Sh_w=10$. For higher values of Sherwood numbers, the variation in the concentration with axial length z is similar to the behavior expected for Sherwood infinity. It is also observed that with increasing z for positive and negative values of γ, it has been a decrease in the average solute concentration, however this decrease in $C_{av}(z)$ is very close for negative and positive values of γ., indicating that the extraction is not influenced for this parameter. For $\gamma=1$, the $C_{av}(z)$ concentration behaves almost identically to the case of $\gamma=-0.9$. The use of higher values of γ than 1 furnishes similar variations in the concentration $C_{av}(z)$ along the membrane length that those obtained with $Sh_w\rightarrow\infty$. One can see from the comparison of Figs.3 and 4 with Fig. 5 for the behavior of $C_{av}(z)$ concentration along the axial length, that the extraction of the solute is more efficient when the Sherwood number is closer to infinite values, as is the case for $Sh_w=10$.

Also, from Figs. 3 to 5, comparisons with those results of Urtiaga et al. (1992) are shown, and excellent agreements are verified, this way furnishing a direct validation of the present methodology employed in the present work.
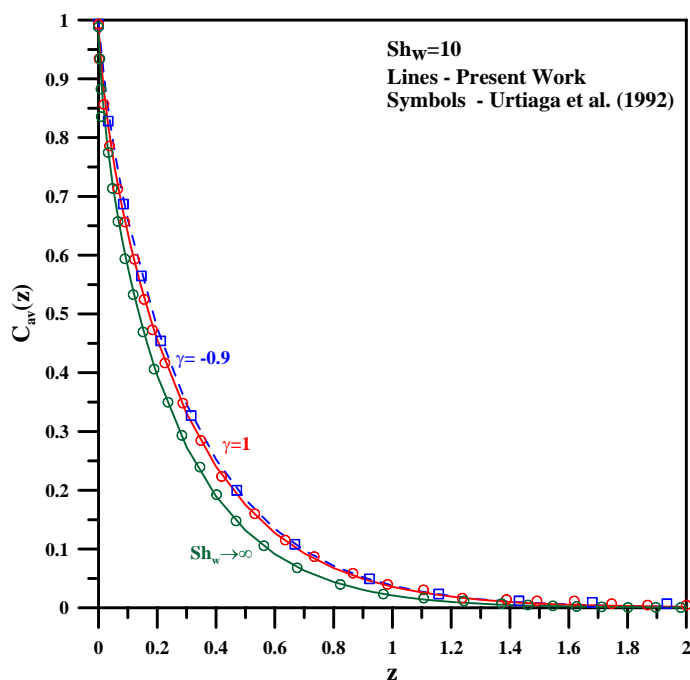
Figure 5. Comparison of the average solute concentration along the dimensionless axial length for Sh_w=10 and different values of the γ parameter.

4. CONCLUSIONS

A study of membrane extraction process of solute by using hollow-fiber supported liquid membranes (HFSLM) was developed in the present work. The mathematical modeling of physical problem was done through the equations of mass conservation of chemical species by considering variable solute distribution coefficient, which were solved through the Generalized Integral Transform Technique (GITT), which provided reliable and cost effective simulations for the considered cases. Also, it was verified that the present GITT solution was in an excellent agreement with that of Urtiaga et al. (1992), this way offering a direct validation of the present results. The analysis also shown that a variable distribution coefficient has important influence on the mass transfer separation in hollow-fiber mass transfer devices as the Sherwood number is less than 10 and the γ parameter greater than 1. Therefore, to predict the performance of a liquid membrane module, the variation of the distribution coefficient should be taken into account.

5. ACKNOWLEDGEMENTS

6. REFERENCES

Cotta RM., 1993, "Integral Transforms in Computational Heat and Fluid Flow", CRC Press, Boca Raton.
Gherrou, A. and Kerdjoudi, H., 2002, "Removal of Gold as $Au(Tu)_2^+$ complex with a Supported Liquid Membrane Containing Macrocyclic Polyethers Ligands as Carriers", Desalination, Vol. 144, pp. 231.
Habert, A. C.; Borges, C. P.; Nobrega, R., 2006, "Processos de Separação por Membranas", E-papers Serviços Editorais Ltda, pp. 9.
IMSL LIBRARY, MATH/LIB., 1991, Houston, TX.
Mikhailov MD, Ozisik MN., 1984, "Unified Analysis and Solutions of Heat and Mass Diffusion", Wiley, New York.
Loiacono, O.; Drioli, E. and Molinari, R., 1986, "Metal Ions Separation and Concentration with Supported Liquid Membranes", Journal of Membrane Science, Vol. 28.
Prakorn, R.; Kwanta, N.; Ura, P., 2004, "Recycling of Cr (VI) by Membrane Solvent Extraction: Long Term Performance with the Mathematical Model", Korean Journal Chemical Engineering, Vol. 21(6), pp. 1212.

Sheng, S., Mastuyama, H. and Teramoto, M., 2004, "Ce(III) Recovery by Supported Liquid Membrane using Polyethylene Hollow Fiber Prepared via Thermally Induced Phase Separation", Sep. and Purif. Tech., Vol. 36, pp. 17.

Urtiaga, A. M.; Ortiz, M. I.; Irabien, A. J., 1990, "Phenol Recovery with Supported Liquid Membranes. I.", Inst. Chem. Eng. Symp. Ser., No. 119, pp. 35-46.

Urtiaga, A. M., 1991, "Applicación de las Membranas Liquidas Soportadas a la Recuperacidn de Fenol en Módulos de Fibras Huecas", Ph.D. Thesis, Universidad del Pais Vasco, Bilboa, Spain.

Urtiaga, A. M.; Irabien, A.; Stroeve, P., 1992, "Effect of a Variable Solute Distribution Coefficient on Mass Separation in Hollow Fibers", Ind. Eng. Chem. Res., Vol. 31, pp. 1362-1366.

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