Description and approximation of mass-transfer in pervaporation process on the base of nonequilibrium thermodynamics approach

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ABSTRACT

Pervaporation is a nonequilibrium membrane process. The pressure or chemical potential gradients are the factors that determine the irreversibility of membrane transfer in pervaporation. In this work, we consider the opportunity of describing and approximating pervaporation data using a nonequilibrium thermodynamic approach. Pervaporation curves for a wide range of feed solution concentrations have been built based on data on a few binary systems. The thermodynamic properties of feed solutions were calculated using vapor–liquid equilibrium data. The sigmoidal Boltzmann function, Gauss function and Praal equation were used to approximate vapor–liquid equilibrium data. Approbation of proposed variants in the construction of pervaporation curves was carried out for five binary systems: ethanol–water at 50 °C and 60 °C, acetone–water at 30 °C, benzene–cyclohexane at 25 °C, methanol–methyl-tert-butyl ether at 25 °C, and ethanol–butanone at 55 °C. The agreement between calculation results and experimental data is in the limits which are sufficient for applied estimations.

1. Introduction

Pervaporation, or evaporation through a membrane, is one of the main membrane separation processes that are of significant industrial importance [1–3]. In practical applications the pervaporation process is carried out with the use of non-porous polymeric membranes and in vacuum mode. In these cases the driving force of the process is the gradient or difference of upstream and downstream pressures. This difference of the pressures on the membrane sides causes the gradient of chemical potentials or partial pressures of components. Accordingly, pervaporation should be considered a nonequilibrium process. The first works that describe the pervaporation process on the basis of a nonequilibrium thermodynamics approach were papers by Kedem and colleagues (see e.g. [4]). The significance of the application of nonequilibrium thermodynamics to membrane processes in general has been repeatedly emphasized in subsequent papers and books by various authors [1]. Nevertheless the limitation of full pervaporation and thermodynamic data necessary for application of nonequilibrium theory retarded the appropriate calculation and modeling methods. In this paper we present analysis data on the pervaporation of binary solutions using a linear approach of nonequilibrium thermodynamics. Of course the use of linear phenomenological laws

should limit the generality of the proposed estimation method. Nevertheless, the results of fulfilled calculations are consistent with experimental data, at least for applied purposes. We also did not apply the common vapor–liquid equilibrium (VLE) models for the description of thermodynamic properties of feed solutions (i.e. the initial mixture that should be separated): the approximation of VLE data was carried out with the use of sigmoidal Boltzmann function, Gauss function and Praal's equation. Such an approach was chosen to simplify the calculation procedure.

Also discussed are some important practical aspects, including the problem of determining thermodynamic forces in a vacuum mode of pervaporation.

2. Theoretical approaches and approximation method

The nonporous membranes used in pervaporation are of a diffusive type. The description of mass-transfer in such systems needs to obtain the values of diffusion coefficients. We consider the case when the dependence of diffusion coefficients on local composition within the membrane can be valued as negligible. In the opposite case the calculation of this dependence requires additional correlations, e.g. the Rautenbach–Albrecht model [5]. Diffusion is determined not only by a coefficient diffusion of pure substances but also by reciprocal influence of components in the case of a binary mixture. In general, the nature of this influence depends on the composition of a feed mixture. Dependence on pressure as a

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driving force of membrane mass transfer in pervaporation can be presented as values of partial pressures that correspond with values of chemical potentials of components. Therefore, the phenomenological equations for the combined fluxes of substances $J_i(i = 1, 2)$ and thermodynamic forces in the case of isothermal pervaporation of binary mixtures can be presented in the well-known form [5]:

$$J_1 = -L_{11}\frac{d\mu_1}{dz} - L_{12}\frac{d\mu_2}{dz}$$
$$J_2 = -L_{21}\frac{d\mu_1}{dz} - L_{22}\frac{d\mu_2}{dz}, \tag{1}$$

where μ_i is the chemical potential of substances i, L_{ik} are kinetic (phenomenological) coefficients, which connect with diffusion coefficients, and $\left(-\frac{d\mu_1}{dz}\right)$ is the constituent of gradient μ_i (thermodynamic force) along the space axis z. Fluxes of substances J_i through the unit area can be determined by equation $J_i = \frac{dm_i}{d\tau}$, where m_i is the amount of substances i and τ is the time. In the context of discontinuous nonequilibrium thermodynamics [6–8], the gradients of chemical potentials can be presented as a difference of μ_i values for two opposite membrane sides. For practical purposes the chemical potentials may be presented with the use of partial pressures of components: $\mu_i = \mu_i^\circ(T) + RT\ln p_i$, where $\mu_i^\circ(T)$ is a standard value of chemical potential which depends on temperature only; R is gas constant. In this paper we consider the isothermal pervaporation processes. Correspondingly, the difference of μ_i can be written as a difference of logarithm of partial pressures p_i. In this work we presumed that the driving forces could be expressed by partial pressures in feed only. We simplified in this way for two reasons. Firstly, we assumed that the values of partial pressures of components in the feed mixture would have a significant contribution to the values of thermodynamic forces in vacuum mode of pervaporation. Secondly, in vacuum mode the total and partial pressure at the down-stream mode of membrane (permeate pressure) vanishes and the chemical potentials of components go to $-\infty$ correspondingly. Obviously, the difference between finite quantity and infinity has no physical meaning. On the other hand, the "infinitesimal values" of partial pressure for different components could be estimated at an arbitrary and equal value. We consider the neglecting of partial pressures of permeate in phenomenological equations as relatively free, an assumption that needs additional justification. In any case, the final conclusion can be made according to calculation results and the comparison with experimental data. Therefore, we used the possibility to present pervaporation fluxes in the following form:

$$J_1 = -L_{11}\ln p_1 - L_{12}\ln p_2; \quad J_2 = -L_{21}\ln p_1 - L_{22}\ln p_2, \tag{2}$$

where L_{ik} are appropriate kinetic coefficients.

An equation that describes the ratio of fluxes of the species can be obtained by combining the Eq. (2):

$$\frac{J_1}{J_2} = \frac{L_{11}\ln p_1 + L_{12}\ln p_2}{L_{21}\ln p_1 + L_{22}\ln p_2}, \tag{3}$$

In the case of fluxes ratio the time terms are reduced and the left side of Eq. (3) includes the differentials of component amounts only. The obtaining phase (the product of pervaporation, permeate) in a vacuum condition of pervaporation is continuously withdrawn, as in open phase processes. As a result the permeate contains the infinitesimal amounts of both components and $m_i \cong dm_i$. Therefore, in the first approximation, the ratio of fluxes could be presented as ratio of amounts of substances in permeate and following equation holds:

$$\frac{y_1^{(p)}}{y_2^{(p)}} = \frac{L_{11}\ln p_1 + L_{12}\ln p_2}{L_{21}\ln p_1 + L_{22}\ln p_2}, \tag{4}$$

where $y_i^{(p)}$ is the molar fraction of component i in permeate. Accordingly, the composition of permeate is a function of the values of partial pressures of substances in the feed mixture. Eq. (4) is determined by using several assumptions but it can be applied to modeling of pervaporation and the approximation of pervaporation curves. For the calculation of kinetic coefficients, one needs limited data on pervaporation for some range of the feed solution. Hereafter, we proposed that kinetic coefficients are constant for the whole composition range. Additional facilitated conditions are Onsager reciprocal relations for kinetic coefficients:

$$L_{12} = L_{21}$$

For the sake of simplicity, we consider the systems with the vapor whose behavior is close to ideality. In such cases, by neglecting vapor nonideality, partial pressure is determined with the following:

$$p_1 = Py_1; \quad p_2 = Py_2,$$

where P is the total pressure of feed solution. Taking into account that molar fractions in binary systems are connected by the relationship

$$y_1 + y_2 = 1$$

the Eq. (4) obtains the following form that include only molar fractions of component 1 both for feed mixture and in permeate:

$$\frac{y_1^{(p)}}{1 - y_1^{(p)}} = \frac{L_{11}\ln Py_1 + L_{12}\ln P(1 - y_1)}{L_{12}\ln Py_1 + L_{22}\ln P(1 - y_1)},$$

where we took into account Onsager relations and link between partial and total pressure. As a result the following equation for the composition of permeate holds:

$$y_1^{(p)} = \frac{\frac{L_{11}\ln Py_1 + L_{12}\ln P(1 - y_1)}{L_{12}\ln Py_1 + L_{22}\ln P(1 - y_1)}}{1 + \frac{L_{11}\ln Py_1 + L_{12}\ln P(1 - y_1)}{L_{12}\ln Py_1 + L_{22}\ln P(1 - y_1)}},$$

or, after simple transformation:

$$y_1^{(p)} = \frac{1}{1 + \frac{[(L_{22}/L_{21}) + 1]\ln P + \ln(y_1) + (L_{22}/L_{21})\ln(1 - y_1)}{[(L_{11}/L_{21}) + 1]\ln P + \ln(1 - y_1) + (L_{11}/L_{21})\ln(y_1)}}, \tag{5}$$

To optimize calculations by Eq. (5) we present dependence $P(y_1)$ in an analytical form. For interpolation of the data sets on the pressure dependence, we applied sigmoidal Boltzmann function (6) and Gauss function (7):

$$P(y_1) = A_2 + \frac{(A_1 - A_2)}{1 + e^{\frac{y_1 - t_0}{t}}}, \tag{6}$$

$$P(y_1) = y_0 + \frac{A}{w\sqrt{\pi/2}}e^{-2\frac{(y_1 - x_c)^2}{w^2}}, \tag{7}$$

where
A_1, A_2, t_0, t и y_0, x_c, w, A are variable parameters that do not depend on composition. The choice of Eqs. (6) and (7) is justified by the fact that these functions best described the dependence of total pressure on in composition of vapor in systems under consideration. In any case, the final results do not depend on these functions and their parameters.

For approximating the data on dependence of vapor composition on the composition of the feed solution, we applied the Praal's equation:

$$y_1(x_1) = \frac{cx_1(a - x_1)}{cx_1(a - x_1) + x_2(b + x_1)}, \tag{8}$$

where x_i is the mole fraction of component i in the feed mixture and a, b, c are variable parameters, not dependent on composition.

Our procedure in calculating the kinetic coefficients and the construction of pervaporation curves consists of following steps: