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The membranes (Nafion and LDPE) in binary liquid mixtures benzene + methanol – sorption and swelling

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ABSTRACT

Sorption studies provide valuable information about the interactions of the components of the liquid mixture with the polymer. In the present paper, the behaviour of Nafion and low-density polyethylene membranes in binary mixtures benzene + methanol was examined with respect to their application in separation processes. The individual sorption isotherms, the separation factors, and the composition of the swollen membranes were derived from the experimental data. The results confirm that Nafion as a polar material sorbs the more polar component of the mixture (methanol) preferentially to the less polar component (benzene) whereas non-polar polyethylene prefers non-polar benzene in the whole concentration range. Volume measurements of the swollen membranes indicate that the ideal sorption behaviour cannot be considered for the selected systems.

1. Introduction

Since large amounts of solvents are used in industrial applications, the minimisation of their environmental impacts calls for the improvement of current technologies for solvent regeneration or finding new possibilities in this field. However, the distillation process, commonly used for the solvents separation, is energy-consuming, and its selectivity may be limited by the vapour–liquid equilibrium, especially in cases of azeotropic mixtures. If the process can be replaced by the membrane separation, these difficulties might be overcome. The problem is the choice of suitable membrane. It is necessary to consider the selectivity of the membrane, as well as its price and durability. The sorption data may help when designing the separation process and choosing the suitable membrane.

The aim of this work is to compare the selectivity of two membranes of different nature for non-polar–polar organic mixtures as such as benzene + methanol, often encountered for instance in the pharmaceutical industry. Nafion usually shows a high selectivity for organic mixtures. On the other hand, with hydrophobic membranes, such as polyethylene, one cannot expect a very high selectivity, as they do not possess any functional groups to create a difference in interaction between the two components of the separated mixture. Nevertheless polyethylene in the role of the separation membrane is a very cheap material.

Both materials under study are used in the form of the foil. Nafion is a polymer with perfluorovinyl pendant side chains ended by sulphonic acid groups (Fig. 1a). The poly(tetrafluoroethylene) backbone guarantees an outstanding chemical stability in both reducing and oxidizing environments. The sulphonic exchange groups on the side chains have very high acidity [1,2]. Nafion membrane is used in fuel cells, membrane reactors, gas dryers, production of NaOH, electrodialyses, etc. [3–7]. Polyethylene is a smooth-chained polymer with simple structural unit (Fig. 1b). In numerous applications the membranes are immersed in liquid, which significantly affects their properties (namely swelling and transport properties of permeates) [8–11].

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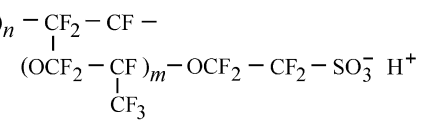
a



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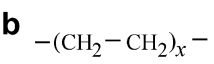

Fig. 1. Structural units of (a) Nafion, (b) polyethylene membranes. The index m is usually equal unity, so that the value of n determines the ratio of polar to non-polar material in the membrane and varies from 5 to 11.

2. Theory

The sorption of a binary liquid mixture (components 1 and 2) in a polymer (component 3) is characterised by two parameters: the swelling degree and the preferential sorption [12–25].

2.1. The swelling degree

On immersion into a liquid the polymer imbibes certain amount of liquid. This process can be quantified by the swelling degree, i.e., the relative mass increase:

$$Q = \frac{m_3 - m_{3,0}}{m_{3,0}} \tag{1}$$

where m_3 is the mass of the swollen polymer membrane and $m_{3,0}$ is the mass of the dry membrane.

2.2. The preferential sorption and the composition of binary mixture sorbed in the polymer

When a polymer is in contact with a binary liquid mixture, in most cases one of the mixture components is more sorbed into the polymer. The extent of this phenomenon is characterised by the preferential sorption, i.e., by the excess number of moles of certain component sorbed in the polymer compared to its number in the bulk solution having the same total number of moles of liquid mixture n^s the mixture sorbed in the polymer. If, for example, the component 2 is preferentially sorbed, the preferential sorption Ω_2 related to unit of mass of dry polymer (in mol g^{-1}) is given by the relation

$$\Omega_2 = n^s(x_2^s - x_2^b) \tag{2}$$

where x_2^s is the molar fraction of the component 2 in liquid sorbed in the polymer, x_2^b the molar fraction of this component in the bulk binary liquid surrounding the polymer. The total number of moles of substances sorbed in one gram of polymer n^s from Eq. (2) can be expressed as

$$n^s = \frac{Q}{\overline{M}^s} = \frac{Q}{x_2^s M_2 + (1 - x_2^s)M_1} \tag{3}$$

where M_1 and M_2 are the molar masses of pure components 1 and 2, and $\overline{M}^s$ is the average molar mass of binary sorbed liquid. Preferential sorption Ω_2 is available from experimental data using equation

$$\Omega_2 = \frac{N_0}{m_{3,0}} \cdot (x_{2,0}^b - x_2^b) \tag{4}$$

where $N_0 = m_0/(x_{1,0}^b \cdot M_1 + x_{2,0}^b \cdot M_2)$ is the initial mole number in m_0 grams of the binary solution brought in contact with $m_{3,0}$ grams of polymer, $x_{i,0}^b$ and x_i^b are the molar fractions of the component i ($i = 1$ for benzene and $i = 2$ for methanol) in bulk initial and equilibrium solutions, respectively.

The dependence of the preferential sorption on the bulk solution composition at constant temperature is called the isotherm of concentration change or composite isotherm.

The combination of Eqs. (2) and (3) allows determination of the molar fraction of the preferentially sorbed component in the polymer phase from experimental data on preferential and total sorptions (Eqs. (1) and (4))

$$x_2^s = \frac{Qx_2^b + \Omega_2 M_1}{\Omega_2(M_1 - M_2) + Q} \tag{5}$$

2.3. The individual isotherms

In many applications it is necessary to have information not only on the total sorbed amount (n^s) but also on the amounts of single components sorbed in the polymer (so called individual sorptions n_1^s and n_2^s) at different bulk solution compositions. Knowing the composition of the sorbed liquid as a function of bulk solution composition (Eq. (5)) and the total sorbed amount n^s (Eq. (3)), the individual isotherms can be gained

$$n_1^s = x_1^s \cdot n^s \tag{6}$$

$$n_2^s = x_2^s \cdot n^s \tag{7}$$

2.4. The separation factors

The effectiveness of the separation processes can be expressed by the separation factors

$$\alpha_{21}^{sb} = \frac{x_2^s/x_1^s}{x_2^b/x_1^b} \tag{8}$$

for the sorption equilibrium and

$$\alpha_{21}^{g\ell} = \frac{y_2/y_1}{x_2/x_1} \tag{9}$$

for the vapour–liquid equilibrium (x_i and y_i are the molar fractions of the component i in the liquid and vapour phases, respectively).

2.5. The composition of the swollen polymer

The composition of the ternary phase, i.e., swollen polymer, is expressed in weight fractions, because the molar mass of the polymer is not known. The weight fraction of polymer (component 3) in the ternary system (superscript ter) is given by the equilibrium swelling degree as

$$w_3^{ter} = \frac{1}{1 + Q} \tag{10}$$

and weight fractions of components 1 and 2 are calculated from the individual sorptions:

$$w_1^{ter} = \frac{n_1^s \cdot M_1}{1 + Q} \tag{11}$$