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Determination of water/polymer interaction parameter for membrane-forming systems by sorption measurement and a fitting technique

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Abstract

The water/polymer interaction parameter plays an important role in the thermodynamic description of membrane-forming water/solvent/polymer solutions with the Flory-Huggins (FH) model. In order to discuss reasons for the wide variety of values for this parameter reported in the literature, interaction parameter was determined utilizing two different methods for polysulfone, poly(ether sulfone), cellulose acetate and poly(ether imide) (PSU, PES, CA, and PEI). In a "direct" determination, water sorption isotherms have been measured and analyzed with the FH model. In a second, "indirect", method an optimal parameter value was found by fitting experimental cloud point data of ternary polymer systems with the FH model. Liquid–liquid equilibrium (LLE) calculations have been carried out under the assumption that the water/solvent and solvent/polymer interactions are correctly described by known composition dependent interaction parameters. For a given polymer, the water/polymer interaction parameters resulting from fits of ternary systems with different solvents agree well. But the obtained values are smaller than the ones resulting from the sorption experiment. The difference is smaller for a more hydrophilic polymer with a higher water uptake than for hydrophobic polymers with a lower uptake. Reasons for this difference will be discussed.

Keywords: Membrane preparation; Thermodynamics; Nonsolvent-induced phase separation; Water sorption; Water/polymer interaction parameter

1. Introduction

Since several decades the immersion precipitation process has been employed to prepare asymmetric membranes [1–8]. In this process, a moderately concentrated solution of polymer (10–30 wt.%) is immersed into a nonsolvent bath, e.g. water. Then immediately a liquid–liquid phase separation takes place. The diffusive exchange of nonsolvent and solvent through the resulting interface leads to changes in the composition, and the polymer solution may become instable. Subsequently liquid–liquid demixing may start, and a polymer-rich and a polymer-poor phase may be formed. The specific thermodynamic situation and the kinetic progress of this liquid–liquid demixing process determine the final morphology of a specific polymer membrane [9–12].

For the thermodynamic analysis of the phase behavior in a ternary nonsolvent(1)/solvent(2)/polymer(3) system, often Tompa's extension [13] of the classical FH model is used. The Gibbs free energy of mixing ΔG in a ternary system can be formulated as

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12}(u_2) n_1 \phi_2 + \chi_{23}(\phi_3) n_2 \phi_3 + \chi_{13} n_1 \phi_3 \quad (1)$$

Abbreviations: PSU, polysulfone; PEI, poly(ether imide); PES, poly (ether sulfone); CA, cellulose acetate

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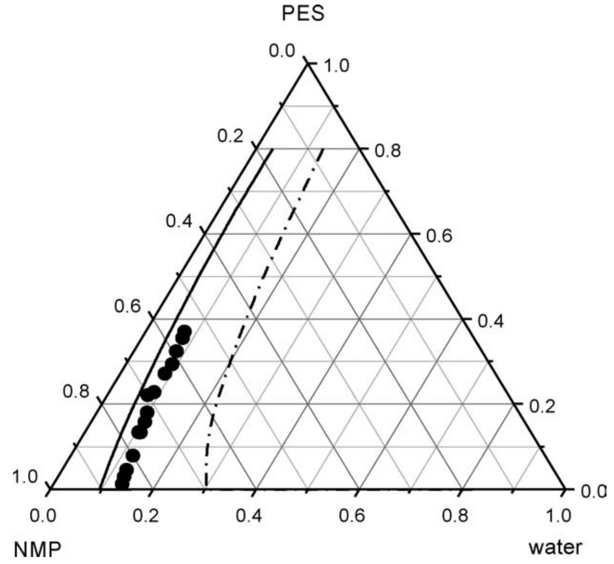

Fig. 1. Comparison of calculated binodal curves obtained by different water/polymer interaction parameters reported in the literature (cloud points (●). (- - -) $\chi_{13} = 2.7$ [12], (—) $\chi_{13} = 1.5$ [14] (for other parameters see Table 3).

where R is the gas constant; T, the absolute temperature, n_i and ϕ_i are the number of moles and the volume fraction of component i, respectively. $\chi_{12}(u_2)$ is a generalized nonsolvent(1)/solvent(2) interaction function depending on the volume fraction $u_2 = \phi_2/(\phi_1 + \phi_2)$ of a pseudo binary mixture. Also the parameter for the solvent(2)/polymer(3) interaction, $\chi_{23}(\phi_3)$, is assumed as a concentration dependent interaction function. In contrast, χ_{13}, the parameter for the nonsolvent(1)/polymer(3) interaction, is often considered to be a constant. Based on Eq. (1), the phase diagram of the ternary system can be calculated provided that the (partly concentration dependent) parameters χ_{12}, χ_{23} and χ_{13} are known.

The literature shows that especially the nonsolvent/polymer interaction parameter χ_{13} is difficult to determine. This is problematic because χ_{13} has a considerable effect on the size and the location of the miscibility gap in a ternary phase diagram. An example for this problem is presented in Fig. 1 for the ternary system water(1)/NMP(2)/PES(3).

Fig. 1 shows calculated binodal curves, obtained for two different χ_{13} values for the water/PES interaction parameter. The interaction parameters were obtained from different experiments. The smaller value, $\chi_{13} = 1.5$, was determined by light scattering and viscosity measurements of the ternary system at low polymer concentrations [14,15]. The higher value $\chi_{13} = 2.70$ resulted from swelling measurements [12] at a high polymer concentration. Both predicted binodal curves deviate considerably from the experimental cloud points. Obviously the optimum χ_{13} accurately describing the experimental data should be somewhere between the two values mentioned above (see below). It should be mentioned that the two other interaction parameters χ_{12} and χ_{23}, necessary for the phase equilibrium calculations, do not reveal any considerable deviation in different reference sources.

The main objective of our study is to determine the water/polymer interaction parameter χ_{13} for several membrane forming polymers with two methods on the basis of the FH model. First we have measured sorption isotherms of water for four polymers. These measurements are, in principal, identical with the common swelling experiments, but they provide a set of data which are a function of the partial vapor pressure and therefore of the volume fraction of water. They are also not affected by inaccuracies of the swelling experiment with respect to adhered water on the polymer sample. An application of the FH model to this binary system should give direct access to the water/polymer interaction parameter. As a second (indirect) method, 'optimal' χ_{13} values were determined from ternary systems by best-fit representation of sets of experimental cloud points. To predict the optimal value, phase equilibrium calculations have been performed where only χ_{13} was varied while the other two interaction parameter functions, χ_{12} and χ_{23}, have been assumed as constant. The comparison of χ_{13} values obtained from water sorption experiments and from the ternary LLE fits often show a considerable disagreement. Reasons for this discrepancy will be discussed below.

2. Experimental

2.1. Materials

The four polymers used for the sorption measurements are common materials for membrane formation: PEI (type Ultem® 1000, General Electric, USA), PSU (type Ultrason®S3010, BASF, Germany), PES (type Ultrason®E6020, BASF, Germany), and CA (39.8 wt.% acetyl content, Sigma-Aldrich, Germany). The samples were dried before use in an oven for 4 h at 100 °C. Characteristic data of the polymers are listed in Table 1.

2.2. Preparation of polymer films for sorption measurements

The polymer samples were dissolved in dichloromethane (except CA: solved in acetone) at room temperature under

Table 1
Characteristic data of the polymers used in sorption experiments

Materials	Specific volume (cm^3/mol)	Molecular weight (g/mol)	Density (g/cm^3)
PSU	31,000	39,000[a] [12]	1.24 [12]
PEI	25,000	32,800[a] [16]	
	14,000	18,000[b] [17]	1.287 [18]
PES	36,000	49,000[a] [12]	1.37 [12]
CA	23,000	30,000[c]	1.31 [19]

[a] Weight molecular weight.
[b] Number molecular weight.
[c] Data of supplier.