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Use of inverse gas chromatography to account for the pervaporation performance in the microemulsion breakdown[☆]

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Abstract

Mass transfer phenomenon that occurs in the pervaporation process when applied to the microemulsion breakdown, was confirmed by the results of inverse gas chromatography. The stationary phase for this study was polydimethylsiloxane (PDMS), a hydrophobic polymer employed as a membrane in the pervaporation technique. The retention times of the different molecule probes (toluene, cyclohexane, and *n*-butanol) gave an insight into the extent of the interactions between each of these molecules and the stationary phase; these molecules were the components of the two microemulsions in study. The infinite dilution conditions allowed to determine the thermodynamic and the chromatographic parameters γ^{∞} (the infinite dilution activity coefficient), the Flory-Huggins parameter interactions χ_{12}^{∞}, and V_g^0 (the specific retention volume), respectively. The magnitudes of the latter parameters threw some light on the permselectivity of the membrane in the pervaporation operation.

Keywords: Inverse gas chromatography; Interaction parameters; Pervaporation; Microemulsion; PDMS membrane

1. Introduction

Pervaporation has been vastly recognized as an energy-saving process to separate organic components from aqueous or organic mixtures [1,2]. In this line, the recovery of organic compounds from wastewater has gained a special attention [3]. Lately, we applied this technique to break down a microemulsion, a highly ordered system [4–6], to monitor the oxidation of primary alcohols [7], and to separate azeotropic mixtures [8]. Its use to control some equilibrated organic reactions was claimed [9]. In the pervaporation operation, as depicted in Fig. 1, the feed mixture is maintained in contact with the upstream side of a dense membrane and the permeate (or the pervaporate) is continuously removed from the downstream side of the membrane in vapor state by a vacuum pump. The used membrane would alter the vapor–liquid equilibrium (VLE).

As unanimously believed, the membrane remains indubitably the basic key component for the pervaporation performance. Of the aspects of the membrane integrity, the chemical nature in terms of organic functional groups within the backbone or as pendent moieties, hence hydrophobicity and hydrophilicity and in-between, determines its effectiveness in the pervaporation process; for example, the polyvinylalcohol membranes are more hydrophilic due to the hydroxyl groups (OH) present in the polymer structure. The design of a separative membrane destined to the pervaporation process includes: slightly crosslinked polymers, polymer blends, interpenetrating networks, and best of all chemically modified polymers. The latter ones were conveniently made to increase either the hydrophobicity or the hydrophilicity with regard to the aim at applying

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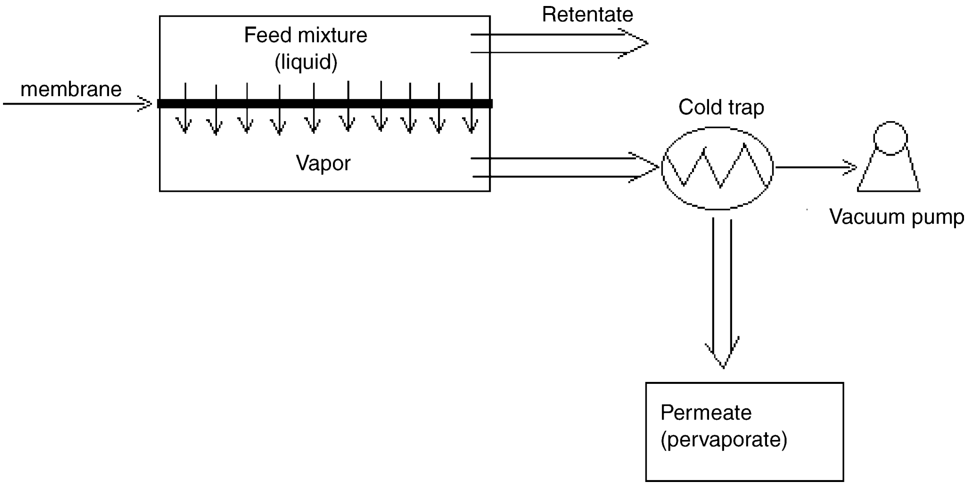

Fig. 1. Basic principles of the pervaporation technique.

the pervaporation. The existing or deliberately introduced functional groups within the membrane will selectively interact with the molecules to be separated.

In the goal of providing a better understanding of the pervaporation performance when operating for the microemulsion breakdown, the extents of the infinite dilution activity coefficient γ^{∞} and the interaction parameters of Flory-Huggins, χ_{12}^{∞}, were thought to give a better insight. To measure these interaction parameters, the inverse gas chromatography (IGC) was employed because it is a reliable tool for quantifying the extent of interactions. According to the value of the interaction parameter, one can select among others the appropriate membrane for a pervaporation work. One of the many uses of inverse gas chromatography is its application in polymers-related phenomena. In fact, it has been applied to determine the solubility parameters of polymers and oligomers [10,11], the diffusion coefficients in crosslinked polymers [12], the polymer–polymer interaction parameters [13], and the characterization of conducting polymers [14,15].

In our previous work [4–6], polydimethylsiloxane (PDMS) was evaluated as a membrane in the pervaporation for the microemulsion breakdown. For a matter of a better understanding of the results obtained in the pervaporation, PDMS was examined as a sorbent (or solvent) in the inverse gas chromatography study. The molecule probes were toluene, cyclohexane, and *n*-butanol, which were the ingredients of the microemulsions to be collapsed by pervaporation technique. Therefore, the dilution activity coefficient γ^{∞}, the interaction parameters χ_{12}^{∞} and the thermodynamic factors were experimentally determined by IGC. The results were discussed in light of those of the PDMS swelling and the pervaporation parameters, the total flux and the enrichment factor. In the pervaporation process, the permselectivity is linked to the extent of the interactions of the permeating species with the pervaporative membrane. Such interactions may be indirectly quantified via the magnitudes of the infinite dilution activity coefficients of the sorbates vis-à-vis to the sorbent (the membrane). Yet, the values are but indicative as the IGC does not really reconstitute the pervaporation process because, in this process, the molecules (probes) are in liquid form in contact with the membrane, but, they are in gas phase in IGC. The PDMS used as a solvent in IGC is in rubbery form ($T_g = -123\,^{\circ}$C). Also, the thermodynamic parameters, ΔH_a and ΔG_a, provided by IGC study would give an insight into the pervaporation performance as the absorption of the molecules in study by the PDMS membrane is an important step. Indeed, the composition of the pervaporate depends mostly on the absorption extents of the different components in the feed.

2. Experimental

2.1. Chemicals

Rhodorsil (PDMS/crosslinking agent system, 2% by weight of crosslinking agent) was provided by Rhodia (ex-Rhône-Poulenc). Toluene, cyclohexane, *n*-butanol were supplied by Prolabo, Fluka, and Aldrich, respectively, and were 99% purity (no further purification was done). Water was bidistilled before use. Sodium dodecylsulfate (SDS) was provided from Prolabo and purified by recrystallization from absolute ethanol.

2.2. Pervaporation technique

2.2.1. Apparatus

The pervaporation apparatus used in this work was previously described [8]. It is comprised of the following parts: a stainless steel pervaporation cell (capacity of 125 cm^3); a pervaporation pyrex-made receiving set fitted with vapor traps; a primary vacuum pump (10^{-1} mmHg), Trivac type.

2.2.2. Membrane preparation

A suitable amount of Rhodorsil was spread evenly over a clean teflon-plate surface by means of an appropriate