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Review

Ionic liquids in separations of azeotropic systems – A review

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ABSTRACT

Efforts to make existing separation methods more efficient and eco-friendly may get a boost from the use of a relatively new class of compounds known as ionic liquids (ILs). The separation of azeotropic mixtures has conventionally been one of the most challenging tasks in industrial processes due to the fact that their separation by simple distillation is basically impossible.

This paper provides a critical review of methods using ILs as azeotrope breakers. Three separation processes were addressed: liquid–liquid extraction, extractive distillation, and supported liquid membranes. We examine the azeotrope breaking potential of ILs and compare their performance to that of conventional solvents. A systematic analysis of the influence of the structure of ILs on their azeotrope breaking capacity contributes to the establishment of guidelines for selecting the most suitable ILs for the separation of specific azeotropic mixtures.

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List of symbols

T	temperature
P	pressure
az	azeotrope
IL, ILs	ionic liquid, ionic liquids
LLE	(liquid + liquid) equilibria
VLE	(vapor + liquid) equilibria
$\alpha_{ij}^{\mathrm{VLE}}$	relative volatility (component i/component j) from (vapor + liquid) equilibria data
y_i, y_j	mole fraction of the component i or j in the vapor phase
x_i, x_j	mole fraction of the component i or j in the liquid phase (for VLE data the mole fraction is ionic liquid free basis)
$S_{\mathrm{IL}}^{\mathrm{VLE}}$	selectivity from (vapor + liquid) equilibria data
$\alpha_{ij}^{\text{with IL}}$	relative volatility from VLE data using as entrainer ionic liquid
$\alpha_{ij}^{\text{without IL}}$	relative volatility from VLE data without ionic liquid (azeotrope)
β^{LLE}	distribution coefficient from (liquid + liquid) equilibria data
$x_{\mathrm{Solute}}^{\text{IL Phase}}$	mole fraction of the solute in ionic liquid phase (LLE data)
$x_{\mathrm{Solute}}^{\text{Organic Phase}}$	mole fraction of the solute in organic phase (LLE data)
S^{LLE}	selectivity from (liquid + liquid) equilibria data
$x_{\mathrm{Inert}}^{\text{IL Phase}}$	mole fraction of the inert in ionic liquid phase (LLE data)
$x_{\mathrm{Inert}}^{\text{Organic Phase}}$	mole fraction of the inert in organic phase (LLE data)
E^{LLE}	extraction efficiency from (liquid + liquid) equilibria data
$C_{\mathrm{Solute}}^{\text{IL Phase}}$	concentration of solute in ionic liquid phase (LLE data)
$V_{\mathrm{Solute}}^{\text{IL Phase}}$	volume of solute in ionic liquid phase (LLE data)
$C_{\mathrm{Solute}}^{\mathrm{Mix}}$	concentration of solute in the initial azeotropic mixture (LLE data)
$V_{\mathrm{Solute}}^{\mathrm{Mix}}$	volume of solute in the initial azeotropic mixture (LLE data)
E^{EP}	extraction efficiency from extraction process data
$w_{\mathrm{Inert}}^{\mathrm{Feed}}$	mass fraction of the inert in feed stream (extraction process data)
$w_{\mathrm{Inert}}^{\mathrm{Raffinate}}$	mass fraction of the inert in raffinate stream (extraction process data)
$w_{\mathrm{Inert}}^{\mathrm{Equilibrium}}$	mass fraction of the inert in one equilibrium stage (theoretical data)
SLMs, SILMs	supported liquid membranes, supported ionic liquid membranes
S^{MEM}	selectivity from supported liquid membranes data
$Perm_{\mathrm{Solute}}$	permeability of the solute in supported liquid membranes
$Perm_{\mathrm{Inert}}$	permeability of the inert in supported liquid membranes
α^{MEM}	separation factor from supported liquid membranes data
$p_{\mathrm{Solute}}^{\mathrm{Permeate}}$	partial pressure of the solute in the permeate
$p_{\mathrm{Inert}}^{\mathrm{Permeate}}$	partial pressure of the inert in the permeate
$p_{\mathrm{Solute}}^{\mathrm{Feed}}$	partial pressure of the solute in the feed
$p_{\mathrm{Inert}}^{\mathrm{Feed}}$	partial pressure of the inert in the feed
w, wt	mass fraction
THF	tetrahydrofuran
t	ton
€	euro
h	hour
mol	mole
n	alkyl chain length
ETBE	ethyl tert-butyl ether
C_6, C_7	hexane, heptane

1. Introduction

1.1. Azeotropes

Increasing concern about environmental issues, as well as the establishment of new regulations, has recently directed the attention of the scientific community to novel processes based on greener technologies. In many areas of industry, solvent mixtures accumulate due to recycling difficulties. The separation of these mixtures into their pure components is necessary so that they can be reused. However, most of these solvent mixtures contain azeotropes and, thus, their separation by simple distillation becomes impossible. Azeotropes are involved in common chemical processes including the production of methyl acetate, terahydrofuran, ter-methyl amyl ether, isopropanol, and vinyl acetate. Additionally, due to their growing popularity, biofuel processes typically produce fermented products that form azeotropes with water which is abundant in the fermentator. Among those products, ethanol is the most important example, due to its excellent properties as alternative fuel. However, compounds such as butanol also form aqueous azeotropic mixtures.

Several potential processes for separating azeotropes have come to light such as azeotropic distillation, extractive distillation, pressure swing distillation, liquid–liquid extraction, adsorption, membranes. Extractive distillation is the most common process for removing one of the components in the azeotropic system. Its greatest constraint is the tremendous energy costs required to achieve a fluid phase system. Therefore, liquid–liquid separation,