

Abstract

The nascent field of biofuels derived from renewable lignocellulosic resources offers a promising solution to the finite supply of fossil fuels and the ensuing climatic, economic and political challenges. However, aspirations of large scale and scalable biorefining of bio-butanol from multicomponent Acetone-Butanol-Ethanol (ABE) fermentation broths through organophilic pervaporation are still challenged, in part, by a limited knowledge on the effect of by-products ethanol and acetone on final recovery. This study, therefore, involves experimental investigations on multicomponent permeation in pervaporation followed by the modeling and quantification of the impact of coupling phenomena on the selective transport of butanol via a diverse portfolio of semi-empirical, statistical, and theoretical frameworks. Equilibrium sorption, pure and mixture permeation experiments were conducted using a commercial polydimethylsiloxane (PDMS) membrane (PERVAP-4060) with individual solvent content ≤ 6 wt.% over a temperature range of 303.15–323.15 K, relevant to fermentation processes.

Initially, modified solution-diffusion models are customized to emulate temperature and concentration dependence of permeation in binary and ternary feed mixtures. After initial screening of thermodynamic models and simulation of activity coefficients and volume fractions, a rationally designed experimental and statistically validated empirical investigation of sorption characteristics and the influence of coupling on fluxes in quaternary ABE mixtures using sorption and flux isotherms followed. Finally, Maxwell-Stefan (MS) diffusion formulations, combined with the UNIQUAC thermodynamic model, are extended to multicomponent ABE feed solutions to resolve coupling into its thermodynamic and kinetic (diffusive) constituents. A generalized and explicit analytical derivation for calculation of thermodynamic correction factors by UNIQUAC model is proposed, allowing estimation for any number of permeants.

The membrane is observed to be most intrinsically selective towards butanol in all systems and compositions. However, coupling effects were observed to limit permeation, especially at higher solvent concentrations. Analysis of phenomenological parameters reveal that while the additional plasticization by other penetrants benefits butanol permeation, their presence also induced a reduction in the free volume expansion by butanol itself. Furthermore, though sorption isotherms reveal that butanol volume fractions in the membrane remain unaffected by feed composition, flux isotherms also reaffirm that the positive coupling due to additional plasticization decreases at higher solvent concentrations, suggesting other physical associations or cluster formation between penetrants to be the causative factor. Subsequently, a detailed hit-and-trial based strategy is implemented to evaluate the relevance of membrane plasticization, cluster formation and interspecies frictional interactions on effective diffusivities. The optimal model fit is found to be insensitive to variation in MS cross-diffusivities, affirming the trivial contribution of correlation effects between penetrants, provided the expressions for

self-diffusivities are adequately tailored for membrane plasticization and clustering. Notably, while only butanol clustering suffices for binary mixtures, additional aggregates involving butanol-water, water-water, and butanol-acetone/ethanol are suggested to play a crucial role in steering diffusivities in ternary solutions.

Overall, by a careful manipulation of solvent ratios – for instance at lower butanol to second component ratios in feed; multicomponent coupling effects were demonstrated to significantly enhance butanol permeances through the polymeric membranes, achieving nearly twice the values observed in binary systems. In contrast, minimal coupling is experienced at equimolar conditions, allowing multicomponent pervaporation to be satisfactorily modeled as binary separation in such limiting cases. Additionally, the modelling of quaternary ABE fermentation solutions was also simplified to ternary mixtures by showing that mutual interactions between acetone and ethanol have minimal impact on butanol transport utilizing Response Surface Methodology based statistical analysis. Furthermore, a deeper understanding of the physico-chemical origins of coupling effects was achieved, particularly the synergy between membrane plasticization and kinetic coupling mechanisms. These insights can guide the development of superior energy-efficient membrane materials with improved diffusivity and sorption selectivities by optimizing the free-volume-diffusivity paradigms for enhanced targeted recovery from complex industrial feed mixtures.