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Predicting the Vapor–Liquid Equilibria Phase Envelope for Nonideal Mixtures of Cyclopentanol and Cyclopentyl Methyl Ether

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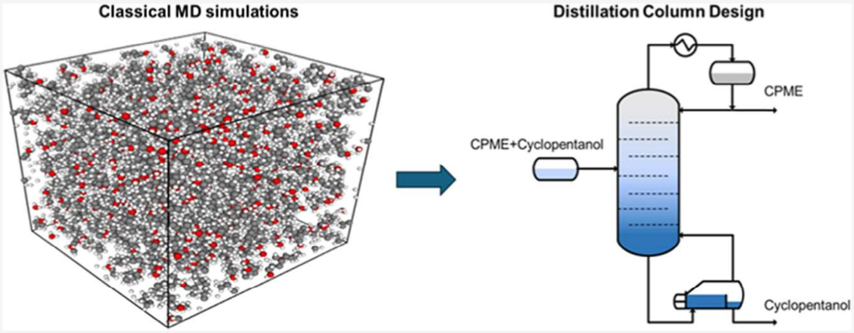

ABSTRACT: Cyclopentyl methyl ether (CPME) is an underexplored green alternative to commonly used, relatively toxic, and highly volatile organic content containing ethereal solvents. Traditional CPME synthesis requires energy-intensive azeotropic distillation. Optimizing a distillation column requires sets of rigorous experiments to generate a reliable vapor–liquid equilibria (VLE) data set. Albeit Grand Canonical Monte Carlo calculations remain a hallmark method to calculate VLE, its computational cost for nonideal binary mixtures is significant. We present a less-demanding approach using classical molecular dynamics simulations with the two-fluid theory and nonrandom two-liquid local composition model to derive the VLE profile of CPME and cyclopentanol. These VLE profiles are found to be in good qualitative agreement with the experiments. Shorter time scale (10 ns), small system size (121 molecules), affordable computational cost (~500 CPU hours), and qualitative consistency with experiments highlight its applicability. Additionally, simulations reveal a strong hydrogen bond (H-bond) between cyclopentanol–cyclopentanol and CPME–cyclopentanol (vs the absence of an H-bond between CPME–CPME) as a possible reason for the lower volatility of cyclopentanol-rich mixtures. The applicability of the simulated VLE profile is finally demonstrated in generating a preliminary design for a distillation column using the McCabe-Thiele approach, along with necessary precautions near the azeotropic point.

■ INTRODUCTION

Cyclopentyl methyl ether (CPME) has recently gained significant traction as a green solvent and extraction media alternative to widely used ethereal solvents for organic syntheses, as it is environmentally benign and hydrophobic, and has low volatile organic content, reduced susceptibility to peroxide formation, and increased pH stability under both acidic and basic conditions.[1,2] These properties have popularized its use in a wide range of synthetic chemical transformations for C–C bond formation using Grignard reagents and other organolithium-driven reactions.[3,4] CPME is remarkably stable under reactive conditions involving Lewis acids like Beckmann rearrangement and Brønsted bases as compared against conventional cyclic ethers like tetrahydrofuran (THF) that are susceptible to ring opening.[4] Further, peroxide formation is significantly suppressed with CPME, requiring one-fifth the amount of peroxide inhibitor (butylated hydroxy toluene ~ 50 ppm) vis-à-vis conventionally used THF and Me-THF.[5] CPME is additionally resistant to H abstraction and associated degradation pathways by commonly used initiators like azobis(isobutyronitrile) (AIBN), making it a versatile solvent for radical addition chemistries.[5]

The industrial scale synthesis of CPME involves the methylation of cyclopentanol in the presence of dimethyl sulfate/zeolites or by methanol addition across the double bond of cyclopentene under acidic conditions.[2] The reaction mixture containing CPME–cyclopentanol–H_2SO_4 is purified through aqueous extraction of sulfuric acid, while cyclopentanol–CPME is retained in the organic phase. Attaining critically pure CPME from a CPME–cyclopentanol mixture poses a significant challenge due to their similar polarity and closely spaced boiling points ($T_{b(CPME)}$: ~379 K, $T_{b(cyclopentanol)}$:

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