



Separation of methyl acetate + methanol azeotropic mixture using ionic liquid entrainers



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HIGHLIGHTS

- Capability of two ILs to break the methyl acetate–methanol azeotrope was examined.
- VLE in the methyl acetate + methanol + IL systems was determined.
- New convenient headspace GC methodology was employed.
- Using binary data only, NRTL predicts well the effect of ILs on separation factor.
- [BMPYR][DCA] and [EMIM][SCN] as entrainers outperform other ILs previously tested.

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ABSTRACT

Two ionic liquids (ILs), namely 1-butyl-1-methylpyrrolidinium dicyanamide [BMPYR][DCA] and 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN], were studied as agents for the separation of the methyl acetate + methanol azeotropic mixture by extractive distillation. Isothermal vapor–liquid equilibria of the ternary systems with the ILs and all the constituting binary subsystems were measured by headspace gas chromatography (HSGC) to examine the effect of the IL additives on the separation factor. Two HSGC methods were combined to this end: one employing a commercial headspace autosampler and the other employing our own setup with external equilibrium cell and forced circulation of the vapor phase through the GC sampling loop. The HSGC methodology developed herein presents distinct advantages compared to conventional dynamic measurements using recirculation stills. The measurements were conducted at 327.31 K, a temperature close to the normal boiling point of the methyl acetate + methanol azeotropic mixture, and at various compositions covering well the composition ranges of involved binaries and ternaries, particularly at compositions keeping constant IL contents. The ample experimental data allowed us to test the performance of several activity coefficient models and data treatment strategies. Using binary information only and the NRTL model gave fairly accurate predictions of the effect of ILs on separation factors. We found that both [BMPYR][DCA] and [EMIM][SCN] increase considerably the methyl acetate/methanol separation factor, breaking the azeotropic behavior at rather low levels of IL mole fractions (>0.043 and 0.087, respectively). As potential entrainers to separate methyl acetate from methanol by extractive distillation, [BMPYR][DCA] and [EMIM][SCN] outperform other ILs previously tested for this purpose in the literature.

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1. Introduction

The azeotropic mixture of methyl acetate and methanol is formed in some industrially important manufacturing processes, as the production of methyl acetate or poly(vinylalcohol), and presents a difficult separation problem. Various strategies proposed to overcome it involve extractive [1] and azeotropic [2] distillations,

reactive distillation [3], selective adsorption [4], and use of membranes [5]. The extractive distillation using as extractive agents to break the azeotropic behavior higher boiling organic solvents [6–8], salts [9,10], and most recently ionic liquids [11–13] appears to be the most popular and straightforward technology.

The use of ionic liquids (ILs) as entrainers in extractive distillation was first reported by Arlt et al. [14,15]. These substances composed of organic cations and anions with low melting points combine complementarily some characters of organic solvents and inorganic salts which leads to their favorable technological and environmental properties as broad liquid and thermal stability temperature ranges, negligible vapor pressure, and excellent

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solventy for a variety of materials that can be controlled by almost countless structure variations of composing ions. ILs can be thus tailored for a concrete application case to obtain their best performance, in particular high separation selectivity and capacity, low viscosity, low heat capacity, etc. The general advantage of IL entrainers consists of the fact that they can be introduced on the highest stage of the distillation column without contaminating the overhead product and completely recovered from the bottoms product by a simple evaporation or stripping of the volatile component.

As concerns the methyl acetate + methanol system, three ILs have been examined as possible entrainers so far, namely 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][OTF] [11], 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] [12], and 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF₆] [13]. All were found to be capable of breaking the azeotropic behavior of methyl acetate + methanol mixture and providing its separation. Nevertheless, neither of these IL entrainers appears to provide optimal performance that would qualify it for a real industrial application: these ILs are either too viscous ([OMIM][PF₆], [EMIM][Ac]) which would excessively increase power requirements for their pumping and limit heat and mass transfer rates, or contain fluorine ([OMIM][PF₆] and [EMIM][OTF]) which would imply corrosion and environmental risks. Inspecting the current portfolio of commercially available ILs, it turns out that other IL structures might yield more convenient properties including the separation selectivity itself.

For the present study we selected two halogen-free ILs, 1-butyl-1-methylpyrrolidinium dicyanamide [BMPYR][DCA] and 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] the chemical structures of which are shown in Fig. 1.

These ILs exhibit low viscosities (34 mPa s [16] and 22 mPa s [17], respectively, at 298.15 K) and due to their low molecular masses (208.31 g mol⁻¹ and 169.25 g mol⁻¹, respectively) their heat capacities should be also relatively low (439 J K⁻¹ mol⁻¹ and 259 J K⁻¹ mol⁻¹, respectively, at 298.15 K, as estimated by method of Farahani et al. [18]). As indicated by previous measurements of infinite dilution activity coefficients of ours [19] for [BMPYR][DCA] and Domanska and Marciniak [20] for [EMIM][SCN], these ILs show a very strong affinity to methanol, while their interactions with aliphatic hydrocarbons are quite unfavorable, which forms the basis for their separation selectivity. The selectivities of the present ILs for methyl acetate/methanol separation are expected to be high and exceed those for the ILs studied in the literature, which can be inferred from their infinite dilution values β_{12}^{∞} (323.15 K) obtained either from direct measurements of limiting activity coefficients ([BMPYR][DCA]: $\beta_{12}^{\infty} = 4.45$) [19] or estimated by the ion-specific Abraham solvation model [21] ([EMIM][SCN]: $\beta_{12}^{\infty} = 6.7$, [EMIM][OTF]: $\beta_{12}^{\infty} = 1.4$, [OMIM][PF₆]: $\beta_{21}^{\infty} = 1/\beta_{12}^{\infty} = 1.9$).

In this work, isothermal vapor–liquid equilibria for two ternary systems methyl acetate(1) + methanol(2) + IL(3) (IL = [BMPYR][DCA] or [EMIM][SCN]) and the five constituting binary subsystems are measured and the effects of ILs on the methyl acetate/methanol separation factor determined. For the VLE measurements we implemented two new static headspace gas chromatography (HSGC) techniques avoiding the need of explicit GC calibration and offering further advantages compared to the dynamic boiling technique using conventional recirculation stills employed by previous authors.

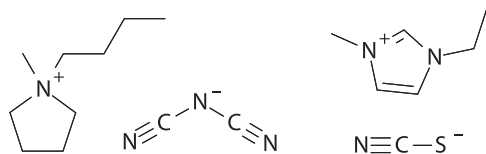


Fig. 1. Chemical structure of the ionic liquids investigated.

2. Theoretical background

2.1. Essential concepts

Two indicative quantities, the separation factor (or relative volatility) α_{12} and the selectivity β_{12} , are conveniently used to describe the separation effect of extractive solvents on binary azeotropic behavior. The relative volatility of component 1 respect to component 2 is defined as

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} \quad (1)$$

where y_1 (y_2) and x_1 (x_2) are the equilibrium mole fractions in vapor and liquid phase of the more volatile (less volatile) component, respectively. Thus, in the vapor–liquid partitioning of the components, the higher the value α_{12} , the more effective the separation, while when $\alpha_{12} = 1$ no separation of components occurs. On considering the condition of vapor–liquid equilibrium

$$\varepsilon_i y_i p = \gamma_i x_i p_i^s \quad (2)$$

α_{12} can be expressed as follows

$$\alpha_{12} = \frac{\gamma_1 p_1^s \varepsilon_2}{\gamma_2 p_2^s \varepsilon_1} \quad (3)$$

where p is the total pressure, γ_i are activity coefficients of respective components in the liquid mixture, p_i^s their pure liquid saturated vapor pressures, and ε_i combined vapor phase nonideality and Poynting corrections.

The selectivity β_{12} is defined as a ratio of the activity coefficient of the more volatile component and that of the less volatile component in the mixture with a separation agent (component 3)

$$\beta_{12} = \frac{\gamma_1}{\gamma_2} \quad (4)$$

The separation factor is proportional to the selectivity and the higher the value of β_{12} in a given solvent, the more effective this solvent in achieving the separation. Obviously, β_{12} alone is not an indicator of the VLE separability of the components, but merely rates relatively the power of solvents to achieve it. Since β_{12} typically increases with the content of the solvent, just the infinite dilution values β_{12}^{∞} are used for such ratings.

2.2. Headspace gas chromatography using an autosampler (HSGC-AS)

Consider a standard vial for use with commercial HSGC autosamplers which is partially filled with a binary liquid mixture of volatile organic compounds (VOCs) 1 and 2 and equilibrated with the vapor phase which contains besides the VOCs also nitrogen as a HSGC working gas. The headspace analysis is generally based on the determination of chromatographic responses (peak areas) A_1 and A_2 corresponding proportionally to the equilibrium contents (mole fractions) y_i of volatile components in the vapor phase

$$A_i = k_i y_i \quad (5)$$

By taking the ratio of responses

$$\frac{A_1}{A_2} = \frac{k_1 y_1}{k_2 y_2} = k_{12} \frac{y_1}{y_2} \quad (6)$$

we can define the response coefficient $k_{12} = k_1/k_2$ the knowledge of which is sufficient to obtain from measured A_1 and A_2 the binary vapor-phase composition. Obviously, a calibration measurement, e.g. via the total vaporization technique (TVT) [22], is needed to determine k_{12} . In this work we however employ a convenient alternative procedure avoiding additional calibration measurements. For the purpose we take advantage of the fact that the liquid phase

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