



Separation of ethyl acetate and ethanol azeotrope mixture using dialkylphosphates-based ionic liquids as entrainers



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ABSTRACT

Isobaric vapor-liquid equilibrium (VLE) data for the ternary systems of ethyl acetate + ethanol + 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), ethyl acetate + ethanol + 1-butyl-3-methylimidazolium diethylphosphate ([BMIM][DEP]) and ethyl acetate + ethanol + 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]) were measured at 101.3 kPa. The results showed that all the three ionic liquids (ILs) produced remarkable salting-out effect, leading to the increase of the relative volatility of ethyl acetate to ethanol. Hence, the azeotropic point of ethyl acetate and ethanol could be eliminated with the addition of a certain content of ILs. The separation effect of the three ILs follows the order of [EMIM][DEP] > [BMIM][DEP] > [BMIM][DBP]. Then, the experimental VLE data were well correlated with the nonrandom two-liquid (NRTL) model. Finally, the σ -Profiles of solvents and ILs were used to analysis the micro-mechanism of the different separation performance of the three investigated ILs.

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1. Introduction

Ethyl acetate is an important solvent and widely used in the chemical industry. In recent years, the Fischer esterification reaction of acetic acid [1] and the ethanol dehydrogenation method [2] have been used to produce ethyl acetate. In those processes, the mixture of ethyl acetate and ethanol would inevitably at atmospheric pressure form a minimum azeotrope [3] which is impossibly separated by conventional distillation. Thus, some special separation technologies have been employed to separate the azeotrope, such as azeotropic distillation, pressure-swing distillation, reactive distillation, extractive distillation, liquid-liquid extraction, and membrane separation. Among them, extractive distillation is the most widely used process, in which a third component (entrainer) is added to enhance the initial relative volatility and to make the separation easier. Therefore, the key to extractive distillation is to select a highly effective entrainer [4–6].

During the past few years, ionic liquids (ILs) have become attractive options (alternatives) for entrainers in extractive

distillation due to their remarkable physicochemical properties [7–14]. The negligible vapor pressure and high thermal stability make it easy to recover and reuse after the separation process. Existing in liquid state over a wide temperature range allows them to pass through process equipments without clogging up pipes. Last but not the least, ILs can be “designed” by judicious combination of cation and anion, leading a specific and effective entrainer for a given azeotropic system. Obviously, ILs have the unique advantages over conventional organic solvents and inorganic salts.

In terms of the ethyl acetate and ethanol azeotropic system, many ILs have been used as entrainers to improve the separation effect of extractive distillation. Orchillés et al. [15] reported that 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][F₃CSO₃]) could eliminate the azeotropic point at 100 kPa when the mole fraction of ionic liquid in liquid phase was greater than 0.20. Qunsheng Li et al. [16–18] investigated the effects of three tetrafluoroborate-based ionic liquids, namely 1-ethyl-3-methylimidazolium tetrafluoroborate([EMIM][BF₄]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM][BF₄]), on the vapor-liquid phase equilibrium (VLE) behavior of ethyl acetate + ethanol at 101.32 kPa. It was found that all the three ILs produced a significant salting-out effect with the mole fraction of ionic liquid greater than 0.20. Rui Li et al. [19] measured the VLE

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data of ethyl acetate (1) + ethanol (2) + 1-ethyl-3-methylimidazolium acetate([EMIM][Ac]) (3) at 101.30 kPa, and found [EMIM][Ac] could break the azeotrope as its mole fraction in liquid phase was greater than 0.10. Yingjie Xu et al. [20] compared the influences of [BMIM][BF₄] and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF₄]) on the VLE behavior of the ethyl acetate (1) + ethanol (2) system. Andreatta et al. [21] studied the abilities of six ILs to break the ethanol + ethyl acetate azeotrope at 313.15 K, including 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][Tf₂N]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPYRR][Tf₂N]), 1-ethyl-3-methylimidazolium methanesulfonate ([EMIM][MeSO₃]), 1-ethyl-3-methylimidazolium methylsulfate ([EMIM][MeSO₄]), and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][CF₃SO₃]). And among those ILs, [EMIM][MeSO₃] and [EMIM][MeSO₄] exhibited the best performance for breaking the azeotrope with $x_3 = 0.025$ at 313.15 K.

As far as we know, the separation performance of ILs is strongly dependent on their structures, including the types of cations and anions, molecular size, side-chain length and so on. They determine the type and strength of the molecular interactions between ILs and solvents. Molecular interactions include electrostatic interaction, hydrogen bond and Van der Waals forces [22,23]. Among them, hydrogen bond is frequently employed to explain the different separation performance of ILs as entrainers in extractive distillation. In the previous work [24–28], the screening charge density profile (σ -profile) were applied to vividly analyze hydrogen bond interactions among different molecules in the mixtures of polar solvents, and the results were in good agreement with experimental data.

In this work, [EMIM][DEP], [BMIM][DEP] and [BMIM][DBP] were employed as entrainers to separate the ethyl acetate + ethanol azeotropic system. The VLE data of the ethyl acetate (1) + ethanol (2) + IL (3) ternary system were measured at 101.3 kPa. Then, the experimental data were correlated with the nonrandom two-liquid (NRTL) activity coefficient model [29]. Finally, the separation performance of the three ILs was discussed by means of the σ -profiles of solvents and ILs, which are able to identify the strength of the hydrogen bond interactions between solvents and ILs.

2. Experimental

2.1. Chemicals

Ethyl acetate and ethanol were supplied by Sinopharm Group CO. Ltd. The purities of all reagents were confirmed to be analytical grade by chromatography. The ILs [EMIM][DEP] and [BMIM][DBP] were synthesized in our laboratory according to the method mentioned literature [30]. The water mass fraction of ILs were determined by Karl Fischer titration and the mass fraction of ILs were measured by liquid chromatography. [BMIM][DEP] was provided by Yulu Chemical. The specifications of chemical samples used are given in Table 1 and the structures of the three ILs are shown in Fig. 1.

2.2. Apparatus and procedure

The isobaric VLE data were measured by an all-glass dynamic recirculating still which has been described in detail in a previous literature [31]. The still is mainly composed of six parts: a vapor liquid boiling chamber, a heating rod, a liquid phase sampling point, a spherical condenser, a thermometer and a vapor phase sampling point. The still has a total capacity of about 100 cm³. The system

pressure was controlled by a gas buffer connected with the still and measured by a manometer with a standard uncertainty of 0.1 kPa. At the beginning, the vapor-liquid boiling chamber was filled with a sufficient concentration of sample solution. The heating rod was used to heat the liquid to boil, the rough surface of which prevent the liquid from bumping. The vapor is separated from the liquid in the vapor-liquid chamber and condensed in the spherical condenser then refluxed into the vapor-liquid chamber for continuous circulation. The system temperature was measured using a standard and calibrated thermometer with a standard uncertainty of 0.05 K. The system reached equilibrium when the system temperature remained unchanged more than 30 min, then analysis samples can be taken from the liquid phase sampling point and the vapor phase sampling point.

All the solutions were gravimetrically prepared with a digital balance (ACCULAB ATL-224-1 China), and the standard uncertainty is 0.0001 g. For the binary system of ethyl acetate + ethanol, some ethanol was added to the pure ethyl acetate until a very diluted solution was obtained. For each ternary system, the mixture of ethyl acetate and scheduled mole fraction of IL was prepared, where the mixture of ethanol and the same mole fraction of IL was added, trying to keep a constant mole fraction of IL in each series. But for [EMIM][DEP] and [BMIM][DEP], they are not miscible with ethyl acetate at room temperature. Fortunately, adding a very small amount of ethanol could generate a one phase ternary system. So we must prepared the ternary solution of ethyl acetate + ethanol + IL firstly and then different quantities of the ethanol + IL mixture were added to keep constant the mole fraction of IL in each series.

In this experiment, the contents of ethyl acetate and ethanol in every gas and liquid samples were placed in headspace sampler (G1888 Network headspace sampler, Agilent Technologies) and then analyzed by the gas chromatography (Agilent GC7890A) with a thermal conductivity detector (TCD), DB-WAXETR capillary column (30 m × 0.32 mm, 1 μ m). The temperatures of column, injector and detector were 338 K, 473 K and 473 K, respectively. Since the ionic liquid has a nonvolatile property, the content of the ionic liquid in the solution was measured by weighing the mass of the liquid phase before and after dried in the vacuum desiccation at 393 K for 48 h. The standard uncertainty of ILs components in liquid phases was 0.001 in mole fraction.

In this work, a quantum chemical calculations based on density functional theory (DFT) was used to obtain the σ -Profiles of ethyl acetate, ethanol and the ions of ILs, the procedures were carried out as the following three steps [32–35]. The first step is to derive the optimized molecular geometry in the ideal gas phase with DFT to confirm the configuration in global energy minimum. For this purpose, every compound was optimized with the VWN-BP method at the version 4.0.0 DNP basis set by employing the DMol3 module implemented in the MS. The second step is to proceed “Energy task” for the geometry optimization output files to obtain the COSMO files, which contains the volume of the cavity, screening surfaces and number of surface segments, etc. In the final step, the σ -profiles was obtained by averaging the surface charge densities from input the COSMO files to the Fortran program “Sigma-average_v2.exe”.

3. Results and discussion

3.1. Experimental data

The binary vapor-liquid equilibrium data for ethyl acetate (1) + ethanol (2) were measured at 101.3 kPa and compared with the reported data [17,20] for the purpose of validating the accuracy of our apparatus and methods. The experimental data are listed in

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