Fluid Phase Equilibria 427 (2016) 90–96

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Isobaric vapor-liquid equilibrium for methanol + methyl ethyl ketone + bis(trifluoromethylsulfonyl)imide-based ionic liquids at 101.3 kPa

Zhuo Li [a], Qunsheng Li [a], Ruiqi Qiao [a], Kun Zhang [a], Xiaolin Song [b], Chunjiang Li [b], Hongjian Tang [b], Yudong Liu [c], *

[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China
[b] Xinjiang Tianye (Group) Co., Ltd., Shihezi, Xinjiang, 832000, China
[c] China Huanqiu Contracting & Engineering Corp., Beijing, 100012, China

A R T I C L E I N F O

Article history:
Received 11 May 2016
Received in revised form
27 June 2016
Accepted 28 June 2016
Available online 1 July 2016

Keywords:
Vapor-liquid equilibrium
Methanol
Methyl ethyl ketone
Ionic liquids
NRTL

A B S T R A C T

Isobaric vapor-liquid equilibrium data for the ternary systems of methanol + methyl ethyl ketone (MEK) + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf$_2$]) and methanol + MEK + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][NTf$_2$]) have been measured at 101.3 kPa using a modified Othmer still. The data obtained were correlated using NRTL model and fitted in well with it. The results showed that the addition of ionic liquids (ILs) into the azeotropic system caused a significant salting-in effect on MEK, thus increased the relative volatility of methanol to MEK and broke the azeotrope. And [HMIM][NTf$_2$] has a stronger effect than [BMIM][NTf$_2$]. The elimination of azeotropic phenomenon could be achieved when the mole fraction of ILs in the liquid phase was 0.05 (about 0.40 in mass fraction) or more. The effect of the ILs in this study was compared with that of some other ILs.

1. Introduction

Recently, ILs have grown in popularity as promising solvents in different fields of separation techniques [1]. In particular, ILs might be utilized as entrainers in extractive distillation for separating azeotropic or close-boiling mixtures, which was first suggested by Arlt et al. [2–4]. Compared with conventional organic solvents and solid salts applied in extractive distillation, ILs possess plenty of advantages determined by their unique physicochemical properties. ILs have almost all the attributes that a perfect entrainer requires, which means they have a relatively wide liquidus region, negligible vapor pressure, good thermal stability, less causticity and excellent solubility in both polar and nonpolar compounds [5–9], etc. Furthermore, the addition of ILs, generally of a small quantity, could remarkably alter the vapor-liquid equilibrium (VLE) of azeotropic systems even to break the azeotropic point, which has been verified experimentally in many literatures [10–23]. The VLE data containing ILs, to which many researchers are devoting nowadays, are essential for studying the separation ability of ILs as entrainers and selecting suitable ILs for a specific separation process.

Methanol and methyl ethyl ketone (MEK) are important solvents as well as raw materials for the synthesis of many compounds. Once mixed, for instance, in the industrial synthesis process of methyl isopropyl ketone and diethyl ketone [24], methanol and MEK will form a completely miscible azeotrope. Several methods have been proposed to separate them, including pressure swing distillation [25] and extraction using n-alkanes as entrainer [26]. As for extractive distillation for separation of methanol and MEK, Privott et al. [27] recommended diethyl ketone as the entrainer, and Li et al. [28] first investigated the feasibility of using IL as the entrainer. As a continuation of predecessors' work, this research is aimed at providing more alternative for entrainer.

In this paper, isobaric VLE data for the azeotropic system of methanol + MEK and the ternary systems containing [BMIM][NTf$_2$] and [HMIM][NTf$_2$] were measured at 101.3 kPa. The effects of the two ILs on the equilibrium behavior were also discussed. And a comparison of their separation ability was made with other ILs reported before.

---

* Corresponding author.
E-mail address: HQCydl@163.com (Y. Liu).

http://dx.doi.org/10.1016/j.fluid.2016.06.048
0378-3812/© 2016 Elsevier B.V. All rights reserved.

2. Experimental section

2.1. Materials

The chemicals used in this study included methanol, MEK, [BMIM][NTf_2] and [HMIM][NTf_2], as listed in Table 1. Methanol and MEK from Beijing Chemical Works, China, were analytical reagents with the mass fraction more than 99.5% checked by gas chromatography (GC). The ILs were provided by Shanghai Cheng Jie Chemical Co. LTD., China, with the mass fraction more than 99% checked by liquid chromatography (LC). The water concentration in methanol, MEK, [BMIM][NTf_2] and [HMIM][NTf_2], measured by Karl Fischer titration, were 250 ppm, 300 ppm, 500 ppm and 530 ppm, respectively. Prior to the experiment, the ILs were further purified with a rotary evaporator operated under a vacuum at 390 K for 24 h to remove volatile solvents. And they were also reused after experiment in exactly the same way. Methanol and MEK were used without further purification.

2.2. Apparatus and procedure

All the VLE data in this paper were measured by a modified Othmer still at a constant pressure (101.3 kPa). The equilibrium still is exquisite in structure and made out of quartz glass, in which stable equilibrium condition can be easily reached. More detail about the apparatus can be found in our previous publications [10,12].

Each sample in the experiment, about 60 mL, was gravimetrically prepared by an analytic balance (Satorius, Germany) with a standard uncertainty of 0.1 mg. The equilibrium temperature was measured using a mercury thermometer whose standard uncertainty was 0.1 K. The measurement of equilibrium content of methanol and MEK in the condensed vapor phase and liquid phase was carried out with GC. The GC (SP7800, China) contained a thermal conductivity detector (TCD) and a stainless steel packed column (Porapak-Q, 3 m × 3 mm). The carrier gas was high-purity hydrogen (99.999%) with a flow rate of 35 $cm^3\ min^{-1}$. The GC was operated in this condition: the injector and detector temperature at 413 K and oven temperature at 403 K. A calibration curve was obtained from a series of standard solutions so as to figure out the mole fraction of methanol and MEK in the samples. By this means the combined standard uncertainty in mole fraction of compositions could be estimated to be 0.002. The samples of liquid phase containing ILs were also injected into the GC directly. The ILs could not be vaporized in GC due to their nonvolatility, thus only the chromatographic peaks of methanol and MEK were observed. In this way, we figured out the mole fraction of methanol and MEK in liquid phase on an IL-free basis. In order to quantify the ILs in liquid phase, samples were dried in an oven for 10 h to remove the volatile components. The content of ILs in liquid phase could be obtained by measuring the mass difference of original samples and treated samples. The standard uncertainty in mole fraction of ILs was 0.001.

3. Result and discussion

3.1. Experimental data

The VLE data for the binary system of methanol (1) + MEK (2) were measured at 101.3 kPa and listed in Table 2, where T is the equilibrium temperature with a unit of K, x_1 and y_1 represent the mole fraction of methanol in the liquid and vapor phase, respectively. At the very beginning of the discussion, all the experimental data were tested and proved to be thermodynamically consistent. As illustrated in Fig. 1, the experimental data agreed well with those published by Privott et al. [27] and Li et al. [28]. Therefore, the experimental method and apparatus used in this study were reliable.

The VLE data for the ternary system of methanol (1) + MEK (2) + IL (3) were measured at 101.3 kPa, as listed in Table 3. The mole fraction of IL was kept constant in each of the three sets of data at $x_3 \approx 0.05$, 0.11 and 0.17. Besides the y-x diagrams and T-x-y diagrams were plotted in Figs. 2 and 3, respectively. By the way, x_1' is the mole fraction of methanol in liquid phase on an IL-free basis.

The activity coefficient, which describes the deviation of a solution from the limiting behavior of Raoult's law [29], was used to study the effect of ILs on phase behavior of the components. When the pressure of system is low, the activity coefficient of component i, γ_i, could be calculated by the following equation

$$\gamma_i = \frac{y_i P}{x_i P_i^s} \tag{1}$$

where y_i and x_i represents the mole fraction of component i in the vapor phase and liquid phase containing IL, respectively; P is the total pressure of system (constant at 101.3 kPa in this study); P_i^s is the vapor pressure of pure component i at the system temperature, which could be calculated by Antoine equation using the Antoine constants from the literatures [30,31]. The relative volatility of

Table 2
VLE data for temperature T, liquid-phase mole fraction x, and gas-phase mole fraction y, for the system methanol (1) + MEK (2) at 101.3 kPa.[a]

T/K	x_1	y_1	T/K	x_1	y_1
352.8	0.000	0.000	338.6	0.548	0.660
349.8	0.039	0.114	338.2	0.599	0.689
347.7	0.079	0.204	338.0	0.641	0.713
345.7	0.121	0.278	337.7	0.688	0.738
344.1	0.176	0.361	337.5	0.740	0.772
342.7	0.222	0.416	337.4	0.791	0.802
341.7	0.280	0.475	337.4	0.852	0.849
340.8	0.326	0.512	337.4	0.900	0.886
340.0	0.393	0.555	337.6	0.956	0.946
339.6	0.437	0.586	337.9	1.000	1.000
339.0	0.486	0.621			

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u(P) = 0.10$ kPa, and the combined standard uncertainties are $u_c(x_1) = u_c(y_1) = 0.002$.

Table 1
Specifications of chemical samples.

Chemical name	CAS	Source	Mass fraction	Purification method	Final water mass fraction	Analysis method
Methanol	67-56-1	Beijing chemical works	0.995	None	0.00025	GC[c], KF[e]
MEK	78-93-3	Beijing chemical works	0.995	None	0.00030	GC[c], KF[e]
[BMIM][NTf_2][a]	174899-83-3	Shanghai Cheng Jie chemical Co. LTD.	0.99	Rotary evaporation under a vacuum	0.00050	LC[d], KF[e]
[HMIM][NTf_2][b]	382150-50-7	Shanghai Cheng Jie chemical Co. LTD.	0.99	Rotary evaporation under a vacuum	0.00053	LC[d], KF[e]

[a] [BMIM][NTf_2] = 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.
[b] [HMIM][NTf_2] = 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.
[c] GC = gas chromatography.
[d] LC = liquid chromatography.
[e] KF = Karl Fischer titration.